ERRATA

Page 13:
Line 2 should begin "C_v =" not "c_v +"

Page 15:
The coefficient $e^{(l-r)}$ should multiply $A_i$ in equation 2:5.

Table 2:1 has been omitted. The coefficients described do appear on page 152 in Table 1 of Appendix A.

Page 18:
$\lambda$ should be defined by $\lambda^2 = \frac{\hbar^2}{2\mu m k T}$

Page 21, Table 5:13:
The terms
\[-2 \frac{T}{T} < U_Q > + \frac{1}{kT^2} (< U_0 U_Q > - < U_0 > < U_Q >)\]
should be added to the right side of equation 2:19. Dr. M.L. Klei has pointed out that the major perturbation contributions to $C_v$ would be given by the expression
\[
\frac{2}{T} \left[ \frac{1}{kT} (< U_0 U_Q > - < U_0 > < U_Q >) - < U_Q > \right]
\]
This correction should eliminate most of the discrepancies between calculated and experimental values of $C_v$ in Table 5.13.

Page 23:
Fluctuations are defined here as terms of the form $< A^2 > - < A >^2$.

Equations 2:26 and 2:27 were inverted in chapter 3 to calculate $C_v$ from the fluctuations observed.

Page 28:
The total momentum probably becomes negative since the /360 always rounds down.
Although the values in these tables are monotone in appearance rather than oscillating they are very stable compared to the statistical error in $V_0$ and $P_0$. However an additional contribution of 5 atm. to the statistical error has been included in the final error bounds.

The error of 68 atm. appears more pleasing when the near vertical slope of the $P$ vs $V$ curve is considered.

The experimental low density PVT data are those of Levelt (1960).

$x_{10}$ should be $x'_{10}$

The end of the first paragraph is meant to indicate that the results of our calculations should be near those of argon, probably within the stated statistical error. This statement is based on conjectures which are plausible but cannot be proven.

Second paragraph, tenth line should read; At high densities the opposite is true.

Second paragraph, last line, "do lead" should read "does lead".

line 5 should read "eqn. 5:23" not "eqn. 5:33".
Page 74:

The last term in equation 5:34 should be replaced by

\[ \frac{NkT}{V} (\delta \text{ im } jn + \delta \text{ in } jm) \]

and the comment following does not apply since the equation has now been properly symmetrized.

Page 78:

\( \nu \) has been used instead of \( \gamma \) in the equation.

Page 79:

A better approximation to \( \frac{\partial P}{\partial T} \) in equation 5:49 would be given by

\[ \frac{\partial P}{\partial T} \approx \frac{Nk}{V} - \frac{1}{\sqrt{kT}} \left( < P_0 U_0 >_0 - < U_0 >_0 < P_0 >_0 \right) \]

\[ - \frac{1}{VT} < P_0 >_0 + \frac{2}{\sqrt{kT}} \left( < U_0 P_0 >_0 - < U_0 >_0 < P_0 >_0 \right) \]

Page 85, Table 5:8, Figure 5:1, Table 5:9:

The pressure \( P \) appearing in the equations on page 85 is not the total pressure \( P_T \) of Table 5:6 but rather \( P_T - P_3 \) since the correction for \( P_3 \) was included in the calculation of \( C_{ij} (U_3) \). Therefore the tabulated values of \( C_{11} \) and \( C_{44} \) should be raised by .06 at 40, 50 and 60°K and by .05 at 70 and 80°K. \( C_{12} \) should be lowered by the same amount at each temperature. This correction for pressure effects will not affect the following arguments concerning the experimental elastic constants. The author is indebted to Dr. M.L. Klein for pointing out this inconsistency.

Page 94:

Sect. 5:7, third sentence. This should begin, "However there are systematic differences". Since these differences lie mainly within the statistical error it is difficult to say whether they are significant.
Table 5:12.

As a result of the above the calculated bulk moduli $B_{TB}$ and $B_{SB}$ should be lowered by .02. The tabulated values of the anisotropy become

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>60a</th>
<th>70</th>
<th>70b</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{SB}$</td>
<td>2.63</td>
<td>2.67</td>
<td>2.64</td>
<td>2.65</td>
<td>2.84</td>
<td>2.74</td>
<td>2.72</td>
</tr>
</tbody>
</table>

These new values of the anisotropy are still quite inconsistent with those of Keeler and Batchelder and the argument is again unaffected.

Page 100:

Line 5 should read "but not to the same extent as $g(r)$.

Page 114:

As a result of the comments on pages 21 and 79, and the conversation with Dr. M.L. Klein it appears probable that $C_v$ can be estimated well at temperatures down to $40^\circ K$. Monte Carlo calculations at lower temperatures could be possible providing the suggested quantum correction is adequate.
THE STATISTICAL MECHANICS
OF
ARGON

A Thesis submitted to the Australian National University
for the degree of Doctor of Philosophy

R. A. Fisher
December, 1971
STATEMENT

Except where acknowledgements are made in the text, all the material contained in this thesis is the work of the candidate.

[Signature]

R. A. Fisher
ACKNOWLEDGEMENTS

The author thanks his supervisor Dr. R. O. Watts for his great help and encouragement while the research work described in this thesis was being carried out. He further appreciates the suggestion of the molecular dynamics study and helpful criticism of the early drafts of this thesis. Dr R. Mills and other members of the Diffusion Research Unit have also aided the author with discussions and encouragement.

Dr. J. A. Barker of the IBM Research Centre, San José should also be thanked for his correspondence and discussions. He has also allowed the use of some unpublished results.

The numerical work was carried out on the IBM /360-50 computer at the ANU Computer Centre. The author thanks Dr. M. R. Osborne for permission to use the computer outside normal working hours. Discussions with the staff of the Computer Centre have been most helpful in improving the efficiency of the programs used. The assistance of the Data Processing Unit and its operators, directed by Mr P. Wilson is greatly appreciated. Many of the calculations were performed while the members of the unit were operating the machine.

Finally the author wishes to thank the Australian National University for the award of a post-graduate scholarship.
ABSTRACT

Liquid and dense gaseous argon has been simulated (using the Barker-Bobetic potential) by means of molecular dynamics techniques similar to those developed by Rahman. The equilibrium properties have been calculated using 108 particles interacting through a truncated potential, together with perturbation theory to correct for the finite size of the system, as well as quantum and three-body effects. Good agreement with the experimental values of the pressure and internal energy has been obtained using these techniques. In addition excellent agreement with values calculated by Barker using Monte Carlo methods has resulted from this work, showing that there are no systematic differences between the two methods. Partly as a result of this work the Barker-Bobetic potential has been modified to give even better agreement with experimental liquid pressures.

The transport properties of argon have also been investigated using the results of this work. The diffusion coefficient has been calculated and the results are in reasonable agreement with experimental values and with the Lennard-Jones results of Levesque and Verlet. It has not proved possible to correct these results so as to represent argon exactly since the perturbation theories developed to date are not suitable. In addition the coefficients of shear and bulk viscosity and thermal conductivity have been studied using the Kubo approach to transport. It has not proved possible to obtain accurate results from this work, or to check the validity of this theory of transport. Research related to this thesis has shown that the assumptions underlying the friction coefficient approach to transport are not valid for argon.

The properties of solid argon at temperatures between 40 and 80°K have been calculated using Monte Carlo methods
and the new Barker potential just mentioned. The calculated pressures and internal energies are in excellent agreement with experimental values. The elastic constants are found to be closer to the Lennard-Jones results than to the experimental values, but the agreement has been quite pleasing here as well. Related properties of solid argon have also been studied in this work.

The radial distribution function for the Barker-Bobetic potential has been calculated and tabulated values have been included in an appendix for use by other workers. Some investigations of the time dependent distributions have also been undertaken and the results discussed. Good agreement has been obtained between the values of the energy and pressure calculated directly and using the radial distribution function.

Both solid and liquid argon have been successfully simulated and the results have established that the present Barker potential combined with the Axilrod-Teller triple-dipole interaction is an excellent model of interactions in argon in two areas of great theoretical interest.
The molecular dynamics results of Chapter 3 have appeared in

Liquid Argon: Monte Carlo and Molecular Dynamics Calculations,
Molecular Physics, 21, 657, (1971).

The study of the friction coefficient, reported in Chapter 4,
The Friction Coefficient Formalism in the Statistical Mechanics of Transport Processes,
will appear in the February issue of the Australian Journal of Physics.

The material in Chapter 5 is being prepared as Solid Argon: Monte Carlo Results along the Solid-Vapour Coexistence Curve, for submission to Molecular Physics.

Parts of Chapter 4 and 6 are being prepared as Diffusion Coefficients and Time-dependent Distribution Functions from the Barker-Bobetic Potential, for submission to the Australian Journal of Physics.
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CHAPTER 1

INTRODUCTION

The description of the macroscopic properties of a system in terms of the microscopic behaviour of its constituent particles has been attempted many times by chemists. Much of the basic research on such problems was completed during the latter half of the 19th century (Gibbs, 1902) or in the early part of this century. Although both the solid and gaseous states were studied at this time the description of liquids proved to be more complex. A large part of the theoretical developments in statistical mechanics has been devoted to calculating the equilibrium and non-equilibrium properties of systems consisting of one species of molecule in the liquid state. If these molecules are monatomic and obey classical mechanics the problem is much simplified and then a knowledge of the interatomic potential function allows the thermodynamic properties of the system to be calculated, at least in principle. In practice such calculations have only become possible with the development of high speed digital computers. (McDonald and Singer, 1970).

1.1 Argon

Argon has been a system of great theoretical and experimental interest for some time (Smith, 1971). In order to compare the properties of a physical system with the results of theoretical calculations it is convenient to use a material which is as simple as possible. Since the rare gas atoms are chemically inert due to their stable electron configurations, their interactions are considerably weaker than those of easily ionized atoms. Their interactions depend on Van der Waals attractive forces and on repulsive forces arising from overlapping electron orbitals. The attractive forces, the London dispersion forces, may be calculated using quantum mechanical perturbation theory. They are related to the instantaneous dipoles and multipoles formed by the orbiting electrons of an atom. The repulsive forces occur when electron orbitals overlap. The source of these forces lies in the fact that electrons are Fermi particles obeying the Pauli exclusion principle. Exchange forces, again described by quantum mechanical perturbation theory, do not appear to be important in argon.
Much interesting work on intermolecular forces appears in the Discussions of the Faraday Society (1965), which is devoted to this subject. Both two-body and many-body contributions to the interactions are discussed in this volume and in the review article of Buckingham and Utting (1970).

Copeland and Kestner (1968) have also investigated in detail the various many-body effects affecting the interatomic forces of heavy rare gases. There is also evidence that these forces can be adequately modelled by considering only interactions between pairs and triplets of atoms (Barker and Pompe, 1968).

Since the argon atom is fairly massive, it is well described using classical statistical mechanics (Bewilogua and Gladun, 1968). Thus it is simpler to deal with than is helium (Murphy and Watts, 1970), where quantum considerations are important. In addition it is more abundant than the heavier rare gases and so is more accessible to experimental workers. For these reasons argon has become a convenient substance for the comparison of experimental and theoretical values.

1:2 Previous Calculations of Fluid Properties

In early work aimed at calculating the thermodynamic properties of liquids, various approximations were made in order to simplify the calculations.

Several theories have been advanced that try to describe the behaviour of liquids by analogy with other states. Lattice theories (Barker, 1963) generally describe liquids as slightly disordered solids. Theories based on the radial distribution function treat the liquid as a dense gas. Several lattice theories of the liquid state have been developed. The cell theory was investigated in detail by Lennard-Jones and Devonshire (1937, 1938). In this theory the liquid is assumed to consist of a group of cells centred on the lattice sites of the related crystal. One atom is contained in each cell and moves freely in it. Later work has found that although this theory does not describe liquid behaviour well (Barker, 1963) it can prove useful in the study of the solid when quantum effects are small (Hoover et al., 1970). The cell theory has been extended from this simple form by treating the fact that
the positions of particles in adjacent cells are correlated and that more than one atom may occupy a cell. This has been treated in the cell cluster theory (De Boer, 1954). Another cell theory divided the liquid into arbitrary cells and allowed multiple occupancy of cells (Kirkwood, 1950). A related model dealt with the fact that atoms in liquid have fewer nearest-neighbours than they do in the solid. The hole theory (Eyring, 1936) described the liquid in terms of a lattice containing holes, or vacant lattice sites. The tunnel model (Barker, 1960, 1961) introduced disorder into the solid state by allowing disorder in one dimension. It has been described as an array of one dimensional fluids (Barker, 1963). This last model probably comes the closest to describing the behaviour of liquids. In general the lattice models have proved more useful in the description of melting (Hoover and Ross, 1971) than of liquids. All of these models describe systems with long range order.

The theories based on the radial distribution function \( g(r) \), all result in the evaluation of an integral equation of some form. It will be seen in Chapter 6 that the thermodynamic properties of a liquid can be obtained once the radial distribution function is known. One approach developed independently by several workers (Yvon, 1935; Born and Green, 1946; Kirkwood, 1935) uses a hierarchy of integral equations relating the two-body distribution function to the three-body distribution function. In order to solve these exact systems a further approximate relation is needed between these distribution functions. Generally the Kirkwood superposition approximation is used (Kirkwood, 1935; Kirkwood and Boggs, 1942). Another approach uses the Ornstein and Zernike (1914) equation for the direct correlation function \( c(r) \). A second relation is needed between \( c(r) \) and \( g(r) \) to solve this equation. Two different approximate relations have been used, the Percus-Yevick approximation (Percus and Yevick, 1958; Percus, 1962) and the Hypernetted Chain approximation (Van Leeuwen, Groenveld and De Boer, 1959; Meeron, 1960; Morita and Hiroike, 1960; Rushbrooke, 1960; Verlet, 1960). In general the Percus-Yevick approximation has proved to be the more successful of these methods (Watts, 1971c). This approach has been used successfully with the Lennard-Jones potential, when the thermodynamic
properties are calculated using the energy equation. (Barker, Henderson and Watts, 1970a,b). More recently the theory has been extended to take three-body interactions into consideration (Rowlinson, 1967; Rushbrook and Silbert, 1967). In any approximate theory the difficulty in the approach lies in separating the errors due to the approximation used from those resulting from using an inaccurate potential function.

Subsequent development of computers has meant that fewer simplifications needed to be introduced into the calculations. Simulation methods were developed that allowed the thermodynamic properties of systems of hard particles to be calculated exactly. These hard sphere systems have been studied using both Monte Carlo (Wood, 1968) and molecular dynamics techniques (Wainwright and Alder 1958).

Using the results of calculations involving hard spheres, the properties of systems interacting through more realistic potentials can be calculated by means of perturbation theory. An early theory developed by Zwanzig (1953) gave accurate results at high temperatures. However at low temperatures the treatment of the repulsive part of the potential was not acceptable and the theory broke down. Rowlinson (1964) showed how the repulsive region could be treated exactly for an inverse n-potential, thus improving the perturbation theory approach.

A different treatment of the repulsive part of the potential, when used with Zwanzig's (1954) theory by Barker and Henderson (1967a,b) gave improved results. This is the most successful approximate method developed to date, giving excellent agreement with machine calculations for the Lennard-Jones potential. Perturbation theory has been further advanced to the consideration of quantum (Kim, Henderson and Barker, 1969) and three-body forces (Barker, Henderson and Smith, 1968, 1969). Good agreement with Monte Carlo results resulted when the perturbation theory was used to calculate the thermodynamic properties of the Barker-Pompe liquid, using hard spheres for the simple potential.

Further advances towards an essentially exact theory of liquid argon began when Rahman (1964) studied the properties of the Lennard-Jones system using molecular dynamics (Rahman, 1969).
The thermodynamic properties of this system have also been calculated using Monte Carlo methods (McDonald and Singer, 1969). Later work (McDonald and Woodcock, 1970) calculated the effects of the Axilrod-Teller triple dipole interaction. In all of this work a system containing a small number of particles was studied and usually the properties calculated were compared with experimented argon results. In some cases comparison has been made with Xenon as well (Verlet, 1967) through use of the law of corresponding states (Guggenheim, 1945). The potentials used (hard sphere, Lennard-Jones) were chosen for computational convenience and have simple computational forms.

1.3 The Interatomic Potential Function Of Argon

In order to calculate the thermodynamic properties of argon using statistical mechanics it is necessary to know the form of the interatomic potential function. Several potential functions have been used, the most common of which is probably the Lennard-Jones potential. The exponential-six, Kihara and Morse potentials have also been extensively studied (Levesque and Vieillard-Barron, 1969; Horton, 1968). In general these potentials have two or three parameters which are fitted to experimental data related to the physical state, solid (Horton, 1968), liquid or gas (Hirschfelder, Curtiss and Bird, 1954) to be investigated. Different parameters are then used for different phases.

The first multiparameter function designed to fit argon specifically was derived by Guggenheim and McGlashan (1960). Later Dymond and Alder (1969) developed a potential function, presented in a tabulated form. Both of these were effective pair potentials for they considered only interactions between pairs of atoms and treated many-body interactions implicitly. Barker and Pompe (1968) developed an advanced form of the potential function by treating both two and three-body interactions explicitly. Coefficients used in the long range attractive part of the two-body potential and the three-body terms were all chosen so as to agree with quantum mechanical values (Leonard, 1968; Bell and Kingston, 1966). This was a significant change from previous work. Barker with various
co-workers has since used this and similar potentials to study the equilibrium properties of liquid argon (Barker, Fisher and Watts 1971), and of solid argon near 0°K (Barker, Klein and Bobetic, 1970).

1:4 Transport Properties Of Argon

The study of non-equilibrium statistical mechanics has proven to be far more complex than the equilibrium work. Several theories have been developed that are designed to give methods for calculating the transport coefficients of a system from a knowledge of the equilibrium state (Rice and Gray, 1965). Kirkwood and various co-workers (Rice and Gray, 1965) have developed a theory of transport based on the concept of a friction coefficient (Kirkwood, 1946), which first appeared in the theory of Brownion motion. A later development of this work, the Rice-Allnatt theory (Rice and Allnatt, 1961) has also been extensively studied.

An alternate theory, the linear response theory of transport has also been developed (Kubo, 1957,1958). The basic premise of this theory is that near equilibrium the deviations of the distribution functions from their equilibrium forms are linear (Green, 1952, 1954; Resibois, 1964; Mori, 1958). The full theory was developed by many authors, references to whom may be found in a review by Zwanzig (1965). In this approach the transport coefficients are generally expressed as time integrals of the autocorrelation function of some property of the system at equilibrium. This is the most appealing theory of transport yet developed, since it is developed using similar assumptions to those used in deriving experimental transport coefficients (de Groot and Mazur, 1962; Pitts, 1962).

The diffusion coefficient has been calculated using this theory by Rahman (1964) and Levesque and Verlet (1970), in conjunction with their molecular dynamics calculations for the Lennard-Jones potential. The agreement with experimental values for argon is reasonable. This is the only transport coefficient that has been calculated for a liquid system using a realistic potential. Bruin (1969) has reported values for several other transport coefficients in the dense gaseous region.
Liquid state results for the viscosity and thermal conductivity are of interest, but the only calculated results at liquid densities that have been reported used the hard sphere potential (Alder, Gass and Wainwright, 1970).

1.5 Argon Crystals

The study of solid state effects is also of great interest, and many calculations have been made based on the lattice dynamics theory of Born and von Karman (1911). This work has been reviewed recently by Horton (1968). Once again a simple two-body potential such as the Lennard-Jones potential has been used to model the argon interactions. The potential parameters are fitted to solid state properties and the solid is then treated as a system of harmonic oscillators. The frequencies of phonons, the thermodynamic properties, and the elastic constants of the solid are calculated. This method is most suitable for calculation at low temperatures (Horton, 1968), as at higher temperatures the method becomes more and more complex due to the increasing importance of anharmonic terms. The difficulty with treating solids at high temperatures has recently been eliminated by work of Squire, Hoover and Holt (Squire et al. 1969; Hoover et al. 1969; Holt et al. 1970) in a series of papers in which they report calculations of the elastic constants for a Lennard-Jones solid using Monte Carlo methods.

Bobetic and Barker (1970) have investigated the Barker-Pompe potential (Barker and Pompe, 1968) at low temperatures using lattice dynamics, calculating both thermodynamic properties and the elastic constants. As a result of this work the Barker-Pompe potential was modified to give a form that is suitable for studies in both the gaseous region and for the solid near 0°K. The same parameters are used for both phases. This is a major advance over previous work since there is no reason to believe that the argon potential changes with the phase of the system. All previous work by using different potential parameters has in effect used a different potential function for the solid, liquid and gaseous regions.

1.6 Scope Of The Present Investigations

From the previous discussion it is apparent that both solid and liquid argon have been investigated extensively using
approximate pair potentials. It was therefore decided to calculate both the equilibrium and the transport properties of liquid argon using molecular dynamics techniques and the accurate potential function of Bobetic and Barker (1970). At the same time a Monte Carlo study of the equilibrium properties of the liquid was commenced by Barker. By using both techniques, systematic differences between the two methods could be studied whilst the molecular dynamics data would allow current theories of transport to be investigated. It was decided to use 108 particles for long model times to allow the long time behaviours of systems to be observed. Comparison could then be made with the short time runs generated using 864 particles as studied by Rahman (1964) and Levesque and Verlet (1970). As no transport studies using an accurate potential are presently available and this is an area of considerable interest. Initially the Kubo theory of transport was investigated, since it was judged to have the soundest theoretical basis. Subsequently the results of these calculations led to an investigation of the assumptions underlying the Kirkwood approach to non-equilibrium phenomena (Kirkwood, 1946) in an attempt to find an adequate theory of liquid transport.

In addition to the liquid state work it was proposed to study the solid state at temperatures from 5°K to the melting point along the melting curve. Providing the quantum effects could be accurately calculated, comparison with low temperature results using lattice dynamics could be made. In addition the thermodynamic properties of argon could be accurately calculated using the potential function proposed. Thus the properties of argon could be studied over the major thermodynamic regions of interest. During the course of the liquid state calculations it was found that a small change in the Barker-Bobetic potential resulted in improved agreement with experimental liquid pressures. As a result this potential was used in the calculation of solid state properties. Calculations by Barker showed that this new potential gave good agreement with gas phase and 0°K properties of argon, as well as with liquid state results. Thus an examination of the new potential at high solid temperatures would show the adequacy of the new potential over an important range of temperatures and densities. Since transport properties were not investigated in this case, the Monte Carlo rather than the molecular dynamics technique was used. This thesis is a discussion of the results of performing the calculations outlined.
CHAPTER 2
STATISTICAL MECHANICS OF FLUID ARGON

This chapter will describe the method of molecular dynamics as used in the calculation of the thermodynamic properties of argon. First the statistical mechanics employed will be developed and secondly the procedures used in the machine calculations will be described.

2.1 Introduction

Statistical mechanics was developed to relate the macroscopic properties of a system to the molecular properties of its constituent particles. It has been applied to both equilibrium (Hill, 1956) and non-equilibrium (Prigogine, 1962) systems. In this work it is assumed that the particles of the system strongly repel each other when close together and attract each other weakly when separated by greater distances. It is further assumed that the particles are spherically symmetric. Rotational and vibrational degrees of freedom are prohibited so that only translational motions in three dimensions contribute to the internal energy of the system.

The interactions between particles are complicated functions of the atomic properties. As Fitts (1966) pointed out the interaction energy $U(1, \ldots, N)$ of a system of $N$ particles may be divided into contributions due to two-body, three-body, ..., $N$-body interactions. In addition external forces such as electrical or gravitational fields acting on the system may contribute. We may write (Fitts, 1966)

$$U(1, 2, \ldots, N) = \sum_{i=1}^{N} u(x_i) + \sum_{i>j=1}^{N} u(x_i, x_j) + \sum_{i>j>k=1}^{N} u(x_i, x_j, x_k) + \sum_{i>j>k>l=1}^{N} u(x_i, x_j, x_k, x_l) + \ldots$$

2.1

where $x_i$ is the position of the $i$'th particle and $u(x_i, x_j, \ldots, x_n)$ is the appropriate $n$-body interaction. If we restrict ourselves to systems involving no external fields and with negligible four-body and higher order interactions, equation 2.1 becomes

$$U(1, \ldots, N) = \sum_{i>j=1}^{N} u(x_i, x_j) + \sum_{i>j>k=1}^{N} u(x_i, x_j, x_k)$$
By neglecting external forces we are assuming that gravitational and electromagnetic fields have negligible effect on the atomic motions. These fields are commonly ignored in experimental work on the inert gases, except where they are important, for example gravitational effects can be noticeable near the critical point. Other experimental work investigates the effect of an electric field on ions (Robinson and Stokes, 1955). These forces have not been considered in this research and are assumed to be zero. If we also invoke the Born-Oppenheimer approximation then $U$ becomes a function of inter-nuclear distances only,

$$U = \sum_{i<j} u(|x_i - x_j|) + \sum_{i<j<k} u(|x_i - x_j|, |x_j - x_k|, |x_k - x_i|)$$

In machine calculations we commonly deal with a system consisting of $N$ identical particles of mass $m$ contained within a volume $V$ resulting in a number density of $\rho = N/V$. We will consider only thermodynamic systems of this type in the following work.

2.2 The Concept of Ensembles

In a system of macroscopic size, the number of constituent particles is so large that the positions and momenta of individual particles are indeterminate. Experimental measurements of the properties of such a system average its behaviour over a period of time (Kirkwood, 1946). This period will be considerably longer than the lifetime of a particular configuration of the constituent particles. Statistical mechanical ensembles attempt to reproduce the average behaviour of macroscopic systems.

Two types of ensemble are commonly generated in computer simulation methods. The first is the canonical ensemble which has a fixed volume, composition and temperature. This ensemble represents a closed thermodynamic system in thermal contact with its surroundings. The second is the microcanonical ensemble in which the composition, volume and total energy are fixed. This ensemble represents a thermodynamically isolated system. Experimental studies use both these thermodynamic systems. Other ensembles may also be defined. For example,
the grand canonical ensemble is useful for some work in statistical mechanics (Hill, 1956). Simulation work has also used the NpT-ensemble (Wood, 1968) in which the pressure is constant.

An ensemble is a collection of replica systems. Each system is allowed to take up any configuration allowed in the thermodynamic system it is modelling. The number of systems in an ensemble is assumed to be so large that the number of systems in a particular configuration is proportional to the probability of the real system appearing in that configuration. It is a fundamental postulate of statistical mechanics that the average behaviour of the systems in the ensemble will reproduce the observed behaviour of the real system (Hill, 1956, p.9).

In the canonical ensemble each system has a fixed volume V containing N particles and is at temperature T. In the microcanonical ensemble the total energy E rather than the temperature is fixed. The following derivations of equations relating ensemble averages to thermodynamic properties is valid for both ensembles except where explicitly stated, providing we ignore terms of order $\frac{1}{N}$. In the limit $N \to \infty$, $V \to \infty$, $\frac{N}{V} = \rho$ (const.), the ensembles are equivalent.

2.3 Equilibrium Statistical Mechanics

To derive the equations for equilibrium thermodynamic values using statistical mechanics we begin with the definition of the canonical partition function for a classical system of N particles,

$$Q_N = \frac{1}{h^{3N}N!} \int \cdots \int \frac{e^{-H/kT}}{V} d^3N \mathbf{r} d^3N \mathbf{p} \quad 2:3$$

where $h$ is Planck's constant, $k$ is Boltzmann's constant and $H$ is the Hamiltonian of the system. For a classical system of identical particles of mass $m$ interacting through a potential $U$

$$H = \frac{1}{2m} \sum_{i=1}^{N} \mathbf{p}_i \cdot \mathbf{p}_i + U(1, \ldots, N) \quad 2:4$$

Substituting in 2:3 and integrating over the momenta

$$Q_N = \left(\frac{2\pi m k T}{h^2}\right)^{3N/2} \frac{1}{N!} \int \cdots \int \frac{e^{-U/kT}}{V} d^3N \mathbf{r} \quad 2:5$$
It is also convenient to define

\[ Z = \int \ldots \int_{V} e^{-U/kT} d^{3N} \xi \]

and

\[ Z < X > = \int \ldots \int_{V} X e^{-U/kT} d^{3N} \xi \]

which defines the expected value or ensemble average of the property \( X \), providing \( X \) is a function only of the coordinates of the atoms in the system. It can be shown that the Helmholtz free energy of the system is given by

\[ F = -kT \log Q_{N} \]

(Landau and Lifshitz, 1959, sec. 31) and may be identified with the free energy of the thermodynamic system. The thermodynamic properties of the system may then be derived as derivatives with respect to temperature and volume. As examples, the pressure is defined by

\[ P = -(\frac{\partial F}{\partial V})_{T} \]

the internal energy of the system by

\[ E = -T^{2} (\frac{\partial}{\partial T} (\frac{F}{T}))_{V} = F - T (\frac{\partial F}{\partial T})_{V} \]

and the specific heat at constant volume by

\[ C_{V} = (\frac{\partial F}{\partial T})_{V} \]

The internal energy due to interatomic interaction is

\[ E^{*} = E - \frac{3}{2} NkT \]

where we have taken off the contributions due to the kinetic energy of the system.

In terms of ensemble averages

\[ P = -(\frac{\partial F}{\partial V})_{T} = \frac{2}{3V} kT \log Q_{N} = \frac{kT}{Z} \frac{\partial}{\partial V} \frac{3Z}{3V} + \frac{NkT}{V} \]

\[ = \frac{NkT}{V} + \frac{kT}{Z} \int \ldots \int_{V} \frac{\partial U}{\partial V} e^{-U/kT} d^{3N} \xi \]

or

\[ P = \frac{NkT}{V} - < \frac{\partial U}{\partial V} > \]

Similarly

\[ E = \frac{3}{2} NkT + < U > \]
and

\[ C_v + \frac{3}{2}Nk + \frac{3}{3T} < U > \]

\[ C_v = \frac{3}{2}Nk + \frac{1}{kT^2}(<U^2> - <U>^2) \]

2:4 Atomic Interactions in Argon

It can be seen from the previous section that the thermo­
dynamic properties of a system can be calculated by averaging
over the appropriate ensemble. (The free energy is a simple
function of an ensemble average.) Such averages require a
knowledge of the interparticle potential function \( U(x_1, \ldots, x_N) \).

In section 2:1 we assumed its form to be

\[ U(x_1, \ldots, x_N) = \sum_{i<j} u_{ij} + \sum_{i<j<k} u_{ijk} \]

Early work in this field used model potential functions that
were chosen for their computational convenience. In some cases
their parameters were adjusted to fit one or two properties
or argon. The first potentials studied using simulation methods
were those of the 'hard particles',

\[ u(r) = \begin{cases} 
\infty & r \leq \sigma \\
0 & r > \sigma \\
u_{ijk} = 0 & \end{cases} \]

(Wainwright and Alder, 1958; Alder et al. 1960; Alder et al.,
1968) and the 'square-well particles'

\[ u(r) = \begin{cases} 
-\varepsilon & \sigma < r \leq \lambda \sigma \\
\varepsilon & r > \lambda \sigma \\
u_{ijk} = 0 & \end{cases} \]

(Alder, 1966).

\( \lambda, \varepsilon \) and \( \sigma \) are adjustable parameters representing the width
and depth of the potential well, and the particle diameter
respectively. For use in the study of argon \( \lambda = 1.5 \).

A more realistic approximation to the interatomic potential
is the Lennard-Jones potential

\[ u(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) \]

For comparison with experiment \( \varepsilon \) and \( \sigma \) are adjusted to give
agreement with experimental results for the particular state
(solid, liquid or gas) being examined. However when agreement
with liquid argon results is desired using this potential, the
best choice of \( \varepsilon \) and \( \sigma \) results in a coefficient for \( r^{-6} \) which
is twice the value of that obtained for the dipole-dipole inter­
action, calculated using quantum mechanics (Leonard, 1968).
Thermodynamic values obtained from these and other potentials have also been studied extensively using various approximation techniques (Barker, 1963; Yvon, 1935; Percus and Yevick, 1958; Van Leeuwen, Groeneveld, and de Boer, 1959). Evaluations of these techniques suffered because it was difficult to separate the effects of the approximate potential from those of the approximations used in the statistical mechanics. Comparison with molecular dynamics and Monte Carlo results allowed errors arising from the approximations to be determined. Since Guggenheim and McGlashan (1960) showed that actual interactions in liquid argon are quite different from those of a Lennard-Jones liquid, the quantitative agreement between Lennard-Jones and experimental results is fortuitous. The Lennard-Jones potential approximates the interatomic in two ways, first by assuming a simple mathematical form for the two-body interactions and secondly by ignoring many-body effects. Early attempts to develop more realistic two-body potentials generally resulted in poorer agreement with experiment. (Levesque and Vieillard-Barron, 1969). In recent developments aimed at deriving an accurate potential function specifically for argon interactions two approaches have been used. One, used by Dymond and Alder (1969), is to assume that interatomic interactions can be approximated by implicitly averaging many-body effects in calculating a two-body potential. Spectroscopic and molecular beam data (Tanaka and Yoshino, 1970; Lee and Parson, 1970) have shown this potential to be unsatisfactory in this area (Dymond, 1971). When used in lattice dynamics work other anomalies appeared such as negative specific heats under certain conditions (Bobetic and Barker, 1970). In addition since this potential is a numerical rather than an analytic function, its derivatives are not uniquely defined. Thus, some assumptions must be made before it can be used in simulation. Recently Dymond and Alder (1971) have published work dealing with many-body interactions explicitly.

The second approach, used by Barker and various co-workers is to derive exact two-body and three-body potential functions. The two-body potential is fitted to experimental data dependant only on two-body interactions. This pair potential developed by Barker and Pompe (1968) and later improved by Bobetic and Barker (1970) gives excellent agreement with experiment for
the thermodynamic properties of solid argon at low temperatures and for the thermodynamic properties and transport data of dilute gaseous argon. In addition it agrees well with recent spectroscopic data of Tanaka and Yoshino (1970) and molecular beam scattering data of Lee and Parson (1970). Barker and Bobetic's two body potential is used throughout this work. It has the analytic form

$$u_{ij} = \varepsilon \sum_{i=0}^{5} A_i (R-1)^2 \sum_{j=0}^{2j+6} C_{2j+6} R_j^2$$

where $R$ is the ratio $\frac{r_i - r_j}{R_m}$ and $R_m$ is the atomic separation at the potential minimum. The constants used are listed in Table 2:1. $\delta$ is a small constant which eliminates a pole at $R = 0$. The coefficients $C_{2j+6}$ are obtained from quantum mechanical calculations (Leonard, 1968) and are the multipole attraction coefficients of $r^{-6}$, $r^{-8}$ and $r^{-10}$. In Figure 2:1 this potential is compared with the Lennard-Jones potential.

It is worth noting that all the potentials discussed here have the form $u_{ij} = \varepsilon \phi \left( \frac{r_i}{R_m} \right)$. The important point is that in the Barker-Bobetic and Dymond-Alder potentials $\varepsilon$ and $\sigma$ are constants independent of phase and temperature. In the earlier potentials $\varepsilon$ and $\sigma$ were parameters adjusted to fit a particular phase or temperature range of argon and their values changed considerably as the temperature and phase are altered.

Many-body forces and their contributions to the thermodynamic properties of argon have been studied a great deal (Copeland and Kestner, 1968). Most of the literature seems to concern their effects in the solid state. References appear in Bobetic and Barker (1970) to much of this work. In total it suggests that the major contribution to many-body effects is the triple dipole interaction described by Axilrod and Teller (1943). Other contributions seem insignificant in solid argon and even weaker in the liquid state.

The Axilrod-Teller potential is the three-body potential used in Barker's work. It has the analytic form

$$u_{ijk} = \frac{\gamma}{r^3 s^3 t^3} (1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3)$$

where atoms $i$, $j$ and $k$ are separated by distances $r$, $s$ and $t$ and $\theta_1$, $\theta_2$ and $\theta_3$ are the interior angles of the triangle with
Figure 2:1

Potential functions for argon.

--- Lennard-Jones potential.

-- Barker-Bobetic potential.
sides of length $r$, $s$ and $t$. The coefficient $\gamma$ is chosen as the value calculated by Leonard (1968), $73.2 \times 10^{-84}$ erg cm$^{-9}$. This is close to the value reported by Bell and Kingston (1966).

The excellent agreement with experimental gas and solid data resulting from calculations (Bobetic and Barker, 1970) using this combination of two and three-body potentials is strong evidence for the validity of ignoring other many-body interactions. A further test consists of calculating the thermodynamic values for the liquid state. This has been done using molecular dynamics calculations as reported here. Concurrently Monte Carlo calculations have also been carried out (Barker, Fisher and Watts, 1971). This paper appears as Appendix A of this thesis.

2:5 Molecular Dynamics Calculations

Molecular dynamics calculations have been described by several authors and the details are now generally well known (Wainwright, and Alder, 1958; Rahman, 1964; Verlet, 1967). The method used in this work is very similar to that of Verlet. The main differences are that:

a) 108 rather than 864 particles have been used;
b) 5000 rather than 1200 configurations have been generated;
c) a more realistic potential function has been used.

The model used treats the liquid as a group of 108 particles, interacting through a spherically symmetric two-body potential function, contained in a cubic box of volume $V$. Initially they are placed on the equilibrium lattice sites of a crystal and their momenta selected such that they have random directions and a Maxwellian distribution of speeds. The particle motions are then integrated through time. After the system has reached equilibrium, the subsequent configurations are recorded, and thermodynamic values are calculated as averages over different configurations. Since the total energy, number of particles, and volume are fixed, these configurations form a microcanononical ensemble.

Edge effects due to the finite volume are reduced by assuming periodic boundary conditions. The walls of the cube are then
"transparent" to the particle motions. However, when a particle leaves the cube, an "image" with the same momenta enters at the corresponding point on the opposite face. The liquid is thus periodic. If there is an atom at position \((X,Y,Z)\) then there are also particles at \((X±nL, Y±mL, Z±oL)\) \((m,n,o\) integral) where \(L^3 = V\) with the same momentum. If we record the position only of particles with coordinates between 0 and \(L\), we can generate an infinite fluid from this record.

It is necessary for the efficient calculation of results that the interaction potential should be of finite range, so that only a finite number of interactions are considered. This distance should be less than \(L/2\) so that a particle does not interact with two "images" of another atom. In this work we have used the potential

\[
u_{ij} = \begin{cases} U_{ij} & r < R \\ 0 & r \geq R \end{cases}
\]

where \(U_{ij}\) is the Barker-Bobetic potential and \(R\) is either 8.4165 Å or \(L/2\). \(R = L/2\) was chosen for one liquid and one dense gas point, and at the highest density where \(L/2 < 8.4165\) Å. In order to calculate results based on the full Barker-Bobetic potential we must now develop a method of averaging properties using configurations generated by the truncated potential.

### 2.6 Perturbation Expansion of The Free Energy

In Section 2.2 we obtained the classical Helmholtz free energy as:

\[
F_c = -kT \log \left( \frac{2\pi m kT}{\hbar^2} \right)^{3N/2} \frac{\mathcal{Z}}{N!}
\]

If the system we are studying is classical and has only two-body interactions, we can calculate its properties using molecular dynamics. Argon interactions, however, are quite long ranged and three-body interactions are not negligible. Although its de Broglie wavelength is small compared to helium for example, we must also deal with the fact that it obeys the laws of quantum mechanics. Therefore a perturbation method is used to calculate the required properties of argon in terms of our molecular dynamics results. We first expand the quantum free energy, which is the trace of the density matrix, about its classical value.
The Wigner-Kirkwood expansion (Green, 1951) may be used to
give the free energy as a power series in \( \hbar \).

\[
F = F_c + i \hbar F_1 - \hbar^2 F_2 - i \hbar^3 F_3 + \hbar^4 F_4
\]

It can be shown (Landau and Lifshitz, 1959; Hansen and Weis,
1969) that \( F_1 = F_3 = 0 \) and

\[
F_2 = -\frac{1}{96} \pi^2 \frac{N}{m \kappa T} \sum_{i=1}^{N} \frac{\partial^2 U}{\partial \xi_i^2}
\]

\[
= -\frac{1}{96} \pi^2 \frac{N}{m \kappa T} \left< \sum_i \nabla^2 \xi_i U \right>
\]

where \( \nabla^2 \) is the Laplacian operator \( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \) evaluated
at \( \xi_i \).  The free energy including quantum effects is thus:

\[
F = F_c + \frac{\hbar^2}{96 \pi^2 m \kappa T} \left< \sum_i \nabla^2 \xi_i U \right>
\]

We now suppose that \( U \) can be divided into several contributions:

\[
U = U_o + U_2 + U_3
\]

In this work \( U_o \) is the truncated two-body potential used in
the previous section, \( U_2 \) is the contribution from interactions
with \( r > R \) and \( U_3 \) is the three-body triple-dipole potential.

\[
U_o = \sum \xi_{ij} \quad (r_{ij} < R)
\]

\[
U_2 = \sum \xi_{ij} \quad (r_{ij} > R)
\]

\[
U_3 = \sum \xi_{ijk}
\]

We now substitute for \( U \) in equation 2:9

\[
F = +\frac{3NkT \log \lambda + kT \log N}{2}
\]

\[
-kT \log \int \int e^{-U_o/kT} (1 - U_2 + \ldots) (1 - U_3 + \ldots) d^3 \xi
\]

\[
+ \frac{\hbar^2}{96 \pi^2 m \kappa T} \int \int \sum_i \nabla^2 \xi_i (U_o + U_2 + U_3) e^{-U_0/kT} \times
\]

\[
(1 - U_2 + \ldots) (1 - U_3 + \ldots) d^3 \xi
\]

\[
\int \int e^{-U_0/kT} (1 - U_2/kT + \ldots) (1 - U_3/kT + \ldots) d^3 \xi
\]
Introducing the notation,

\[ Z_o = \int \int e^{-U_o/kT} d^3N \]

\[ Z_o \langle X_o \rangle = \int \int X e^{-U_o/kT} d^3N \]

and neglecting terms of the form

\[ h^2U_2, U_2U_3, h^2U_3, \text{ and higher order in } h^2, U_2 \text{ and } U_3 \]

this becomes

\[ F = kT \log N! + 3 NkT \log \lambda \]

\[ -kT \log \int \int e^{-U_o/kT} d^2 \]

\[ \frac{h^2}{96 \pi^2 mkT} \quad < \Sigma \frac{V^2}{i} U_0 > \]

\[ \frac{1}{kT} \frac{U_o}{kT} \]

\[ 2:11 \]

We now have the free energy for the complete Barker-Bobetic potential in terms of ensemble averages depending only on the truncated two-body potential. Such an ensemble is generated during the molecular dynamics calculations. The development is in terms of the canonical ensemble, but is also valid for the microcanonical ensemble, excepting for terms of order \( \frac{1}{N} \) (Rahman, 1964). Other thermodynamic properties can now be calculated by taking appropriate derivatives of equation 2:11.

\[ E^* = -T^2 \left( \frac{3}{\beta T} \frac{E}{T} \right) V - \frac{3}{N} NkT \]

\[ = kT^2 \left( \frac{3}{\beta T} \left( Z_o \left( 1 - \frac{U_2}{kT} - \frac{U_3}{kT} \right) \right) \right) \]

\[ \frac{< U_o > < U_o >}{Z_o \left( 1 - \frac{U_2}{kT} - \frac{U_3}{kT} \right)} \]

\[ + \frac{3}{\beta T} \frac{< U_o >}{T} \quad \text{where we define} \]

\[ < U_o > = \frac{h^2}{96 \pi^2 mkT} \quad \Sigma \frac{V^2}{i} U_o \]

\[ 2:12 \]

If we make use of the relations

\[ \frac{3}{\beta T} \frac{< X_o >}{Z_o} = Z_o \frac{3}{\beta T} \int \int X e^{-U_o/kT} d^3N - \int \int X e^{-U_o/kT} d^3N \frac{Z_o}{\beta T} \]

\[ = \left( \frac{< UX_o >}{kT^2} - \frac{< X >}{kT^2} \frac{< U_o >}{kT^2} \right) \]
and
\[ \frac{1}{Z} \frac{\partial Z}{\partial T} = \frac{1}{kT} < U_0 >_0 \]

\[ E^* = < U_0 >_0 + < U_2 >_0 + < U_3 >_0 - \]
\[ \frac{1}{kT} \left( < U_2 U_0 >_0 - < U_2 >_0 < U_0 >_0 + < U_3 U_0 >_0 - < U_3 >_0 < U_0 >_0 \right) \]
\[ + \frac{b^2}{96\pi^2 mkT} \left[ 2 \left( \sum_i \nabla_i^2 U_0 >_0 - \sum_i \nabla_i^2 U_0 >_0 < U_0 >_0 \right) \right] \]

2:13

The pressure is calculated from
\[ P = - \left( \frac{\partial F}{\partial V} \right)_T \]

We use the "scaling" procedure for differentiating with respect to volume described by Born and Green (1947) to derive the result.

\[ PV = NkT + < P_0 >_0 + < P_2 >_0 + < P_3 >_0 + \]
\[ + < P_0 >_0 - \frac{1}{kT} \left( < U_3 P_0 >_0 - < U_3 >_0 < P_0 >_0 + < U_2 P_0 >_0 - < U_2 >_0 < P_0 >_0 + < U_3 P_0 >_0 - < U_3 >_0 < P_0 >_0 \right) \]

2:14

in which we define
\[ P_0 = - \frac{1}{3} \sum_{i<j<k} \frac{\partial}{\partial r_{ij}} U_{ijk} = 3 \frac{\partial}{\partial t} \]

2:15

\[ P_2 = - \frac{1}{3} \sum_{i<j} \frac{\partial}{\partial r_{ij}} U_{2} \]

2:17

\[ P_{\Omega} = - \frac{1}{3} \sum_{i<j} \frac{\partial}{\partial r_{ij}} U_{\Omega} \]

2:18

The second form of equation 2:15 follows (Graben, 1968) from Euler's theorem on homogeneous functions since \( U_3 \) is a homogeneous function of degree - 9 in its arguments \( r, s \) and \( t \).
The specific heat at constant volume may also be calculated

\[ C_V = \frac{3}{2} N k + \frac{\beta E^*}{\beta T} \]

\[ C_V = \frac{3}{2} N k + \frac{1}{kT^2} \left( <U_2^2> - <U_o>^2 > \right) \left( 1 + \frac{<U_2^*>}{kT} + \frac{<U_3^*>}{kT} \right) \]

\[ + \frac{1}{kT^2} \left( 1 + \frac{<U_o^*>}{kT} \right) \left( 1 + \frac{<U_o^*>}{kT} > \right) \]

\[ \left( <U_2^*> + <U_3^*> \right) > \]

\[ + \frac{1}{kT^2} \left( 2 + \frac{<U_o^*>}{kT} \right) \left( <U_o^*> + <U_o^*> \right) \]

\[ - \frac{1}{kT^3} \left( <U_2^2_U_o^*> + <U_3^2_U_o^*> + <U_3^2_U_o^*> - <U_o^*> \left( <U_2^2_U_o^*> + <U_3^2_U_o^*> + <U_3^2_U_o^*> \right) \right) \]

This last result is valid only for calculations involving the canonical ensemble. The expression for the specific heat of a microcanonical ensemble is derived in the following section.

This expansion has given the desired equations for \( E^* \), \( P \) and \( C_V \). However, \( U_2, \ U_3, \) and \( U_Q \) all involve an infinite number of atomic interactions. In order to perform the desired calculations we must make some further approximation. If we consider the liquid to be a continuum at interparticle distances greater than \( R_2 \), we may rewrite

\[ <U_2^*> = \Sigma \left< \frac{1}{2} u_{ij} \right> + \frac{N^2}{2V} \int_{\text{R}<r_{ij}<R_2} u_{ij}(r) 4\pi r^2 dr \]

\[ <P_2^*> = -\frac{1}{3} \Sigma \frac{\partial^2 u_{ij}}{\partial r_{ij}} \left< \frac{1}{2} n \right> + \frac{N^2}{2V} \int_{R_2} -\frac{1}{3} \frac{\partial}{\partial r} u_{ij}(r) 4\pi r^2 dr \]

For the other contribution we invoke the continuum approximation at \( R \). Then

\[ \frac{96\pi^2 mkT}{h^2} <U_Q^*> = \Sigma \left< \frac{1}{2} V^2 \right> U_o^* + \frac{N}{2} \int_{R} V^2 u(r) 4\pi r^2 dr \]
\[ \frac{96\pi^2 mkT}{\hbar^2} \langle P_3 \rangle = \langle U - \frac{1}{3} \sum_{i<j<k} \frac{2}{\varphi_{ij}} \varphi_{ij}^2 U_0 \rangle + \frac{N \rho}{R} \int_{R}^{\infty} \frac{r^3}{3} \varphi_{ij}^2 r^2 \, dr \times u(r) 4\pi r^2 \, dr \]

2.23

\[ \langle U_3 \rangle = \langle \sum_{i<j<k} u_{ijk} \rangle + \sum_{r,s,t<R} \rho^2 \int_{r<s<t}^{t>R} g(r) g(s) g(t) u_{ijk} \, dx_{ij} \, dx_{jk} \]

2.24

and,

\[ \langle P_3 \rangle = 3 \langle U_3 \rangle \quad \text{as before.} \]

In equation 2.24 the three-body radial distribution function has been replaced by \( g(r) g(s) g(t) \) using the Kirkwood superposition approximation (Kirkwood, 1934). The radial distribution function \( g(r) \) measures the probability of finding an atom at a distance \( r \) from the origin, when there is an atom at the origin. These distribution functions will be described in Chapter 6 along with the integrals in equation 2.20 - 2.24. Since the integrals are constants independent of the liquid configuration, they do not contribute to the fluctuation terms in equations 2.13, 2.14 and 2.19. The accuracy of the molecular dynamics calculations and the errors arising from the free energy expansion are discussed in the following chapter.

2.7 Calculation of the Specific Heat in the Microcanonical Ensemble

It is in the consideration of fluctuations that the choice of ensemble becomes important. Equation 2.14 gives the expression for the specific heat in the canonical ensemble where the temperature is fixed and the total energy fluctuates. Lebowitz, Percus and Verlet (1967) have derived expressions for the specific heat applicable to the microcanonical ensemble. In this case the temperature fluctuates and the total energy remains constant. Lebowitz et al. begin with the observation that intensive properties of a system, such as the kinetic energy per particle, may be evaluated using any of the phase-space ensembles. In the thermodynamic limit the observed values will be the same in both the canonical and microcanonical ensembles.
In contrast to this result it was found that when fluctuations are considered the expected value of a fluctuation depends on the ensemble in which it is studied. Thus in the microcanonical ensemble,

\[ \langle H^2 \rangle - \langle H \rangle^2 = 0 \]

where \(H\) is the Hamiltonian of the systems. However as we saw in the previous section this quantity is proportional to the specific heat when measured in the canonical ensemble.

Lebowitz et al. (1967) then developed a general formula to describe the difference between fluctuations measured in different ensembles. For intensive variables depending only on the temperature and the space coordinates the differences in this fluctuation as measured in the microcanonical ensemble and the canonical ensemble are proportional to \(C_v\).

By considering the fluctuations of the kinetic energy in the microcanonical ensemble they showed that

\[ \langle K.E. - \overline{K.E.} \rangle^2 = \frac{3N}{2} k^2 T^2 \left(1 - \frac{3}{2C_v}\right) \]

Using the relation

\[ K.E. = \frac{3}{2} N k T \]

this becomes

\[ \frac{\langle T^2 \rangle - \langle T \rangle^2}{\langle T^2 \rangle} = \frac{2}{3N} \left(1 - \frac{3}{2C_v}\right) \]

In addition fluctuations in the internal energy are proportional to fluctuation in the kinetic energy because of the relation \(K.E. + E^* = \text{constant}\).

Therefore we have the equivalent expression

\[ \frac{\langle E^*^2 \rangle - \langle E^* \rangle^2}{\langle T^2 \rangle} = \frac{3Nk^2}{2} \left(1 - \frac{3}{2C_v}\right) \]

2.8 Summary

In this chapter we have developed expressions for the pressure and internal energy of argon using the Barker-Bobetic potential. A perturbation expression for their calculation has been used that is suitable for use with both molecular dynamics and Monte Carlo techniques. In addition two different expressions for the specific heat have been given for use with
the appropriate ensembles. In the following chapter we will discuss the results of using these expressions in combination with molecular dynamics studies of the equilibrium properties of liquid argon.
CHAPTER 3

CALCULATION OF THE EQUILIBRIUM THERMODYNAMIC PROPERTIES OF ARGON

The procedures described in chapter 2 allow the thermodynamic properties of argon to be calculated from the configurations generated using the molecular dynamics methods. In this chapter the numerical procedures used will be discussed and then the results of our calculations will be presented. We begin by discussing the reduced variables used.

3.1 Reduced Variables

It has become quite common in recent studies of simple liquids to perform and often present calculations in terms of reduced variables (Rahman, 1964; Verlet, 1967). These reduced variables are dimensionless quantities chosen such that each is the quotient when the value being represented is divided by a value characteristic of the system. For example the reduced length \( r^* \) is given by \( r/\sigma \). In this case \( r \) is the length and \( \sigma \) is the parameter used in the Barker-Bobetic potential, both in metres. In our calculations we have used

\[
\begin{align*}
\sigma &= 3.3666 \times 10^{-10} \text{ m} \\
\frac{\varepsilon}{k} &= 140.235^\circ \text{K} \\
\text{and } m &= 66.904 \times 10^{-27} \text{kg}
\end{align*}
\]

as our reference values for calculating the reduced units. Here \( m \) is the mass of an argon atom and \( \varepsilon \) and \( \sigma \) are the parameters used in the Barker-Bobetic potential. \( \varepsilon \) measures the depth of the argon-argon potential well and we could define the diameter of an argon atom as \( \sigma \). All the relevant physical properties can then be reduced to dimensionless variables using various combinations of \( \varepsilon, m, \) and \( \sigma \). The basic reduced units are given in table 3.1. It is also possible to represent other quantities as reduced variables and as an example the reduced force is given by

\[
F^* = \sigma F/\varepsilon.
\]
<table>
<thead>
<tr>
<th>Reduced Unit</th>
<th>Physical Unit</th>
<th>Dimensions</th>
<th>Conversion Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r^* )</td>
<td>( r = \sigma r^* )</td>
<td>Length</td>
<td>( 3.3666 \times 10^{-10} ) m</td>
</tr>
<tr>
<td>( T^* )</td>
<td>( T = \frac{\epsilon T^*}{k} )</td>
<td>temperature</td>
<td>( 140.23^0 ) K</td>
</tr>
<tr>
<td>( v^* )</td>
<td>( v = \left( \frac{\epsilon}{m} \right)^{1/2} v^* )</td>
<td>velocity</td>
<td>( 171.6 \text{ m/s} )</td>
</tr>
<tr>
<td>( t^* )</td>
<td>( t = \left( \frac{\epsilon}{\sigma} \right) \frac{1}{\gamma} t^* )</td>
<td>time</td>
<td>( 1.96 \times 10^{-12} ) sec</td>
</tr>
<tr>
<td>( U^* )</td>
<td>( U = \epsilon U^* )</td>
<td>energy</td>
<td>( 1.936 \times 10^{-21} ) J</td>
</tr>
</tbody>
</table>

There are two reasons for using reduced units in these computations. The first of these is mathematical convenience as factors of \( 10^{-84} \) or even \( 10^{-27} \) are unwieldy to use. It is rather simple to eliminate these factors by 'scaling', that is by using a reduced unit, so that all the numbers being used are of order 1. Reduced units are generally necessary when using numerical methods since the internal representation of numbers on the machine restricts the size allowed. For example \( 1 \times 10^{-84} \) is put equal to zero on an IBM machine and so is not acceptable. The second use of reduced variables that is of interest, although not applicable here, is related to the Law of Corresponding States (Guggenheim, 1945). When using the Lennard-Jones potential, the various properties of the system are calculated in terms of reduced variables. Then values of these properties for argon, krypton, and other materials can be calculated using values of \( \epsilon \) and \( \sigma \) appropriate to the system being studied. Hirschfelder, Curtiss and Bird (1954) have tabulated values of \( \epsilon \) and \( \sigma \) for use with the Lennard-Jones potential for a number of different molecules. However since the potential used in this work is appropriate only for argon the law of corresponding states has not been investigated and the reduced units are used here solely for computational convenience.

### 3.2 Molecular Dynamics Calculations

The molecular dynamics techniques developed by Alder and Wainwright (1959, 1962), Alder (1964) and Alder and Einwohner (1965) were appropriate only for hard sphere and square-well
particles. In these cases the collisions occur instantaneously and particles move in straight lines between collisions. Later work using the Lennard-Jones potential (Rahman, 1964; Verlet, 1967, 1968) required programs of a quite different form. In this work the motion of any particles is continuously affected by its interaction with other particles in the system and as in a real system the acceleration of a particle is a smooth function changing continuously as the interactions change. If we assume our particles obey the laws of classical mechanics as formulated by Newton then we have

\[ m \frac{dv_i}{dt} = F_i \quad \text{3.1} \]

\[ \frac{dx_i}{dt} = v_i \quad \text{3.2} \]

where \( x_i, v_i \) and \( F_i \) are the position, velocity and force acting on atom i. If the only forces acting on the particle arise from the interatomic potential \( U \) then

\[ F_i = -\frac{\partial U}{\partial x_i} \quad \text{3.3} \]

We now wish to solve the equations of motion 3.1 and 3.2 for a system of \( N \) atoms enclosed in a volume \( V \) and interacting through the truncated Barker-Bobetic two-body potential. We cannot solve 3.1 and 3.2 as they stand since we do not have suitable expressions for the derivatives. Instead we use a finite difference analogue to these equations. This procedure corresponds to making the time a discrete rather than a continuous entity. The expressions used are (in reduced units)

\[ \mathbf{v}_i^* (t + \delta t) = \mathbf{v}_i^* (t) - \delta t \sum_{j < i} \frac{3u_{ij}^* (t)}{\delta x_i^* (t)} - \mathbf{v}_e (t) \quad \text{3.4} \]

\[ \mathbf{x}_i^* (t + \delta t) = \mathbf{x}_i^* (t) + \delta t \mathbf{v}_i^* (t + \delta t) \text{ Mod } L \quad \text{3.5} \]

In these equations \( \delta t \) is the timestep used in these calculations and corresponds to 10^-14 seconds. As in previous work (Rahman, 1964; Verlet, 1967) this was found to be sufficiently small to allow the particle motions to be calculated accurately.
In fact using timesteps of $5 \times 10^{-15}$ and $10^{-14}$ seconds in two test runs using the same initial conditions produced essentially the same final positions after $10^{-11}$ seconds. This value of $\delta t$, $10^{-14}$ seconds, has been used previously by Rahman (1964) and Verlet (1967), who found this value suitable for the Lennard-Jones system.

In his work Rahman (1964) used a predictor-corrector scheme to integrate the equations of motion of 864 particles, with the potential truncated at $2.25\sigma$ where $\sigma$ is the Lennard-Jones parameter. Verlet later used a central difference scheme to calculate $x_i(t + \delta t)$ from the results of two previous timesteps. He truncated the potential at 2.5 or 3.3$\sigma$. Verlet's method of integration is mathematically equivalent to ours. However it was found not to be as computationally stable as the method described by equations 3:4 and 3:5. These latter expressions gave much better conservation of energy and momentum than Verlet's scheme when used on the IBM/360. Even so it was necessary to correct the total momentum of the system at each timestep. $v_e^*(t)$ the error in the total momentum is calculated by

$$v_e(t) = \frac{1}{N} \sum_{i=1}^{N} v_i^*(t)$$  \hspace{1cm} 3:6

Although the momentum was conserved reasonably well for several hundred timesteps, roundoff error began to accumulate beyond that point and became quite apparent after one thousand timesteps. At that point all three components of the total momentum of the system had become negative. This affected the apparent temperature of the system which is defined by

$$T^*(t) = \frac{1}{3N} \sum_{i=1}^{N} (v_i^*(t))^2$$  \hspace{1cm} 3:7

The correction introduced at each timestep by 3:6 affected only the fifth significant figure of the velocities at any time and it eliminated any systematic violation of conservation of energy or momentum. The total energy of the system fluctuated slightly about its mean value within the range $\pm 0.0001$, this fluctuation being independent of the magnitude of the total energy. It appears to depend for the most part on the magnitude of the potential energy. This can be expected
since the total energy is smaller in magnitude than the internal energy which contributes to it. Total momentum was conserved to five significant figures when eqn. 3:6 was employed. Since Verlet used a machine with a longer word length and did not generate as many time steps, this correction was not needed in his calculations.

The expression mod L in eqn. 3:5 refers to the periodic boundary conditions imposed, described in Chapter 2. In our infinite but periodic system we stored only the positions of particles whose x, y, and z coordinates lay in the range (0, L) where L^3 is the volume V of the cubic box. The modulus function in effect changes the 'image' of a particular atom under consideration when necessary. The potential was usually truncated at 8.42 Å in this work, a value which lies between those used by Rahman and Verlet. The effects of this truncation will be described in the discussion of the various results.

In the molecular dynamics calculations the large amount of computing time involved made it necessary to use the minimum amount of core so that the program could be used as a "background" job in a multi-tasking computer system. This was achieved by careful coding of the programs used.

The other major consideration is the program efficiency or speed of operation. The maximum efficiency was achieved with the aid of several techniques. The first was to use the optimizing compiler FORTRAN H. Programs were first developed using the standard FORTRAN G compiler and then recompiled using FORTRAN H. Two runs using identical initial conditions were performed and the results compared. This produced an additional check on the code generated. A book-keeping device similar to Verlet's (1967) was also developed. It was found however that at high densities approximately 80 of the 10^8 atoms in the cube interacted with a particular atom, and consequently that the bookkeeping device did not increase efficiency when a system containing 10^8 particles was considered. However if 256 or more particles were used and the potential truncated at 2.5 Å, a significant saving in time would result from using the book-keeping device. The saving becomes more pronounced when even larger systems are considered.
It was also found that careful selection of the terms to be calculated using double precision arithmetic led to the same accuracy in terms of conservation of energy and momentum as performing all the arithmetic using double precision. Thus the positions, velocities, and energies of particles could be stored in single precision, without increasing the numerical error. This meant a significant saving in core and in magnetic tape used to record the information. These adjustments were of necessity made on a trial and error basis.

The most significant time-saving feature was developed for use with the Barker-Bobetic potential or any other function with a complex mathematical formula. Instead of evaluating the function \( u(r) \) itself at the desired value of \( r \), the range of \( r \) from 0.8 to 2.5 \( \sigma \) was broken into one hundred segments, equi-distance in \( \frac{1}{r^2} \). The coefficients of the Lagrangian four-point interpolation formulae were tabulated for each of these segments. The energy was then calculated by first finding which segment the value of \( r \) of immediate interest belonged to, and then using the appropriate Lagrangian interpolation formulae such that the required value of \( u(r) \) was found in the middle panel. The first derivative of \( u \) can also be calculated by analytic differentiation of the interpolation formula. The method reproduced the correct values of \( u \) and \( u' \) to five significant figures. It is therefore believed that no additional error has been introduced by using this technique. The saving in time is phenomenal. The energy is evaluated each time using four multiplications, rather than ten multiplications, three divisions, an exponential and a square root. The number of additions is also significantly reduced. Running time was reduced by a factor greater than ten by using this technique. This occurred since the evaluation of the potential is the most time-consuming part of the molecular dynamics calculations.

The reason for selecting distances on the basis of the value of \( \frac{1}{r^2} \) is that the quantity of \( r^2 \) arises naturally in the calculation of the separation of atoms. Fitting to \( \frac{1}{r^2} \) meant that the shortest segments in terms of \( r \) then appeared in the region \( r < \sigma \) where the potential changes most rapidly. Where higher derivatives of \( u \) are used in the calculation, Lagrangian
coefficients of the second and fourth derivative were also tabulated. \( u, u'' \) and \( u^{(iv)} \) were then calculated using the Lagrangian formulae and \( u', u''' \) and \( u^{(v)} \) calculated by analytical differentiation of the Lagrangian formulae for \( u, u'' \) and \( u^{(iv)} \) respectively.

Using this technique it is possible to perform molecular dynamics calculations using the Barker-Bobetic potential at a rate comparable to that obtained using the Lennard-Jones potential. The mathematical simplicity of the potential used is no longer important in the machine calculations. It has been used consistently throughout this work, except in development programs used to check the accuracy of this method.

The internal energy of the liquid arising from the truncated potential was calculated at each timestep and these values recorded along with the instantaneous pressure on a magnetic tape. The position, velocity and energy of each particle was also recorded as was the force acting on it.

The initial calculations were performed on a system at a high density with a temperature of 250K. In order to reach an equilibrium configuration the equations of motion were solved for 2000 timesteps. At this point the system was in a configuration typical of the fluid state. The temperature was then lowered in several stages by dividing each velocity by an appropriate factor. The molecular dynamics calculations then proceeded until the temperature fluctuated about a constant value. This took several hundred timesteps. These initial results for a non-equilibrium configuration were discarded. A chain of some 5000 subsequent timesteps was generated and the values recorded as the results for the equilibrium liquid. These values were used in the later analysis. The next thermodynamic point to be investigated at that density was initialized by taking the last configurations from the previous run. All the velocities were then multiplied by an appropriate value, thus effectively changing the temperature. This system was then brought to equilibrium by integrating the equations of motion for several hundred timesteps. At this point the information generated was once again recorded for a further 5000 timesteps. In this manner results for several temperatures and the same density were generated. In order to begin
Figure 3:1

The Secular Change in Temperature.
calculations at a new density, all the coordinates of the atoms were multiplied by the same factor. This procedure was used to generate configurations of lower density each time, thus preventing two atoms being brought improbably close together, as could happen if the change were to a higher density. Again the system was allowed to reach equilibrium and the subsequent results recorded. The initial high temperature calculations were designed to 'melt' the original solid configuration. After the system had been cooled to temperatures of interest the procedure used kept the system near equilibrium during each change of temperature or density.

The point at which equilibrium is reached in molecular dynamics calculations is rather difficult to define. In their study of hard spheres at several densities Wainwright and Alder (1958) found that the system could spontaneously change from the 'solid' to the 'fluid' state and back again. This effect was not observed with the larger number of particles used here possibly because our densities were always significantly less than the solid densities. The systems started in an equilibrium liquid configuration and remained in this type of configuration at all times. This is most easily demonstrated by examining values of the diffusion coefficients discussed in the next chapter. If the system had solidified, exceptionally low values of the diffusion coefficient would have been observed. When the system being described was disturbed by a change of temperature or density it was found that the temperature changes from one timestep to another were initially monotonic. The temperature thus tended towards a final value which it later oscillated around. The behaviour is shown in figure 3:1. This initial change is the 'secular change of temperature' mentioned by Rahman (1969) in his review article. His definition of equilibrium appears to be appropriate to our calculations, since his system exhibits the same general behaviour. The initial change of temperature comes about as kinetic and potential energy are redistributed to their equilibrium proportions. This redistribution proceeds rapidly, completing in $4 \times 10^{-13}$ sec.
To summarize this section, for a specific temperature and pressure the relevant information about a system of 108 particles interacting through the truncated Barker-Bobetic potential was recorded. The record is about 5000 configurations long and these configurations are all at equilibrium. Finally \( U_0 \) and \( P_0 \), the short range energy and pressure as defined in Chapter 2, were also recorded for each configuration.

3.3 Perturbation Expansion Calculations

It was found that the perturbation terms in equations 2:13 and 2:14 varied much less than \( U_0 \) and \( P_0 \). This is in agreement with the results of Barker et al (1971) where the perturbation terms were obtained using the Monte Carlo method. Therefore \( U_3, U_2 \) and \( U_Q \) were only calculated at every 25th timestep. These results were then used to calculate the internal energy and pressure. The choice of every 25th timestep was made so as to give a total of 200 distinct configurations at which the perturbation terms were investigated. This is rather more configurations than were used by McDonald and Singer (1969) for three-body forces but they did not consider fluctuation terms. Three hundred or more configurations were used in the Monte Carlo calculations of Barker et al (1971). The values appearing in table 3:2 show that 200 configurations are sufficient for this work considering the larger statistical errors in the molecular dynamics results.

<table>
<thead>
<tr>
<th>No.</th>
<th>( U_2 )</th>
<th>( U_3 )</th>
<th>( U_Q )</th>
<th>( P_2 )</th>
<th>( P_3 )</th>
<th>( P_Q )</th>
</tr>
</thead>
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<td>25</td>
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<td>-69.61</td>
<td>89.29</td>
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<td>-216.3</td>
<td>384.0</td>
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<td>88.93</td>
<td>18.43</td>
<td>-219.8</td>
<td>385.4</td>
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<td>382.7</td>
<td>61.1</td>
</tr>
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<td>125</td>
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<td>-217.9</td>
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<td>17.86</td>
<td>-217.3</td>
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<td>17.83</td>
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<td>380.1</td>
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<td>216</td>
<td>-69.26</td>
<td>87.85</td>
<td>17.59</td>
<td>-217.5</td>
<td>379.5</td>
<td>56.9</td>
</tr>
</tbody>
</table>
The long range two-body corrections were calculated in the following manner. We begin with the original cube of side length $L$ containing 108 atoms. For convenience let one atom lie at the origin and the nearest image of another lie at $(X, Y, Z)$. Then in the infinite cube there will also be atoms at $(X \pm L, Y \pm L, Z \pm L)$ interacting with the atom at the origin. If $X^2 + Y^2 + Z^2 < R$, the length at which the potential was truncated, then the atom within the original cube has already been considered. Otherwise it and the 8 images mentioned are included in the sum $U_2$ and $P_2$, providing they are separated from the first atom by a distance less than 1.5$L$. If the separations meet this criterion, then the interaction energies and pressures are calculated; otherwise they are not. The procedure is then repeated for the other 107 atoms in the original cube. Half of the energy sum then belongs to the interaction energy of the atoms in the original cube and half to those outside. The interaction contributing to the pressure $P_2$ is obtained in a similar manner. From the values $U_0$ and $P_0$ of this configuration, stored on magnetic tape, and the values $U_2$ and $P_2$ calculated here, the required fluctuation terms may be calculated.

The interaction terms $U_Q$ and $P_Q$, for pairs of atoms separated by less than $R$ were also calculated from the 200 perturbation configurations and from these results the fluctuation terms were formed. The quantum contributions for interactions with $r > R$ were estimated by setting the radial distribution function equal to 1 and using the equations

$$<U_Q (r>R)> = 2N \rho \pi \int_R^\infty V^2 u(r) r^2 dr$$

$$<P_Q (r>R)> = -2\pi N \rho \int_R^\infty r \frac{3}{3} (V^2 u(r)) r^2 dr$$

The contributions from these terms were included although they are so small that they can safely be ignored (Barker et al. 1971). The derivation of these equations appears in Chapter 6. The term $U_3$ was then calculated for the same 200 perturbation configurations. All triplets of atoms in the original cube were considered, and if each pair was separated by less than $R$ then this interaction was considered in the sum $U_3$. 
The fluctuation terms were again calculated using \( U_0 \) and \( P_0 \), and \( P_3 \) was calculated using the relation \( P_3 = 3U_3 \) derived in Chapter 2. The long range contributions were evaluated using the integral equation introduced in equation 2.24.

The results of these calculations were averaged over the 200 configurations used. In table 3:3 the various contributions to the internal energy are presented for each of the thermodynamic points at which calculations were undertaken. Table 3:5 contains the analogous results for the pressure. In both tables the fluctuation terms are included with their related averages. The term \( NkT \) related to the kinetic energy is included in the truncated pressure term. Thus in the column labelled \( U_2 \) we have tabulated the values

\[
< U_2 >_0 - \frac{1}{kT} \left[ < U_0 U_2 >_0 - < U_0 >_0 < U_2 >_0 \right]
\]

In this expression and analogous ones involving \( U_3, P_2 \), etc., the value for \( < U_0 >_0 \) must be calculated using the same configurations as were used in the calculation of \( < U_2 >_0 \) and \( < U_2 U_0 >_0 \). The reason for this is that the average of \( U_0 \) over a subset of the configurations is generally slightly different from the average of \( U_0 \) over all configurations. If we examine the original development of the perturbation expansion we see that the definition of \( < U_0 >_0 \) used here is the correct one. Since \( < U_0 U_2 >_0 \) and \( < U_0 >_0 < U_2 >_0 \) are of much greater magnitude than their difference, using the wrong definition of \( < U_0 >_0 \) generally results in the fluctuation term becoming very large, often an order of magnitude greater than \( < U_2 >_0 \).

The results of calculations using the methods described here are presented in the following sections.

3:4 Internal Energy of Argon

The various contributions to the internal energy of argon arising from the atomic interactions are given in table 3:3. In table 3:4 the total potential energy from this is compared with the values calculated by Barker, using the Monte-Carlo methods (Barker et al. 1971) and with experimental measurements. The experimental values are the same as those appearing in Barker et al. (1971) which is included as appendix A to this work. The experimental values were derived by Barker using
### TABLE 3:3

**CONTRIBUTIONS TO THE INTERNAL ENERGY OF ARGON**

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two different methods. The first procedure recalculated the values of the internal energy $E^*$ from the PVT data of Streett and Stavely (1969), correcting an error of 20 cal/mole in their published values. The second set of data are believed to be the best estimates available for the internal energy of liquid argon. A full description of the method by which they were obtained appears in the appendix to Barker et al. (1971). The procedure used was adopted to reconcile differences between the experimental values of the specific heat along the saturation curve $C_\sigma$ derived from different experiments. The values of $C_\sigma$ measured by Walker (1958) and Jones and Walker (1956) and those calculated by Streett and Stavely (1969) using the equation

$$C_\sigma = (\frac{3E^*}{\partial T})_\sigma + 1.5 Nk + P (\frac{3V}{\partial T}_S)_\sigma$$

differ by up to 22%. This is unlikely to be due to an error in the measurement of $C_\sigma$. The final values listed under "present" in table 3:4 were derived from a value of -1545 cal./mole for the latent heat at the boiling point after consideration of six different experimental values. The values of $C_\sigma$ were then increased by 4.5% and $U_1$, the internal energy along the saturation curve was then recalculated. The internal energy was then calculated using $U_1$ and the PVT data and procedure of Streett and Stavely (1969). These results should be the best estimates for $U$ available from present experimental values. The experimental error is estimated at ±15 cal/mole.

The agreement between the three sets of data is excellent throughout. The calculated values using both molecular dynamics and Monte Carlo techniques lie within the range of experimental error except for one point at the lowest density considered where the difference between the calculated value and the experimental value, interpolated from Levelt's (1960) tables is 22 cal/mole. The excellent agreement between the molecular dynamics and Monte Carlo results indicates that there is no systematic difference between the methods. The statistical error in the Monte Carlo results for the internal energy (Barker et al. 1971) was estimated at ±2 cal/mol.
**TABLE 3.4**

**COMPARISON OF RESULTS FOR THE INTERNAL ENERGY OF ARGON**

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<th>( T^0 \text{K} )</th>
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<th>( U_{MC} )</th>
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<th>( U_{EXPT(b)} )</th>
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<td>- 586</td>
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<td>- 532</td>
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<td>91.92</td>
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<td>- 455</td>
<td>- 463</td>
<td>- 463</td>
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</table>
The error in the molecular dynamics calculations has been estimated using the standard statistical error, similar to that described by Wood (Temperly, Rowlinson and Rushbrook, 1968). The expected error in the calculated values of some property \( X \) should be less than \( \Delta X \) defined by

\[
\Delta X = \pm \left( \frac{1}{m-1} \sum_{i=1}^{m} (\bar{X} - \bar{x})^2 \right)^{1/2}
\]

Here \( \bar{X} \) is the average value of \( X \) over 100 configurations and \( \bar{x} \) is the average of \( X \) over all configurations. \( m \) is the number of values of \( \bar{X} \) available from the full 5000 molecular dynamics configurations generated. Using this formula we have calculated the expected error in the temperature and energy at four points. These are listed in table 3:4 along with the average values.

In the liquid region the temperature is known to \( \pm 2^\circ K \) whilst in the dense gas region the error is larger at \( \pm 5^\circ K \). Similar behaviour is observed for the internal energy, where the error is \( \pm 8 \) cal/mole in the liquid region and \( \pm 20 \) cal/mole in the gas state. The agreement with Monte Carlo results indicates that these error bounds are probably rather conservative.

Barker et al. (1971) found that the pressures predicted by the Barker-Bobetic potential were slightly high in the liquid state. On the other hand the pressures obtained from the Barker-Pompe potential (1968) were found to be too low. Therefore a new potential was suggested of the form

\[
U = U_{BB} + x (U_{BP} - U_{BB})
\]

where \( U_{BP} \) and \( U_{BB} \) are the Barker-Pompe and Barker-Bobetic potential respectively. This new potential gave pressures that were in excellent agreement with experimental pressures using Monte Carlo methods and \( x = .25 \). All the molecular dynamic calculations used the Barker-Bobetic potential. However since the two potentials differ only slightly it was decided to investigate the new potential using perturbation theory; by treating the difference between the Barker-Pompe potential and the Barker-Bobetic potentials as a perturbation on the Barker-Bobetic potential we obtain another three terms in equation 2:12 in the perturbation expansion for \( U \) described in Chapter 2. These have the same form as those involving \( U_2 \), with \( U_2 \) replaced by \( .25 (U_{BP} - U_{BB}) \). We may then calculate
the internal energy for the latest potential of Barker et al. (1971), a linear combination of the Barker-Bobetic and Barker-Pompe potentials. It was found that at 103.1° and 26.26 cm³/mole the Barker-Pompe, Barker-Bobetic and present Barker potential give internal energies of -1454, -1442 and -1445 cal/mole respectively. At 83.6° and 28.85 cm³/mole the corresponding values are -1426, -1421 and -1422 cal/mole. The three potentials thus give essentially the same value for the internal energy, confirming the results obtained using the Monte Carlo methods (Barker et al. 1971). As a final point we note that our agreement with experimental values is much better than was found using the Lennard-Jones potential (McDonald and Singer, 1969; Verlet, 1967). In fact since our results lie within the experimental error bounds we cannot really improve upon them.

3.5 Equation of State of Argon

The various contributions to the pressure of argon are presented in table 3.5. In table 3.6 the total pressure is compared with the Monte Carlo results of Barker (Barker et al. 1971) and the experimental values of Streett and Stavely (1969). The agreement between the two methods of calculation is excellent throughout, being consistently within the error bounds of the molecular dynamics calculations. Agreement with experimental values is also quite pleasing. The greatest discrepancy occurs at T = 103°, V_M = 27.85 cm³ where the pressure is 68 atm high. The error bounds on the pressure have been calculated for the truncated-two body potential using the statistical formula, equation 3.11 from the previous section. We thus consider fluctuation of the terms

\[ P_0 V = NkT - \left< \frac{\partial U_0}{\partial V} \right> \]

Unlike the Monte Carlo study both T and \( \left< \frac{\partial U_0}{\partial V} \right> \) fluctuate at each time step. The error is then the sum of the errors in both terms. In fact the error bounds were found for \( \frac{P_0 V}{NkT} \) since there is likely to be some correlation between the two terms in equation 3.13.

It appears that the calculated pressures in the liquid state are slightly high on average compared with experiment.
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<th>$P_3$</th>
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Therefore we have investigated the effect of using the new Barker potential described in the previous section. Using similar perturbation techniques to those described previously, we found that at $T = 103^\circ K$, $V_M = 26.26 \text{ cm}^3$ the pressure is reduced by 108 atm when the new potential is considered. At $T = 83^\circ K$, $V_M = 27.85 \text{ cm}^3$ the reduction is 79 atm. The pressure is thus significantly reduced by use of this potential. These perturbation calculations have confirmed the Monte Carlo results reported in Barker et al. (1971), and when combined with those points indicate that the new potential gives results that are in excellent agreement with experiment. Considering both our results and those described in Barker et al. (1971) future investigators should use the new potential.

McDonald and Singer (1969) found that for the Lennard-Jones potential on average their values for the pressure (using 108 particles) were some 20 atm lower than those of Verlet (1967) (using 864 particles) and somewhat more scattered about the experimental values. No such systematic difference between our results and those of Barker is apparent, but it should be noted that we have both used the same number of particles. On the other hand the correction for the long range two-body interactions has been made using perturbation theory in our case and the uniform liquid approximation by Barker. A comparison of the results for this quantity indicates that the error bounds on his approximation of ±10 atm are reasonable. Truncation of the potential at 2.5σ rather than at 4σ does not seem to have had any systematic effect on the final results obtained either. Individual contributions to the pressure and the energy have been compared as calculated by the two methods. The differences between these contributions for the two methods is often somewhat greater than the differences between the totals. There appears to be some compensation of errors between the different techniques. The effect of different numbers of particles could be investigated but again the amount of computation needed is formidable.

It appears then that the results obtained are very satisfactory. The Barker-Bobetic potential has given better agreement with experiment than the Lennard-Jones potential, as expected, and use of the new potential gives even better
### TABLE 3:6

**COMPARISON OF RESULTS FOR THE PRESSURE OF ARGON**

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agreement with experimental pressures, without significantly changing the estimates of the internal energy. We have not yet considered the specific heat results, which appear in the following section.

3:6 The Specific Heat of Argon

While the perturbation terms were being calculated, contributions to the specific heat were also obtained. In table 3:7 we find the contributions to $C_V$ obtained using the fluctuation of $U_0$ only, using the temperature fluctuations, and using the canonical ensemble expression, eqn 2:19, without perturbation terms. This last value is included only to show that in fact the choice of an expression appropriate to the ensemble used eliminates significant error in the values calculated. The canonical ensemble expression for $C_V$ seriously underestimates fluctuations in the microcanonical ensemble. Experimental values of the specific heat at constant volume along the saturated vapour pressure curve are also listed although no attempt has been made to correct these for the pressures considered. Because the total energy fluctuates slightly in our molecular dynamics calculations the specific heats calculated from temperature fluctuations are not exactly the same as those calculated from energy fluctuations. This difference gives some estimate of the statistical error in these results. Barker has communicated a value of $C_V$ at $T = 83.6^\circ$, $V_m = 27.85$, calculated using the Monte Carlo method. His value lies between ours in this case. In addition Barker has also calculated the contributions to the specific heat from the perturbation terms. Their effect is to raise the specific heat by less than 3%. Our estimated error is rather greater than this and so we have not used terms to correct our expressions for the specific heat. We do expect our results for the specific heat of argon to be about 2% lower than the correct result at each point in the liquid region. These corrections are unlikely to be significant for gaseous argon.

Our comparison with experimental results is speculative since we are dealing with different thermodynamic points.
### TABLE 3:7

**SPECIFIC HEAT OF ARGON**

All values in Units of cals deg⁻¹ mole⁻¹

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<th>( C_V(E) )</th>
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</tbody>
</table>
Our values for the specific heat are larger than those determined experimentally. It is difficult to say more than this without knowing the statistical error bounds on our results. From the values tabulated these must be less than 5 cal/mole/deg. Finally, since the specific heat is related to the variance of the energy and temperature, any numerical error resulting from roundoff or finite differencing will tend to increase our calculated specific heats. This effect is apparent in a comparison of the specific heats calculated by Barker (1971) with ours. His statistical error is smaller than ours and his specific heats are also smaller than ours, by about 0.4 cal/mole on average. This has been attributed to the greater statistical error in our calculations, rather than a systematic difference between the two methods used.
CHAPTER 4
DIFFUSION, VISCOSITY AND THERMAL CONDUCTIVITY OF ARGON

The equilibrium properties of fluid argon have already been discussed. The success of these calculations was most encouraging, and we therefore extend our investigations to the study of non-equilibrium properties. Three of the properties of interest in the study of argon are the coefficients of diffusion, viscosity and thermal conductivity. As we will show, the necessary information for the calculation of these coefficients using currently accepted theories was recorded during our calculation of equilibrium properties. The theory of linear transport will be described and then the results of our calculations will be compared with experimental measurements. Since the diffusion coefficient is the simplest of the three properties both to describe and calculate, we will discuss it first.

4:1 The Self-Diffusion Coefficient

The diffusion coefficient was first discussed from a molecular viewpoint by Einstein in 1905, in connection with his theory of Brownian motion. He used the theory to describe the motion of a macroscopic particle in a fluid of microscopic atoms. The approach has been extensively studied by many authors since that time (Zwanzig, 1965). This subsequent work has resulted in an expression for the diffusion of one particle in a fluid of identical particles. In this case, we no longer have the large mass difference inherent in Brownian motion although the mathematical expression remains unchanged. The derivation discussed here, due to Helfand (1960), was chosen to convey a physical picture of the process rather than for its mathematical rigour. More rigorous derivations of the results are described in the review paper of Zwanzig (1965).

We consider a canonical ensemble whose time behaviour is known. Subsets of this ensemble are chosen such that at time \( t = 0 \), the \( i \)th particle in each member has the same \( x \) coordinate, \( x_i^0 \). The proportion of systems in the subensemble which have \( x \) coordinate \( x_i^t \) at time \( t \) is given by the conditional probability \( C_i(x, t|x_i^0) \ A_x \ dx \) where \( A_x \) is the cross-sectional
area perpendicular to $x$. $C_i$ is then the concentration of systems in the subensemble characterised by $x_{io}$ whose $i$th particle lies in the plane $x = x_{it}$. This concentration will obey the continuity equation

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot J_i$$  

where $J_i$ is the particle diffusion current. We now make the assumption that for sufficiently long times, $J_i$ obeys the macroscopic diffusion law

$$J_i = -D\nabla C_i$$

which defines the diffusion constant. Combining equations 4:1 and 4:2 gives Fick's law for diffusion,

$$\frac{\partial C_i}{\partial t} = \frac{1}{\delta x^2} \frac{\partial}{\partial x^2} C_i$$

In order to solve this equation for $D$ we apply the initial and boundary conditions

$$C_i(x, 0 | x_{io}') = \delta(x - x_{io}') / A_x$$

and

$$C_i(\pm \infty, t | x_{io}') = 0,$$

where $\delta(x)$ is a delta-function.

The first condition follows since at time $t = 0$ all the particles in the subensemble are at $x_{io}'$. Since no particle can reach $x = \pm \infty$ in finite time from $x_{io}'$, the second condition is also valid. The solution of 4:3 with the initial and boundary conditions 4:4 and 4:5 is

$$C_i(x, t | x_{io}') = \frac{1}{2A_x \pi Dt} \exp \left[-\frac{(x - x_{io}')^2}{4Dt}\right]$$

We may consider this Gaussian function to be the broadened form of the original delta function and that it defines our knowledge of the $x$ coordinate of atom $i$ at time $t$, given that at time zero its $x$ coordinate was $x_{io}'$.

The spread of a Gaussian is characterised by its second moment, $M_2$ in this case

$$M_2 = \int_{-\infty}^{\infty} (x - x_{io}')^2 C_i(x, t | x_{io}') \, dx = \frac{2}{A_x}$$
If we now reassemble our original ensemble and integrate over initial positions of atom \(i\), the second moment becomes an ensemble average divided by the area spanned by the subensembles.

\[ M_2 (x_i - x'_{i0}) = \langle (x_i - x'_{i0})^2 \rangle = \frac{2Dt}{A_x} \quad 4:7 \]

The equation for the diffusion coefficient is then

\[ D = \frac{1}{2t} \langle (x_i - x'_{i0})^2 \rangle \quad 4:8 \]

Substituting

\[ (x_i - x'_{i0})^2 = \int_0^t \int_0^t v(s) v(r) \, dr \, ds \]

and changing variables to

\[ a = \frac{r + s}{2} \]
\[ b = \frac{r - s}{2} \]

we obtain

\[ 2t \int_0^t \int_0^t v(a+b) v(a-b) \, db \, da \quad 3(a,b) \]

Since our results are independent of time origin

\[ = \int_0^t \int_0^t v(2b) v(o) \, db \, da \quad 3(a,b) \]

Thus

\[ D = \int_0^t \frac{(1 - b)}{t} \langle v(b) v(o) \rangle \, db \]

Providing the velocity autocorrelation \(\langle v(b) v(o) \rangle\) vanishes sufficiently strongly for infinite time, we may extend the upper limit of integration to \(\infty\). We then have

\[ D = \int_0^\infty \langle v(b) v(o) \rangle \, db \quad 4:9 \]

The form of the velocity autocorrelation function at high and low density appears in figure 4:1.

Diffusion is typical of transport processes in several ways.
Figure 4:1

The Velocity Autocorrelation Function.
The great difference between transport and equilibrium properties is that the time evolution of the system must be known before transport can be studied. Equilibrium properties can be calculated from ensembles with no information about the time evolution of the systems in the ensemble. Transport coefficients involve correlations between the properties of a system at different times. Molecular dynamics calculations by their very nature provide the required information about time development. In the next chapter equilibrium properties of the solid are calculated using Monte Carlo methods, and as we shall see this method gives no information about the time development of the system. The length of time over which we consider our time dependent correlations is also important. In equation 4:8 the time \( t \) must be less than the Poincare recurrence time (Huang, 1965, p.88) which we expect to be very long. It must also be long enough so that the hydrodynamic process in equation 4:3 is valid. Uhlenbeck and Ornstein (1930) in work on the Langevin equation, estimate that this is valid for

\[
4:10 \quad t \gg \frac{m}{D/kT}
\]

The result for the onset of hydrodynamical behaviour, eqn. 4:10 has been quoted as applying to self-diffusion as well as Brownian motion (Helfand, 1960). In the following sections it will be seen that other transport coefficients have pairs of expressions analogous to equations 4:8 and 4:9. We will first describe the results of our calculations of the self-diffusion coefficient of argon.

4:2 Calculation of the Self-Diffusion Coefficient

The molecular dynamics calculations used to simulate fluid argon were described in Chapter 2. The coordinates and velocities stored on tape were analysed to calculate diffusion coefficients in the following manner. Both equations 4:8 and 4:9 were extended by averaging over the three coordinates and all 108 particles, giving an average of 324 values for a particular time origin and correlation time \( t \). When using equation 4:8, we averaged over 167 initial times separated by \( 1.5 \times 10^{-13} \) seconds. The expectation \( \left< (x(t) - x(0))^2 \right> \) was then calculated for 400 values of \( t \) between \( 1 \times 10^{-11} \) seconds and \( 1.4 \times 10^{-11} \) seconds. The slope of these values plotted against time, was then calculated by the method of
least squares. For comparison 400 estimates of D from equation 4:8 were calculated and averaged to give another estimate of D. There was no significant difference between these two values. The value of $10^{-11}$ seconds satisfies equation 4:10 since the value of $mD/kT$ is approximately $10^{-12}$ seconds for dense gaseous argon and $10^{-13}$ seconds for the liquid. The results of these calculations appear in Table 4:1. $D_{AV}$ refers to the average of calculations of D at various times using equation 4:8, $D_{LSQ}$ was calculated as the slope of the least-squares fit to $<(x(t) - x(o))^2>$ vs. t. The use of periodic boundary conditions meant that the positions stored on the tapes were not all for the same image of a particular particle. Therefore before using equation 4:8 we generated positions for one set of images of the 108 particles using an initial configuration and the recorded velocities. A record 3900 time-steps long was formed. If this had not been done there would have been discontinuities in the positions, drastically altering the diffusion coefficient. Diffusion coefficients were also calculated using the extended form of equation 4:9 for values of t from 0 to $10^{-12}$ seconds at intervals of $5 \times 10^{-14}$ seconds, and from $10^{-12}$ to $10^{-11}$ seconds at intervals of $2 \times 10^{-13}$ seconds.

The velocity autocorrelation function was formed at these points and then integrated by application of Simpson's rule. The values calculated appear in table 4:1 as $D_{AUTO}$.

Comparing the values $D_{AV}$, $D_{LSQ}$ and $D_{AUTO}$, we see that there is no systematic difference between the three methods of calculating the diffusion coefficient. It is believed that the most accurate values are given by the column labelled $D_{LSQ}$. Averaging the values of D as in $D_{AV}$ ignores the fact that neighbouring estimates are highly correlated with each other. The values of $D_{AUTO}$ are subject to a certain amount of error since the velocity autocorrelation function is nearly zero over a major part of the region studied, at least in the liquid state. Due to statistical fluctuations some of the calculated values are not zero. Summing a large number of values that sum to nearly zero can lead to a greater percentage error than summing similar terms that add to a larger number.
<table>
<thead>
<tr>
<th>$T^0\text{K}$</th>
<th>$V_M$</th>
<th>$D_{AV}$</th>
<th>$D_{LSQ}$</th>
<th>$D_{AUTO}$</th>
<th>$D_{EXPT\ (135 \text{ atm})}$</th>
<th>$D_{MD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>89.6</td>
<td>26.26</td>
<td>.98</td>
<td>.80</td>
<td>.71</td>
<td>1.39</td>
<td>1.01</td>
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<tr>
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<td>27.04</td>
<td>1.52</td>
<td>1.55</td>
<td>1.45</td>
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<tr>
<td>87.9</td>
<td>27.04</td>
<td>1.50</td>
<td>1.50</td>
<td>1.32</td>
<td>1.27</td>
<td>1.38</td>
</tr>
<tr>
<td>94.1</td>
<td></td>
<td>1.43</td>
<td>1.37</td>
<td>1.28</td>
<td>1.71</td>
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</tr>
<tr>
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<td></td>
<td>1.51 (b)</td>
<td>1.39 (b)</td>
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<td>1.46</td>
<td>2.54</td>
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</tr>
<tr>
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<td>27.85</td>
<td>1.74</td>
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<tr>
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<td>2.46</td>
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<td>156.9</td>
<td>57.45</td>
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<td>20.4</td>
<td>21.3</td>
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<td></td>
</tr>
<tr>
<td>168.9</td>
<td>65.66</td>
<td>24.0</td>
<td>27.6</td>
<td>26.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>159.1</td>
<td>70.71</td>
<td>24.6</td>
<td>25.8</td>
<td>25.9</td>
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<td></td>
</tr>
<tr>
<td>158.7</td>
<td>76.60</td>
<td>24.9</td>
<td>25.6</td>
<td>27.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>159.1</td>
<td>91.92</td>
<td>33.8</td>
<td>29.6</td>
<td>33.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.4 (b)</td>
<td>26.8 (b)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Thus we believe that the most accurate calculations here are those using the mean square fluctuation approach. The error in autocorrelation function calculations has been discussed by Zwanzig and Ailawadi (1969). Application of Zwanzig and Ailawadi's theoretical development to the velocity autocorrelation function by Levesque and Verlet (1970) resulted in an estimated error bound of ± 5% for 864 particles and 1200 timesteps. For 108 particles and 3900 timesteps as used here the expected error is about ± 9% for the liquid values.

Two additional values of $D_{LSQ}$ and $D_{AV}$ are given at $94^\circ K$ and 27.04 cm$^3$/mole and $159^\circ K$ and 91.92 cm$^3$/mole. These values were calculated using a least squares fit to $<(x(t) - x(o))^2>$ vs. t for values of t between $5 \times 10^{-12}$ and $9 \times 10^{-12}$ sec., and are denoted by (b) in table 4.1. From these values and those tabulated by Levesque and Verlet it appears that the onset of hydrodynamic behaviour occurs more quickly than equation 4:10 implies. This has been assumed previously by Levesque and Verlet (1970) and the plot given by Rahman (1964) of $<(x(t) - x(o))^2>$ also supports this result, for the plot becomes linear very quickly.

In table 4.1 we have also listed values of $D_{MD}$. These were calculated from Levesque and Verlet's (1970) results for the diffusion coefficient using their interpolation formula

$$D \times 10^5 = \frac{0.005712}{\rho^2} T + 0.8236 - 6130 \rho$$

This empirical formula was fitted to his results for the diffusion coefficient. It was converted to physical units from his reduced units and values of D calculated at the same temperatures and densities as those used in this work. Levesque and Verlet (1970) state that this formula overestimates D by at least 5% for T <120$^\circ K$, and so we have lowered all their values by this amount. Their results are very similar to those reported here. On the basis of this comparison the diffusion coefficient does not seem to be very sensitive to the form of the intermolecular pair potential.

The experimental values for a pressure of 135 atm. were calculated using the interpolation formula suggested by Naghizadeh and Rice (1962).

$$D = 0.89 \times 10^{-3} \exp (-373/T)$$
This formula was obtained by a least squares fit to their experimental diffusion coefficients of argon, obtained at 135 atm. Since the diffusion coefficient decreases with increasing pressures we would expect their values to lie consistently above ours. This result has not been observed. If we use their formula at 12 atm, \( D = 1.16 \times 10^{-3} \exp\left(-352/T\right) \), to obtain the diffusion coefficient at 84°C we obtain the value \( 1.74 \times 10^{-5} \text{ cm}^2/\text{sec} \). This differs from the result of Cini-Castagnoli and Ricci (1960) at .92 atm. and 84°C of \( 1.53 \times 10^{-5} \text{ cm}^2/\text{sec} \). Besides discussing some of the experimental difficulties involved in measuring the diffusion coefficient of argon, Mills (1970) quotes an extrapolated value of \( 1.77 \times 10^{-5} \text{ cm}^2/\text{sec} \) for Naghizadeh and Rice at .92 atm and 84°C. In addition to the experimental disagreements mentioned a further point must be noted. The experimental values represent the tracer diffusion of one isotope of argon in another. The molecular dynamics calculations give results for the self diffusion of a liquid interacting through the truncated Barker-Bobetic potential. Since we are not using the full potential for argon our results do not represent argon values. It is expected however that they will be quite close to the desired values. The reason for our apparently high values may be explained either by experimental error or by this last comment.

It was originally intended to correct our diffusion results to give argon values by means of a perturbation theory. Two such perturbation theories have been developed to date, the first by Frisch and Berne (1965) and the second by Watts (1971b). Unfortunately subsequent work by Watts (1971a) has shown that the first is invalid and the second theory has also been shown to be incorrect (Harris, 1971). Further theoretical developments are necessary before the self-diffusion coefficient of argon can be extracted from our results.

It can be seen that the values calculated show a reasonable temperature and pressure dependence. Under the restrictions implied by the previous discussion there is good quantitative agreement with the tracer diffusion coefficient of argon.
The diffusion coefficients reported here could be calculated with greater accuracy by using the full 5000 timesteps and more initial times. However the considerable expenditure of computer time needed to do this does not appear to be justified at the present time for the following reasons. We cannot correct for long range and three body effects on the diffusion coefficient, since no computationally feasible perturbation theory is available. The perturbation theory given by Harris (1971) appears to be correct but it is too complex to be implemented. In addition to these improvements in the theory further experimental work should also be undertaken to see whether systematic differences can be detected between experimental and calculated values. The theoretical results given here are sufficiently accurate for this purpose. Further analysis of this data may be justified at some future date, but not before major advances in both theory and experiment have occurred.

In their study of the transport coefficients of a hard sphere fluid, Alder, Gass and Wainwright (1970) report several qualitative features of the diffusion coefficient that are of interest. These appear in figure 4:1 describing the shape of the velocity autocorrelation function. The density dependence of their autocorrelation function is qualitatively similar to ours. At low densities the negative portion of the velocity autocorrelation does not appear in our results or theirs, and the equivalent Langevin autocorrelation function lies below the observed function. At low densities the opposite is true. The shape of the velocity autocorrelation function at high densities is similar in form for hard spheres, the Barker-Bobetic potential, and the Lennard-Jones potential (Rahman, 1964; Levesque and Verlet, 1970). It is only the small difference in detail that do lead to different quantitative results.

In order to compare our results with those derived using the Langevin equation, in figure 4:1 we have plotted the velocity autocorrelation predicted by the Langevin approach for the values of \( D \) studied. At all densities this approach predicts that the velocity autocorrelation function will take the form of a decaying exponential.
Detailed studies of the form of the decay of the velocity autocorrelation function for a system of hard spheres have been reported by Alder and Wainwright (1970). In their work they show that the velocity autocorrelation function decays to zero as \((nt)^{-d/2}\) where \(n\) is the viscosity and \(d\) the dimensionality of the system being studied. They also described a vortex motion observed in their molecular dynamics calculations for hard discs (Alder and Wainwright, 1970). Andriesse (1970) then showed that a decay of the form \((nt)^{-d/2}\) applied to argon resulted in improved agreement between experimental and calculated values of the dynamic structure factor \(S_g(Q,\omega)\) described in Chapter 6. This gives experimental evidence that the long term decay of the autocorrelation function for argon shows the same behaviour. It is simpler to obtain a high accuracy in the velocity autocorrelation functions using hard spheres since the calculations proceed more rapidly than in our work. The 5000 timesteps obtained by us gives insufficient accuracy in our liquid results to enable this effect to be studied.

Another area that has been studied by several workers is the derivations of memory functions (Mori, 1965; Zwanzig, 1961). They have been studied in connection with molecular dynamics and the study of diffusion, using both the Lennard-Jones potential (Levesque and Verlet, 1970) and Stockmayer potential (Harp and Berne, 1970). In this approach the time evaluation of the autocorrelation function is modelled using arguments similar to those appearing in the theory of Brownian motion. Varied success is reported in these papers on the application of approximate memory functions to the study of real systems.

The calculated diffusion coefficient as a function of time is also of interest. This shows how diffusion varies before hydrodynamic behaviour begins. In figure 4:2 at high densities the value of the diffusion coefficient is plotted as a function of time. It rises from zero to a peak value and then falls steadily for some time. Similar behaviour was observed by Alder, Gass, and Wainwright (1970) at high densities. Using the mean-square fluctuation approach it was found that the value of \(D\) reached a maximum at \(1.5 \times 10^{-13}\) sec. In some
Figure 4.2

The short time behaviour of the high density diffusion coefficient.
cases it was still falling to its true value after \(4 \times 10^{-12}\) seconds. It was thus approaching its true value from above. It was because of this behaviour that \(D\) was calculated using \(\langle (x(o) - x(t))^2 \rangle\) with \(t\) greater than \(10^{-11}\) seconds in our reported values. At lower densities it was found that \(D(t)\) approached its true value from below in about the same time as in the case just discussed. An example appears in figure 4:3. In figures 4:2 and 4:3 the long time value from table 4:1 is also shown.

In addition from our results the temperature dependence of this behaviour can also be seen. The difficulty in relating hard sphere results to real systems lies in the fact that in this case time temperature dependence is not observed. Hard sphere systems are defined using only time and density. With the real system this is not so and results can be examined for separate time and temperature dependence. Our statistics for the short time behaviour are rather poor here (the averages are over 100 points and 40 initial times). In the liquid the maximum of its \(D(t)\) is reached at or before \(1.5 \times 10^{-13}\) sec. For different points at the same temperature the ratio of the maximum value at \(D\) to its final value is greatest at high temperatures. At lower temperatures the tendency to "overshoot" is less. This may be seen from the two temperatures shown in figure 4:3 at a reduced density of .825.

The diffusion coefficient has been shown to agree qualitatively and quantitatively with Lennard-Jones results. This indicates that it is not sensitive to the pair potential used. Detailed comparison with experimental results must await more extensive experimental work and development of a suitable perturbation theory. We now consider other transport coefficients using the Linear Response Theory.

4:3 Linear Response Theory of Transport

In the following sections the theory underlying the calculation of the coefficients of viscosity and thermal conductivity is discussed and results of various calculations of these coefficients are presented. We begin with the expression for these coefficients as developed by Helfand (1960).
The short time behaviour of the low density diffusion coefficient.

Figure 4:3

$D(t)$

$10^5 \text{ cm}^2 \text{ sec}^{-1}$

$t = 159.1^\circ K$

$V_M = 91.92 \text{ cm}^3 \text{ mole}^{-1}$

$t$
Similar expressions were developed by other workers in a more rigorous manner (Zwanzig, 1965). However, the simple arguments of Helfand have more appeal in view of the final results.

The development presented here is very similar in form to that for diffusion. A hydrodynamical equation is reduced to an equation of the form

$$\frac{\partial X}{\partial t} = K \frac{\partial^2 X}{\partial x^2}$$

where X is a microscopic property of interest and K is a constant proportional to the constant of interest. The derivatives are with respect to time and position respectively. This equation is then solved with appropriate boundary conditions to give an expression for the desired transport coefficient. The procedure will be outlined for the shear viscosity coefficient. The coefficients of bulk viscosity and thermal conductivity are then deduced by considering the appropriate hydrodynamical equation.

The equation of motion for a volume element in a liquid is given by Euler's equation (Landau and Lifshitz, 1956)

$$\frac{\partial}{\partial t} \left( \frac{m}{V} \mathbf{u} \right) = \nabla \cdot (\mathbf{u} \mathbf{u}) + \frac{1}{V} \mathbf{F}$$

where \( \mathbf{u} \) is the velocity of the volume element and \( \mathbf{F} \) is the external force per particle. We assume that the stress tensor \( \sigma \) has the Newtonian form

$$\sigma = -\mathbf{P} + \varrho \left( \nabla \mathbf{u} + \nabla \mathbf{u}^* \right) - \frac{1}{3} \left( \nabla \cdot \mathbf{u} \right) \mathbf{I} + 2\eta \mathbf{E}$$

\( \mathbf{P}, \varrho \) and \( \eta \) are the pressure and bulk and shear viscosities respectively. The rate of shear tensor \( \mathbf{E} \) is defined by

$$\mathbf{E} = \frac{1}{2} \left( \nabla \mathbf{u} + \nabla \mathbf{u}^* \right) - \frac{1}{3} \left( \nabla \cdot \mathbf{u} \right) \mathbf{I}$$

After linearizing equation 4.14 in \( \mathbf{u} \) and consideration of the symmetry of the problem, we obtain the y component of 4.14 as

$$\frac{\partial}{\partial t} \left( \frac{\varrho}{V} \mathbf{u} \right)_y = \frac{\eta}{\rho} \frac{\partial^2 \mathbf{u}}{\partial x^2}_y$$

At this point we form the connection with microscopic properties. Consider a canonical ensemble. We form subensembles as before. However, in this case we group particles on the basis of both their x coordinate and y momentum. The subensemble with characteristic values \( x_{iy0} \) and \( p_{iy0} \) at time \( t = 0 \) has mean y
velocity \( u_y(x, t|x_{io}, p_{io}) \) at position \( x \) and time \( t \).

After a certain period of time we assume \( u_y \) as defined here satisfies the equation of motion 4:1. This forms the connection between statistical mechanics and hydrodynamics for the shear viscosity. The boundary condition for particles in our subensemble represented by \( x_{io} \) and \( p_{io} \) are

\[
\begin{align*}
    u_y(x, 0|x_{io}, p_{io}) &= p_{io} \frac{\delta(x - x_{io})}{\rho A_x} \quad \text{(4:18)}
\end{align*}
\]

and

\[
\begin{align*}
    u_y(t, x_{io}, p_{io}) &= 0 \quad \text{(4:19)}
\end{align*}
\]

The problem to be solved then has the same form as the diffusion equation examined earlier. The solution is

\[
\begin{align*}
    u_y &= \left. \frac{p_{io}}{2A_x (\pi \eta t)^{1/2}} \exp \left( \frac{p (x-x_{io})^2}{4\eta t} \right) \right. \quad \text{(4:20)}
\end{align*}
\]

The second moment of this Gaussian is

\[
\begin{align*}
    M_2(\eta) &= \int_{-\infty}^{\infty} (x - x_{io})^2 u_y \, dx \\
    &= \frac{2p_{io} \eta t}{\rho ^2 A_x} \quad \text{(4:21)}
\end{align*}
\]

The second moment is multiplied by \( p_{io} \) and averaged. To remove the dependence on a particular particle \( i \), we sum over \( i \). The expression for \( \eta \) so obtained is

\[
\begin{align*}
    \eta &= \frac{1}{2Vkt} \Sigma_{i=1}^{N} \Sigma_{j=1}^{N} (x_{jt} - x_{io})^2 p_{jyt} p_{io} \quad \text{(4:22)}
\end{align*}
\]

By applying the law of conservation of momentum this may be simplified to

\[
\begin{align*}
    \eta &= \frac{1}{2Vkt} \Sigma_{i=1}^{N} (x_{it} p_{jyt} - x_{io} p_{jyo})^2 \quad \text{(4:23)}
\end{align*}
\]

\( \eta \) may also be expressed in terms of the autocorrelation of \( J(\eta) \) where

\[
\begin{align*}
    J(\eta) &= \Sigma_{i=1}^{N} \frac{p_{ix_i} p_{iy}}{m} + x_i F_{iy} + x_i K_{iy} \quad \text{(4:24)}
\end{align*}
\]

Here \( F \) is the force due to the intermolecular potential and \( K \) the force due to external fields. The result is (Helfand, 1969)

\[
\begin{align*}
    \eta &= \frac{1}{Vkt} \int_{0}^{\infty} <J_0(\eta) J_t(\eta)> \, dt \quad \text{(4:25)}
\end{align*}
\]
These expressions can now be evaluated by using configurations generated from molecular dynamics calculations. Before continuing with the discussion the expressions for the other coefficients will be described.

We return to the hydrodynamic equation of motion and consider the \( x \)-component. Again considering the symmetry of the problem and linearizing we have the expression
\[
\frac{\delta u_x}{\delta t} = \frac{\phi}{\rho} \frac{\delta^2 u_x}{\delta x^2} - \frac{1}{\rho} \frac{\delta P}{\delta x} \quad 4:26
\]
where \( \psi = \phi + \frac{4}{3} \eta \).

The term in \( P \) may be dropped at this point (Helfand, 1960). Briefly this is justified since the molecular motions do not change the pressure. Using the same arguments as before we have
\[
\psi = \phi + \frac{4}{3} \eta = \frac{1}{2VkT} \left\langle \sum_{i=1}^{N} (x_{it}P_{ix} - x_{i0}P_{ixo}) \right\rangle^2 \quad 4:27
\]
In its autocorrelation form this becomes
\[
\psi = \frac{1}{VkT} \int_{0}^{\infty} \langle J_0(\psi) J_t(\psi) \rangle \, dt \quad 4:28
\]
where
\[
J_t(\psi) = \sum_{i=1}^{N} \left( \frac{P_{ix}P_{ix}}{m} + x_{ix}F_{ix} \right) - PV \quad 4:29
\]
The more rigorous result (Zwanzig, 1965) replaces the contribution \( PV \) by
\[
V \left[ P - \frac{3P}{3N} (N - \langle N \rangle) + \frac{\partial P}{\partial E} (E - \langle E \rangle) \right]
\]
Thus while eqn. 4:29 is not exact for a canonical ensemble since the energy fluctuates, it is exact for the microcanonical ensemble. The thermal conductivity \( \kappa \) is treated by considering the equation for the flow of energy
\[
\frac{m}{V} \left( \frac{\partial E'}{\partial T} + u \cdot \nabla E' \right) = \kappa \nabla u - \nabla \cdot i_E \quad 4:30
\]
The linear law of energy flow is then
\[
i_E = - \kappa \frac{C}{V} \nabla E' \quad 4:31
\]
The heat capacity \( C_V \) is, as before, defined by \( C_V = (\frac{\partial E}{\partial T})_V \) and \( i_E \) is the energy flow. \( E' \) is the difference between the energy of particle \( i \) and its average value \( \langle E_i \rangle \) where
\[
E_i = \frac{P_i^2}{2m} + \sum_{i<j} u_{ij} \quad 4:32
\]
The energy flow equation is now linearized and the non-dissipative term \(-\frac{p^3}{\partial x}\) is dropped to leave the diffusion type equation

\[
\frac{\partial E'}{\partial t} = \frac{V}{m} \frac{\kappa}{C_v} \frac{\partial^2 E'}{\partial x^2} \quad 4:33
\]

We solve as before to obtain

\[
\kappa = \frac{1}{2\sqrt{\pi} T^2 t} \langle \sum_{i=1}^{N} (E'_{it} - E'_{io})^2 \rangle \quad 4:34
\]

In its autocorrelation form this becomes

\[
\kappa = \frac{1}{\sqrt{\pi} T^2} \int_0^\infty \langle J_{\kappa}(\kappa) J_{\kappa}(\kappa) \rangle \, dt \quad 4:35
\]

where

\[
J_{\kappa}(\kappa) = \frac{d}{dt} \sum_{i=1}^{N} x_i E'_{i} \quad 4:36
\]

In principle now we can calculate \(\eta, \phi\) and \(\kappa\) from our molecular dynamic results. This has been attempted for both forms of each equation. We consider first the results using the autocorrelation function approach.

**4:4 The Transport Autocorrelation Functions**

The autocorrelation functions have been investigated as averages over several hundred initial times. It proved impossible to obtain a reasonably stable form for these functions with this number of initial times. This seems reasonable in view of the fact that several hundred initial times must be considered before obtaining the velocity autocorrelation with sufficient accuracy to integrate it accurately. It should also be remembered that with the function we may average over 10^8 different particles. In principle then we might expect to need 100,000 initial times in the average before obtaining reasonable results for the viscosity. This number is impossible to achieve due to the excessive amount of computation needed (about 300 hours per point on the IBM 360/50). The velocity autocorrelation function is close to its final form however, even when only a few initial times are considered. We might hope then that after using one or two hundred initial times the form of the viscosity autocorrelation function for realistic potentials would become apparent.
Some work has been reported for hard spheres (Alder, Gass, and Wainwright, 1970), but they have not studied the autocorrelation functions, except as related to diffusion. The results of this work indicate that these methods are unlikely to be successful without a tremendous amount of computation.

More averages could be extracted from the molecular dynamics results, for example, by considering all possible initial times. Verlet has done this in his studies of the diffusion coefficient. Because of the results reported in the following section this refinement was not considered to be worth the computational effort with the available facilities.

4:5 Mean Square Deviation Expressions for Transport Coefficients

We now consider the alternate expressions for the viscosity. Here only the velocities and positions are considered explicitly. The equations of this type, 4:23, 4:29, and 4:36 are more amenable to computation than the autocorrelation functions. This has already been found in the case of diffusion. Bruin (1969) has published results for one temperature and pressure near the critical point. In his work he used 64 particles in conjunction with the Lennard-Jones potential to represent argon. Unfortunately no statistics are included giving the number of initial times considered. He has studied the gas rather than the liquid state. His agreement with experiment is reasonable for the point considered.

To begin with the shear viscosity was studied at 15 of the points for which molecular dynamics results were obtained. The results of calculations using equation 4:23 were averaged over the six possible combinations of components, \( x_p y', y_p x', x_p z', z_p x', y_p z', z_p y' \). The mean square displacements were averaged over 200 initial times. The results \( x_i p_{iy} - x_{io} p_{iy} \) for the expectation were then
<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>$V_M$</th>
<th>$\eta_{AV}$</th>
<th>$\eta_{LSQ}$</th>
<th>$\eta_{EXPT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>89.6</td>
<td>26.26</td>
<td>1.38</td>
<td>1.48</td>
<td>25.</td>
</tr>
<tr>
<td>103.1</td>
<td></td>
<td>1.55</td>
<td>1.65</td>
<td>16.</td>
</tr>
<tr>
<td>87.9</td>
<td>27.04</td>
<td>1.40</td>
<td>1.47</td>
<td></td>
</tr>
<tr>
<td>94.1</td>
<td>27.04</td>
<td>.31</td>
<td>.30</td>
<td>21.</td>
</tr>
<tr>
<td>105.0</td>
<td></td>
<td>.33</td>
<td>.34</td>
<td>16.</td>
</tr>
<tr>
<td>83.6</td>
<td>27.85</td>
<td>.37</td>
<td>.39</td>
<td></td>
</tr>
<tr>
<td>89.7</td>
<td></td>
<td>1.44</td>
<td>1.53</td>
<td>25.</td>
</tr>
<tr>
<td>103.2</td>
<td></td>
<td>.44</td>
<td>.45</td>
<td>16.</td>
</tr>
<tr>
<td>96.5</td>
<td>28.73</td>
<td>.41</td>
<td>.43</td>
<td>20.</td>
</tr>
<tr>
<td>108.9</td>
<td></td>
<td>1.66</td>
<td>1.70</td>
<td>15.</td>
</tr>
<tr>
<td>147.0</td>
<td></td>
<td></td>
<td></td>
<td>5.</td>
</tr>
<tr>
<td>156.9</td>
<td>57.45</td>
<td>1.85</td>
<td>1.96</td>
<td></td>
</tr>
<tr>
<td>168.9</td>
<td>65.66</td>
<td>2.01</td>
<td>2.16</td>
<td></td>
</tr>
<tr>
<td>159.1</td>
<td>70.71</td>
<td>1.73</td>
<td>1.86</td>
<td></td>
</tr>
<tr>
<td>158.7</td>
<td>76.60</td>
<td>2.12</td>
<td>2.21</td>
<td></td>
</tr>
<tr>
<td>159.1</td>
<td>91.92</td>
<td>2.47</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 4.2

SHEAR VISCOSITY OF ARGON
(units are $10^{-4}$ poise)
plotted against time and a least squares fit used to calculate the resulting slope of the curve $\langle \sum_{i=1}^{N} (x_i \cdot y_i - x_{i0} \cdot y_{i0})^2 \rangle$ versus $t$. The line plot was 3600 timesteps long and the slope of the last 2000 points was calculated by a least square fit to obtain a value of $\eta$.

In addition the value of $\eta$ has been calculated for each of the last 2000 timesteps and these values averaged to give another estimate of the shear viscosity. As in the study of diffusion the positions of the particles were reconstructed so as to remove the effects of the periodic boundary conditions used in the molecular dynamics work. A similar method was used to calculate $\psi$ and $\kappa$.

The results obtained by this method were most unsatisfactory. In Table 4:2 the calculated values of $\eta$ are compared with the experimental values of Hellemans, Zink, and Van Paemal (1970). In Table 4:3 components of the shear viscosity at 5 points are shown as a function of the number of initial times. In Table 4:4 the value of $\psi$ is compared with the experimental results of Nangle, Lansford, and Singer (1966). In Table 4:5 the calculated value of $\kappa$ is compared with experimental values of Ikenberry and Rice (1963).

### Table 4:3

<table>
<thead>
<tr>
<th>t (timesteps)</th>
<th>500</th>
<th>1000</th>
<th>1800</th>
<th>1900</th>
<th>2000</th>
<th>1800</th>
<th>1900</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial times</td>
<td>3200</td>
<td>2600</td>
<td>2000</td>
<td>1900</td>
<td>1800</td>
<td>1900</td>
<td>1800</td>
<td>1900</td>
</tr>
<tr>
<td>$n_\text{xy} \times 10^4$</td>
<td>2.74</td>
<td>1.54</td>
<td>.63</td>
<td>.75</td>
<td>.65</td>
<td>.75</td>
<td>.65</td>
<td>.65</td>
</tr>
<tr>
<td>(poise)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_\text{xz} \times 10^4$</td>
<td>1.15</td>
<td>.61</td>
<td>.81</td>
<td>.66</td>
<td>.49</td>
<td>.66</td>
<td>.49</td>
<td>.49</td>
</tr>
<tr>
<td>(poise)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The value of $\eta$ in the gas phase was approximately correct in agreement with the earlier result of Bruin (1969).
<table>
<thead>
<tr>
<th>$T^0K$</th>
<th>$\psi_{av}$</th>
<th>$\psi_{sq}$</th>
<th>$\psi_{expt}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>89.6</td>
<td>1.56</td>
<td>.64</td>
<td>45.</td>
</tr>
<tr>
<td>103.1</td>
<td>2.05</td>
<td>.5</td>
<td>34.</td>
</tr>
<tr>
<td>87.9</td>
<td>1.83</td>
<td>.13</td>
<td>46.</td>
</tr>
<tr>
<td>94.1</td>
<td>.33</td>
<td>.19</td>
<td></td>
</tr>
<tr>
<td>105.0</td>
<td>.32</td>
<td>.08</td>
<td></td>
</tr>
<tr>
<td>83.6</td>
<td>.34</td>
<td>.12</td>
<td>51.</td>
</tr>
<tr>
<td>89.7</td>
<td>2.3</td>
<td>.8</td>
<td>45.</td>
</tr>
<tr>
<td>103.2</td>
<td>.44</td>
<td>.24</td>
<td>34.</td>
</tr>
<tr>
<td>96.5</td>
<td>.49</td>
<td>.58</td>
<td></td>
</tr>
<tr>
<td>108.9</td>
<td>1.99</td>
<td>.16</td>
<td>31.</td>
</tr>
<tr>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>156.9</td>
<td>1.89</td>
<td>.44</td>
<td></td>
</tr>
<tr>
<td>168.9</td>
<td>2.70</td>
<td>1.16</td>
<td></td>
</tr>
<tr>
<td>159.1</td>
<td>3.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>158.7</td>
<td>2.31</td>
<td>.54</td>
<td></td>
</tr>
<tr>
<td>159.1</td>
<td>2.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 4.5

THERMAL CONDUCTIVITY OF ARGON

(units are $10^{-3}$ watts/m./sec)

<table>
<thead>
<tr>
<th>$T_{\circ}K$</th>
<th>$\lambda_{AV}$</th>
<th>$\lambda_{LSQ}$</th>
<th>$\lambda_{EXPT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>89.6</td>
<td>38.6</td>
<td>10.0</td>
<td>14.0</td>
</tr>
<tr>
<td>103.1</td>
<td>36.2</td>
<td>11.15</td>
<td></td>
</tr>
<tr>
<td>94.1</td>
<td>5.91</td>
<td>4.79</td>
<td>16.0</td>
</tr>
<tr>
<td>105.0</td>
<td>5.79</td>
<td>6.74</td>
<td>14.0</td>
</tr>
<tr>
<td>83.6</td>
<td>8.09</td>
<td>2.51</td>
<td></td>
</tr>
<tr>
<td>89.7</td>
<td>61.2</td>
<td>3.22</td>
<td>13.0</td>
</tr>
<tr>
<td>103.2</td>
<td>8.34</td>
<td>3.24</td>
<td>14.0</td>
</tr>
<tr>
<td>96.5</td>
<td>9.63</td>
<td>6.84</td>
<td></td>
</tr>
<tr>
<td>108.9</td>
<td>36.6</td>
<td>4.30</td>
<td></td>
</tr>
<tr>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>156.9</td>
<td>47.3</td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>168.9</td>
<td>35.2</td>
<td>16.5</td>
<td>4.0</td>
</tr>
<tr>
<td>159.1</td>
<td>40.6</td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>158.7</td>
<td>69.0</td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>159.1</td>
<td>22.2</td>
<td></td>
<td>4.0</td>
</tr>
</tbody>
</table>
However in the liquid phase there was violent disagreement with the experimental results of Hellemans et al (1970). The calculated values of $\psi$ and $\kappa$ are completely untrustworthy. Further investigation revealed that the calculated values depended strongly on the number of initial times considered, and that at least initially the values tended to increase as more and more initial times were considered. This behaviour is quite different from that observed in the study of diffusion, where the calculated values fluctuated about the final result. A new program was developed to calculate the transport coefficients using a least squares fit to find the slope through 40 points selected from various intervals, commencing after several hundred time-steps and using eqns. 4:23, 4:27 and 4:34. Complete results for such a run appears in Table 4:6, with $\eta$, $\psi$ and $\kappa$ appearing as a function of the number of initial times considered. Final values from two other runs are also included. Again the results have been averaged over the various components of the expressions used to improve the averages. Thus the shear viscosity is the average of 6 values and the bulk viscosity and thermal conductivity are averages over 3 components. The intervals for which we derived the slopes corresponding to $\eta$, $\psi$ and $\kappa$ appear before the calculated values. These results do not appear to be converging at all. We cannot calculate the bulk viscosity using

$$\phi = \psi - \frac{4}{3} \eta$$

since $\psi$ is not always greater than $\frac{4}{3} \eta$. If it is possible to obtain reasonable values for the transport coefficients clearly there is no hope of obtaining them without a vast increase in the length of the molecular dynamics runs. No estimate of the amount of computation necessary is possible either.
Table 4:6

η, ψ and κ as a function of the number of initial times considered (arbitrary units)

<table>
<thead>
<tr>
<th>No.</th>
<th>η</th>
<th>ψ</th>
<th>κ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 to 3000 by 50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>1.13</td>
<td>.83</td>
<td>6.59</td>
</tr>
<tr>
<td>400</td>
<td>1.13</td>
<td>3.34</td>
<td>.81</td>
</tr>
<tr>
<td>600</td>
<td>2.26</td>
<td>5.15</td>
<td>3.93</td>
</tr>
<tr>
<td>800</td>
<td>2.60</td>
<td>4.90</td>
<td>6.72</td>
</tr>
<tr>
<td>1000</td>
<td>2.79</td>
<td>4.12</td>
<td>4.80</td>
</tr>
<tr>
<td>1200</td>
<td>2.47</td>
<td>4.20</td>
<td>2.91</td>
</tr>
<tr>
<td>1400</td>
<td>2.76</td>
<td>4.11</td>
<td>7.00</td>
</tr>
<tr>
<td>1600</td>
<td>2.76</td>
<td>3.75</td>
<td>6.68</td>
</tr>
<tr>
<td>1800</td>
<td>2.48</td>
<td>3.49</td>
<td>5.90</td>
</tr>
<tr>
<td>2000</td>
<td>2.35</td>
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<td>1.07</td>
</tr>
<tr>
<td>2200</td>
<td>2.23</td>
<td>3.04</td>
<td>2.26</td>
</tr>
<tr>
<td>2400</td>
<td>1.97</td>
<td>3.20</td>
<td>2.88</td>
</tr>
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<td>1.78</td>
<td>3.14</td>
<td>4.31</td>
</tr>
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<td>2800</td>
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<tr>
<td>3200</td>
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<td>.11</td>
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</tr>
<tr>
<td>3400</td>
<td>-1.44</td>
<td>- .86</td>
<td>69.28</td>
</tr>
<tr>
<td>500 to 1500 by 25</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3900</td>
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<td>1.40</td>
<td>- 5.12</td>
</tr>
<tr>
<td>250 to 1000 by 25</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>4400</td>
<td>.008</td>
<td>3.59</td>
<td>- 4.82</td>
</tr>
</tbody>
</table>

We can however consider the transport studies of Alder, Gass, and Wainwright (1970) using a hard sphere potential.
Even though their system was run for a much longer model time than in this work they had difficulties obtaining satisfactory estimates of the viscosity. They were eventually successful, except for the case of the bulk viscosity which was still subject to a large statistical error. It is because of the larger statistical error in $\phi$ that we have tabulated $\psi$ throughout. Because of the computational difficulties in our work and the time consuming nature of the calculations, the study of these transport coefficients was abandoned at this point at least as far as the Kubo theory was concerned. Although the early results, contained in Tables 4:2, 4:4 and 4:5 seemed to indicate that there were theoretical difficulties with this approach, this view is not supported by the later work. The Kubo approach still seems to be the most attractive theory of transport, but it does not appear to be computationally viable for realistic potential functions. Certainly it is not useful with the facilities presently available at the A.N.U. The only feasible method available for obtaining transport coefficients would be one requiring more theoretical approximations. Therefore the assumptions underlying the friction coefficient approach to transport were examined to see whether this theory was valid for argon.
The previous discussion of transport indicates that the Kubo-type formulations do not give acceptable results at least for shear viscosity. The lack of approximation used in this approach had made it more attractive than some earlier theories. One of these, which has been considered by many workers, originated with Kirkwood (1946). This theory attempts to relate the motion of particles in a fluid to Brownian motion, through a molecular Langevin equation. Suddaby and Gray (1960) obtained conditions under which the friction coefficient as it arises in Brownian motion was compatible with the friction coefficient derived by Kirkwood. Kirkwood has made his friction coefficient proportional to the integral of the force autocorrelation function. Providing certain conditions are obeyed, the Kirkwood approach yields a friction coefficient from which the transport coefficient can be calculated. For spherical particles the friction coefficient is related to the viscosity by

\[ \zeta = 6 \pi \eta r \]  

where \( r \) is the radius of the particles (Edward, 1970). A general discussion of the calculation of transport properties from the friction coefficient can be found in Rice and Gray (1965). Fisher and Watts (1972) have investigated the assumptions underlying the Kirkwood approach to transport. This study was undertaken to check the applicability of the theory in the case of argon. Some of the results will now be discussed. The full paper constitutes Appendix B of this thesis.

We begin by considering the velocity autocorrelation function. This function must decay exponentially if a Langevin equation is to define the motion of a single particle (Wax, 1954). Since our autocorrelation function do not decay in this manner for the liquid state the Langevin equation used by Kirkwood cannot be exact. The definitive evidence for non-Langevin behaviour is the negative portion of the autocorrelation function observed in the molecular dynamics results reported here and by Rahman (1964). Despite the results of Rahman many workers still assume that the Kirkwood
approach gives reasonable results (e.g. Cole, 1970). Apparently the implications of Rahman's work have not been realized.

The reasons for not applying the friction coefficient approach to calculate the transport properties of argon is that the necessary assumptions are not valid.

Fisher and Watts used the molecular dynamics configurations described previously. The force autocorrelation function for liquid argon was calculated as well as the diffusion coefficient at two thermodynamic points. The diffusion coefficients were of course consistent, within the statistical error, with those reported here. They were calculated independently of the work reported in the first sections of this Chapter. The friction coefficient was then calculated using both Kirkwood's equations

$$\zeta = \frac{1}{3kT} \int_0^T \langle F_i (0) \cdot F_i (t) \rangle \, dt$$  \hspace{1cm} (4.38)

and the Einstein relation from Brownian motion

$$\zeta = \frac{kT}{D}$$

where $F_i$ is the force acting on atom $i$ and $D$ is the diffusion coefficient. In Table 4.7 the resulting values of $\zeta$ calculated by both methods are reported. The violent disagreement between these values is indicative that the Kirkwood approach is not useful for argon. The diffusion coefficient agree well with experimental values of argon and with values obtained using the theory of Brownian motion. This is apparent from the earlier discussion in this Chapter. $\zeta$ as calculated from the diffusion coefficient can be quite useful in experimental work on simple non-electrolytes (Edwards, 1970) for the autocorrelation function to give $\zeta$ in terms of the microscopic behaviour.
Reduced diffusion coefficients and friction coefficients from Kubo-Green theory and Kirkwood theory as a function of the upper limit in the time integration.

<table>
<thead>
<tr>
<th>Table 4:7</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Gas</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$</td>
<td>$D^*$</td>
</tr>
<tr>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td>0.11</td>
<td>-</td>
</tr>
<tr>
<td>0.13</td>
<td>-</td>
</tr>
<tr>
<td>0.16</td>
<td>-</td>
</tr>
<tr>
<td>2.08</td>
<td>0.58</td>
</tr>
<tr>
<td>3.09</td>
<td>0.60</td>
</tr>
<tr>
<td>5.02</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Other assumptions underlying the friction coefficient approach were also found to be invalid in the work reported in the Appendix. Thus the friction coefficient approach is not useful in the study of liquid or dense gaseous argon. This view is supported by the work on the Rice-Allnatt theory reported by Collings, Watts and Woolf (1971) using Monte Carlo methods. Therefore no further attempts were made to evaluate the theoretical friction coefficient from the molecular dynamics results or to evaluate the transport coefficients using this approach.

4:7 Summary of Transport in Argon

In this Chapter we have reported attempts to calculate four transport coefficients of dense fluid argon. Calculation of the diffusion coefficient was quite successful. It appears that the expressions for the diffusion coefficient developed both from Brownian motion
studies and linear transport theories are adequate for the study of argon. It is interesting to note that both approaches lead to the same final expression for the diffusion coefficient.

The results given here indicate that the linear transport theory cannot be used to adequately represent the behaviour of the viscosity coefficients in the liquid state. This was surprising after the excellent diffusion results. Since all attempts to use the viscosity formulae failed however, we have not been able to examine the theoretical validity of the approach. Some suggestion of difficulty with these Kubo type formulae for transport has been found in the work of Brown and March (1968). They found that the viscosities of lithium-6 and lithium-7 could only be explained by surrendering one of three assumptions

1. Classical equations of motion.
2. Kubo formulae for transport.
3. Potential energy function independent of atomic mass.

These assumptions are also fundamental to the calculations reported here. Considering our success in other areas assumptions one and three do seem to be valid for argon. Quantum effects are more likely to be important in lithium. However, the adequacy of the Kubo-type formulae does appear to be questioned by their investigation. Investigations performed in conjunction with work reported here have shown that the most popular alternative theory of viscosity is based on assumptions that are not valid for argon. It now appears that the viscosity coefficients cannot be calculated from a realistic potential function together with molecular dynamics techniques using current theories. It seems that there must be a further theoretical advance before successful calculations will be possible. In addition since we have
actually calculated the transport coefficients of the Barker-Bobetic potential rather than of argon, useful perturbation theories need to be developed to correct for the different behaviour of these two fluids.
CHAPTER 5

MONTE CARLO CALCULATION OF THE PROPERTIES OF
SOLID ARGON

The success of the calculations of the properties of dense fluid argon encouraged study of its solid phase. Argon was therefore investigated at thermodynamic points near the solid-vapour coexistence line for selected temperatures from 5 to 85°K. The procedure by which the thermodynamic properties may be calculated and the results of such calculations are given in this chapter. We begin by describing another "exact" method for calculating thermodynamic properties, Monte Carlo integration.

5:1 The Monte Carlo Method

Monte Carlo integration is a statistical method for evaluating integrals. If \( f(x) \) is proportional to the probability of the distribution function of the variable, then the expected or average value of \( g(x) \) is given by

\[
< g(x) > = \frac{\int_a^b g(x) f(x) \, dx}{\int_a^b f(x) \, dx}
\]

5:1

Thus, if we can compute \( <g(x)> \) and the normalising function

\[
\int_a^b f(x) \, dx
\]

then we may evaluate the integral

\[
\int_a^b G(x) \, dx = \int_a^b \frac{G(x)}{f(x)} f(x) \, dx
\]

\[
= <g(x)> \int_a^b f(x) \, dx
\]

5:2

where \( g(x) = G(x)/f(x) \).

The Monte Carlo method consists of:

a) evaluating \( \int_a^b f(x) \, dx \) and,

b) estimating \( < g(x) > \)
f(x), is commonly chosen so as to be easily integrated over [a,b] either analytically or by quadrature. It is also chosen so as to speed convergence by reducing the variance of the individual terms in the average \( \langle g(x) \rangle \). This average is formed by choosing a large number of values \( X_i \) distributed according to \( f(x) \). We now use

\[
\langle g(x) \rangle = \frac{1}{N} \sum_{i=1}^{N} g(x_i)
\]

to obtain an estimate of \( \langle g(x) \rangle \). The larger the value of \( N \) the better this approximation becomes.

For functions of more than three or four variables Monte Carlo integration is usually the only viable numerical method of quadrature. It becomes more attractive as the number of variables increases (Haber, 1970).

In statistical mechanics we often wish to evaluate integrals of the form:

\[
\langle G(r_1, \ldots, r_N) \rangle = \frac{\int \cdots \int G(r_1, \ldots, r_N) e^{-U(r_1, \ldots, r_N)/kT} d^3r_1 \cdots d^3r_N}{\int \cdots \int e^{-U(r_1, \ldots, r_N)/kT} d^3r_1 \cdots d^3r_N}
\]

(5:3)

This is the quotient of two \( 3N \)-dimensional integrals. Clearly if we have 100 or more particles we must use Monte Carlo methods for the quadrature. Comparing equations 5:1 and 5:3 we see that if we can choose our values of \( r_1, \ldots, r_N \) such that the probability of configuration \( r_1, \ldots, r_N \) occurring is proportional to \( e^{-U(r_1, \ldots, r_N)/kT} \),

\[
P(r_1, \ldots, r_N) \propto \exp \left\{ -\frac{U(r_1, \ldots, r_N)}{kT} \right\}
\]

(5:4)

then the average value of \( G(r_1, \ldots, r_N) \) for many such choices of \( r_1, \ldots, r_N \) will be the desired quantity, \( \langle G(r_1, \ldots, r_N) \rangle \). For a system of \( N \) identical particles in a volume \( V \), interacting through a potential function \( U(r_1, \ldots, r_N) \), the rules for choosing configurations \( (r_1, \ldots, r_N) \) were devised by Metropolis et al. (1953).

These rules generate a Markov chain of configurations such that equation 5:4 is satisfied in the limit as the number of configurations becomes infinite (Feller, 1950). The choice of initial configuration then becomes unimportant. The probability distribution function in eqn. 5:3, which is
related to the Helmholtz free energy, is too time-consuming to be evaluated. Thus, while we can calculate various derivatives of the free energy (i.e. other thermodynamic properties) we cannot calculate the free energy itself.

The Monte Carlo method as commonly used in statistical mechanics consists of first choosing an initial configuration of the coordinates of N atoms and then generating a chain of configurations by the following procedure:

1) Calculate $U_p(r_1, ..., r_N)$ for the present configuration $p$.
2) Move a randomly chosen atom $i$ a randomly chosen distance in a randomly chosen direction.
3) Calculate $U_n(r_1, ..., r_N)$ for this new configuration.
4) If $U_n < U_p$ the new configuration is the next one in the chain. If $U_n > U_p$ the new configuration is the next one in the chain if
   \[ e^{-\frac{(U_n - U_p)}{kT}} < r \]
where $r$ is a random number from $[0, 1]$; otherwise the next configuration in the chain is the old one.

The expected value of a thermodynamic property is now its average value over the configurations in the chain generated using rules 1 to 4. In practice the average converges more quickly to its final value if the atoms are only moved a short distance from their original position. Distances are generally chosen randomly from the interval $[0, \delta]$ where $\delta$ is chosen so that about half the new configurations formed are accepted by rule 4. The choice of delta affects only the rate of convergence not the final results. Since we have not considered the equations of motion of the particles, we have no information about the time evolution of the system.

In our calculations we used the truncated Barker potential described in Chapter 2. As in the molecular dynamics calculations we minimized surface effects by applying periodic boundary conditions to a cubic box containing 108 particles. The perturbation theory of Chapter 2 was then used to calculate the pressure, energy and specific heat for the system interacting according to the full Barker potential. It will be further extended in this Chapter to
include corrections for other equilibrium properties of interest in the study of the solid state.

5:2 The Properties of Solid Argon

The fluid state is generally so disordered that there is no convenient internal reference frame. We therefore refer the positions of atoms to a laboratory-fixed cartesian co-ordinate system. However the solid state generally has a strong and persistent order. Solid argon tends to crystallise in a particular type of structure known as the face-centred cubic lattice. Crystals of macroscopic dimensions can be formed with no observable defects or deviations from this lattice structure. (Keeler and Batchelder, 1970) although small regions of hexagonal close-packed structure have been observed in solid argon (Barrett and Meyer, 1964). This long range order is a particular feature of the solid state. Each atom commonly stays nearer its own lattice site than any other. This is in contrast to the liquid where an atom on average moves about $4 \times 10^{-3}$ cm per second from its original position. This distance is much greater for the gas. We have already shown that the arguments of the integrals defining the thermodynamic properties of argon can be expressed as a function of the cartesian co-ordinates of the constituent atoms, e.g. $e^{-F/kT} \propto Z = \int \ldots \int e^{-\sum_{i} X_i^2} / kT \ d^3r$. The orientation and origin of these co-ordinates is unimportant in the study of a liquid. Since the solid has a definite structure it is desirable and very convenient to describe the positions of the atoms relative to their lattice sites in the perfect crystal. If we fix an orthonormal co-ordinate system in the crystal, the basis vectors of this co-ordinate system will change if the shape of the crystal is changed. For a face-centred cubic crystal such as argon we choose these basis vectors to be $(0, 0, 1), (1, 0, 0), (0, 1, 0)$. One lattice site is chosen as the origin, and the basis oriented such that the lattice sites are given by $(\ell, m, n)$ where $\ell, m,$ and $n$ are integers and $\ell + m + n$ is an even number. This defines the unit distance in terms of interatomic spacings.

A homogeneous deformation of a crystal may be defined in the following way. Consider any three co-linear points in the lattice at positions $0$, $X$ and $2X$ respectively.
Then under a homogeneous deformation if the second lattice site is deformed to $X + \delta Y$ then the third is deformed to $2X + 2\delta Y$ while the first remains at $0$. If the original orthonormal co-ordinate system $(X_1, X_2, X_3)$ is deformed to $(X'_1, X'_2, X'_3)$ this deformation may be defined by the non-linear Lagrangian strain tensor (Murnaghan, 1951).

$$\eta_{ij} = \frac{1}{2} (X'_i \cdot X'_j - \delta_{ij})i, j = 1, 2, 3$$

It may be seen immediately that if $X'_i = X_i$ then $\eta_{ij} = 0$ for all $i, j = 1, 2, 3$. In addition $\eta_{ij} = \eta_{ji}$. We reduce the number of subscripts by redefining the $\eta_{ij}$ as follows

$$\eta_1 \equiv \eta_{11} \quad \eta_4 \equiv \eta_{12} = \eta_{21}$$
$$\eta_2 \equiv \eta_{22} \quad \eta_5 \equiv \eta_{13} = \eta_{31}$$
$$\eta_3 \equiv \eta_{33} \quad \eta_6 \equiv \eta_{23} = \eta_{32}$$

We also note that the distance of an atom from the origin when the crystal is under strain is given by

$$r = \left[ \sum_{i=1}^{3} \sum_{j=1}^{3} X_i \cdot X_j (2\eta_{ij} + \delta_{ij}) \right]^{1/2}$$

where $(X_1', X_2', X_3')$ gives the co-ordinates of that atom in the unstrained lattice. Hence

$$\frac{\partial}{\partial \eta_{ij}} = \frac{X_i \cdot X_j}{r} \frac{\partial}{\partial r_{ij}}$$

The elastic constants of conservative, thermoelastic systems are defined by

$$C^T_{ijkl} = \frac{1}{V} \left( \frac{\partial^2 E}{\partial \eta_{ij} \partial \eta_{kl}} \right)_T$$

which defines the second-order isothermal elastic constants and,

$$C^S_{ijkl} = \frac{1}{V} \left( \frac{\partial^2 E}{\partial \eta_{ij} \partial \eta_{kl}} \right)_S$$

which defines the second-order adiabatic elastic constants, (Thurston and Brugger, 1964; Brugger, 1964). These constants relate the stress to the strain when the crystal is deformed under conditions of constant temperature and constant entropy respectively.
We may use the fact that in a crystal
\[
dE = T \, dS + \frac{3}{V} \sum_{j,k=1}^{3} \left( \varepsilon_{jk} \right) d\varepsilon_{jk}
\]
\[
dF = -S \, dT + \frac{1}{V} \sum_{j,k=1}^{3} \left( \varepsilon_{jk} \right) d\varepsilon_{jk}
\]
to obtain a more physical picture of the elastic constants. (Thurston, 1964). If the temperature is held constant while the crystal is deformed the free energy of the strained crystal may be expressed as a Taylor series expansion in \(\varepsilon_{i}^{'}, i = 1, 6\). For a crystal with cubic symmetry (Hoover et al., 1969)

\[
F(\varepsilon) = F_{0} - PV (\varepsilon_{1} + \varepsilon_{2} + \varepsilon_{3})
\]
\[
+ \frac{VCT^{11}}{2} (\varepsilon_{1}^{2} + \varepsilon_{2}^{2} + \varepsilon_{3}^{2})
\]
\[
+ V C_{12}^{T} (\varepsilon_{1} \varepsilon_{2} + \varepsilon_{1} \varepsilon_{3} + \varepsilon_{2} \varepsilon_{3})
\]
\[
+ 2V C_{44}^{T} (\varepsilon_{4}^{2} + \varepsilon_{5}^{2} + \varepsilon_{6}^{2}) + 0(\varepsilon^{3})
\]

Because of the symmetry of the cubic crystal, the coefficients of products of the form \(\varepsilon_{ij} \varepsilon_{kl} \), \(k \neq l\) are zero. The number of coefficients has been reduced further by noting that

\[
\left. \frac{\partial A}{\partial \varepsilon_{1}} \right|_{\varepsilon_{1}=0} = \left. \frac{\partial A}{\partial \varepsilon_{2}} \right|_{\varepsilon_{2}=0} \quad \left. \frac{\partial A}{\partial \varepsilon_{3}} \right|_{\varepsilon_{3}=0} = -P
\]

We have used the relation \(\frac{\partial}{\partial \varepsilon_{ij}} = \delta_{ij} V \frac{\partial}{\partial V}\) where \(\delta_{ij}\) is the Kronecker delta. In addition, again using the symmetry of a cubic crystal

\[
C_{11}^{T} = C_{22}^{T} = C_{33}^{T}
\]
\[
C_{12}^{T} = C_{13}^{T} = C_{23}^{T}
\]
\[
C_{44}^{T} = C_{55}^{T} = C_{66}^{T}
\]

Here the number of subscripts has been reduced by using Voigt (1928) notation

\(e.g.\ C_{11}^{T} = C_{1111}^{T}, C_{12}^{T} = C_{1122}^{T}\)
The effect of crystal symmetry on the number of independent elastic constants, is discussed in several textbooks. Nye (1957) describes the independent elastic constants of several classes of crystal.

The coefficients of eqn. 5:11 are all evaluated under conditions of zero strain. $E$ may also be expanded as

$$E(n) = E_0 - P \nu (n_1 + n_2 + n_3) +$$

$$\frac{V}{2} C_{11}^S (n_1^2 + n_2^2 + n_3^2) + V C_{12}^S (n_1 n_2 + n_1 n_3 + n_2 n_3) + 2V C_{44}^S (n_4^2 + n_5^2 + n_6^2) + O(n^3)$$

In this case the coefficients of $n$ involve adiabatic elastic constants. The six second-order elastic constants for argon are

$$C_{11}^T = \frac{1}{V} \left( \frac{\partial^2 F}{\partial n_1 \partial n_2} \right)_T = \frac{1}{V} \left( \frac{\partial^2 F}{\partial n_2 \partial n_3} \right)_T = \frac{1}{V} \left( \frac{\partial^2 F}{\partial n_3 \partial n_1} \right)_T$$

$$C_{12}^T = \frac{1}{V} \left( \frac{\partial^2 F}{\partial n_1 \partial n_2} \right)_T = \frac{1}{V} \left( \frac{\partial^2 F}{\partial n_2 \partial n_3} \right)_T = \frac{1}{V} \left( \frac{\partial^2 F}{\partial n_1 \partial n_3} \right)_T$$

$$C_{44}^T = \frac{1}{V} \left( \frac{\partial^2 F}{\partial n_4 \partial n_5} \right)_T = \frac{1}{V} \left( \frac{\partial^2 F}{\partial n_5 \partial n_6} \right)_T = \frac{1}{V} \left( \frac{\partial^2 F}{\partial n_4 \partial n_6} \right)_T$$

$$C_{11}^S = \frac{1}{V} \left( \frac{\partial^2 E}{\partial n_2^2} \right)_S = \frac{1}{V} \left( \frac{\partial^2 F}{\partial n_2^2} \right) S = \frac{1}{V} \left( \frac{\partial^2 F}{\partial n_3^2} \right) S$$

$$C_{12}^S = \frac{1}{V} \left( \frac{\partial^2 E}{\partial n_1 \partial n_2} \right)_S = \frac{1}{V} \left( \frac{\partial^2 F}{\partial n_1 \partial n_3} \right) S = \frac{1}{V} \left( \frac{\partial^2 E}{\partial n_2 \partial n_3} \right)_S$$

$$C_{44}^S = \frac{1}{V} \left( \frac{\partial^2 E}{\partial n_4 \partial n_5} \right)_S = \frac{1}{V} \left( \frac{\partial^2 F}{\partial n_5 \partial n_6} \right) S = \frac{1}{V} \left( \frac{\partial^2 E}{\partial n_4 \partial n_6} \right)_S$$

The adiabatic elastic constants have been expressed as adiabatic derivatives of the energy. Our Monte Carlo calculations however evaluate isothermal derivatives of the free energy. Therefore we now derive an expression for $C_{ij}^T$ in terms of isothermal derivatives. Our system may be described using $T$ and the $n_i$ as our independent variables. We use the thermodynamic relations

$$E = F + TS$$

$$dF = \sum_{i=1}^{6} \left( \frac{\partial F}{\partial n_i} \right)_T d\eta_i + \left( \frac{\partial F}{\partial T} \right)_n dT$$
\[ ds = \sum_{i=1}^{6} \left( \frac{\partial S}{\partial \eta_i} \right)_{T} \, d\eta_i + \left( \frac{\partial S}{\partial T} \right)_{\eta} \, dT \]  
5:23

\[ \left( \frac{\partial E}{\partial \eta_i} \right)_S = \left( \frac{\partial F}{\partial \eta_i} \right)_S + S \left( \frac{\partial T}{\partial \eta_i} \right)_S \]  
5:24

Since the \( \eta_i \) and \( T \) are our independent variables

\[ \left( \frac{\partial T}{\partial \eta_i} \right) = 0 \quad i = 1, 6. \]

Also we have from 5:22 and 5:33

\[ dF \left( \frac{\partial S}{\partial T} \right)_\eta - ds \left( \frac{\partial F}{\partial T} \right)_\eta = \sum_{i=1}^{6} \left[ \left( \frac{\partial F}{\partial \eta_i} \right)_T \left( \frac{\partial S}{\partial \eta_i} \right)_T - \left( \frac{\partial S}{\partial \eta_i} \right)_T \left( \frac{\partial F}{\partial \eta_i} \right)_T \right] \, d\eta_i \]

Under adiabatic conditions \( ds = 0 \) and we may write

\[ \left( \frac{\partial F}{\partial \eta_i} \right)_S = \left( \frac{\partial F}{\partial \eta_i} \right)_T - \left( \frac{\partial S}{\partial \eta_i} \right)_T \left( \frac{\partial F}{\partial T} \right)_\eta \]  
5:25

and

\[ \left( \frac{\partial^2 F}{\partial \eta_i \partial \eta_j} \right)_S = \left( \frac{\partial^2 E}{\partial \eta_i \partial \eta_j} \right)_S = \left( \frac{\partial^2 F}{\partial \eta_i \partial \eta_j} \right)_T \]

\[ - \left( \frac{\partial S}{\partial \eta_i} \right)_T \left( \frac{\partial S}{\partial \eta_j} \right)_T - \left( \frac{\partial S}{\partial \eta_i} \right)_T \left( \frac{\partial S}{\partial \eta_j} \right)_T \left( \frac{\partial F}{\partial \eta_i} \right)_T \]  
5:26

We now use the following thermodynamic relations

\[- \left( \frac{\partial^2 F}{\partial T^2} \right)_\eta = \left( \frac{\partial S}{\partial T} \right)_\eta = \left( \frac{\partial S}{\partial T} \right)_V = \frac{C_V}{T} \]

and

\[ \left( \frac{\partial S}{\partial \eta_{ij} T} \right)_T = \left( \frac{\partial S}{\partial \eta_{ij}} \right)_V \delta_{ij} \]

\[ \left( \frac{\partial S}{\partial \eta_{ik} \eta_{jk} T} \right)_T = \left( \frac{\partial S}{\partial \eta_{ik} \eta_{jk}} \right)_V \delta_{ik} \delta_{jk} \]  
5:27

where \( \delta_{ij} \) is the Kronecker delta.

We now have

\[ \frac{1}{V} \left( \frac{\partial^2 F}{\partial \eta_{ik} \partial \eta_{jk} S} \right)_S = \frac{1}{V} \left( \frac{\partial^2 F}{\partial \eta_{ik} \partial \eta_{jk} T} \right)_T + \frac{VT}{C_V} \left( \frac{\partial^2 F}{\partial T^2} \right)_V \delta_{ik} \delta_{jk} \]  
5:27

The adiabatic elastic constants may now be expressed as

\[ C_{S11} = C_{T11} + \frac{VT}{C_V} \left( \frac{\partial^2 F}{\partial T^2} \right)_V \]  
5:28
The second order elastic constants of a crystal with cubic symmetry have now been expressed as derivatives of the Helmholtz free energy. In Chapter 2 we described a perturbation expansion for the free energy and its derivatives for argon in which all the ensemble averages were evaluated using configurations from an ensemble related to the truncated Barker-Bobetic two-body potential. We have generated configurations for the solid using the Monte Carlo method together with this truncated potential. We now combine these results to derive the elastic constants of argon in terms of ensemble averages over the Monte Carlo configurations.

5:3 Perturbation Expansion of the Elastic Constants of Argon

From Chapter 2 the free energy of argon is given by

\[ F = -kT \ln \left( \frac{\lambda^{-3N}}{N!} \right) \int \ldots \int e^{-U_0/kT} d^3N \]

+ \langle U_2 \rangle_o + \langle U_3 \rangle_o + \langle U_Q \rangle_o

Since the free energy is the sum of four terms we may calculate the derivatives of each term separately. We begin with the term involving \( U_0 \) only.

\[ F_o = -kT \ln \left( \frac{\lambda^{-3N}}{N!} \right) \int \ldots \int e^{-U_0/kT} d^3N \]

\[ \frac{\partial F_o}{\partial \eta_{ij}} = -NkT \delta_{ij} - \frac{kT}{\eta_o} \int \ldots \int \frac{\partial}{\partial \eta_{ij}} \left( -\frac{U_0}{kT} \right) e^{-U_0/kT} d^3N \]

\[ = \frac{1}{\eta_o} \int \ldots \int \sum_{k \leq 1} \left( \frac{\partial^2 r_{kl}}{\partial r_{kl}} U_0 \right) T \left( \frac{\partial r_{kl}}{\partial \eta_{ij}} \right) e^{-U_0/kT} d^3N \]

If two atoms in the crystals have cartesian co-ordinates \((x_1, y_1, z_1)\) and \((x_k, y_k, z_k)\), they are separated by a distance \(r_{kl}\) and we define

\[ a_{1kl} = (x_1 - x_k) \]
\[ a_{2kl} = (y_1 - y_k) \]
\[ a_{3kl} = (z_1 - z_k) \]
using equation 5:8. In the following work sums \( \Sigma \) will be over all distinct pairs of particles.

Differentiating 5:33 with respect to \( \frac{\delta F}{\delta \eta_{ij}} \)

\[
\frac{1}{V} \frac{\partial F}{\partial \eta_{ij}} = \frac{1}{V} \left( \frac{\partial}{\partial \eta_{ij}} < \Sigma \frac{u_i}{r} a_{ijkl} a_{kl} > \right) - \frac{\delta F}{\partial \eta_{mn}} \frac{\partial}{\partial \eta_{mn}} - NkT \delta_{ij}
\]

\[
= \frac{1}{V} \left( < \Sigma \left( \frac{u_i}{r^2} - \frac{u_i}{r} \right) a_{ijkl} a_{mkl} > \right) + \frac{1}{V} \int \left( < \Sigma \frac{u_i}{r} a_{ijkl} > < \Sigma \frac{u_i}{r} a_{mkl} > \right)
\]

\[
- < \left( \Sigma \frac{u_i}{r} a_{ijkl} \right) \left( \Sigma \frac{u_i}{r} a_{mkl} \right) > + \frac{2NkT}{V} \delta_{im} \delta_{jn}
\]

The term in \( NkT \) is called the kinetic contribution to the elastic constant. Since this contributes to \( C_{1212} \) but not \( C_{1221} \) and these both contribute to the measured \( C \), we calculate \( C_{44} \) as

\[
C_{44} = \frac{1}{4} \left( C_{1212} + C_{1221} + C_{2112} + C_{2121} \right)
\]

Using the above expressions, we now have

\[
C_{11} (U_0) = \frac{1}{V} \int \left( < \Sigma \frac{u_i}{r} a^2_{1kk} a^2_{2kl} > \right) + \frac{1}{V} \left( < \Sigma \frac{u_i}{r} a^2_{1kk} > \right) \]

\[
+ \frac{1}{V} \left( < \Sigma \frac{u_i}{r} a^2_{2kk} > \right) - \frac{NkT}{V}
\]

\[
C_{12} (U_0) = \frac{1}{V} \int \left( < \Sigma \frac{u_i}{r} a^2_{1kk} > \right) \left( < \Sigma \frac{u_i}{r} a^2_{2kk} > \right) - \frac{NkT}{V}
\]

\[
C_{44} (U_0) = \frac{1}{V} \int \left( < \Sigma \frac{u_i}{r} a^2_{1kk} a^2_{2kl} > \right) + \frac{NkT}{V}
\]
Before discussing the other contributions to the elastic constants we examine the terms in \( C_{11}^T (U_o) \). We call the first term involving \((kT)^{-1}\) the fluctuation term since it has the form of a variance. The term in \( NkT \) has already been called the kinetic term. The other term involving \( (\frac{u''}{r^2} - \frac{u'}{r^3}) \) is called the Born term since this result was first derived by him as the contribution to the elastic constants of a static lattice. (Born and Huang, 1954). Kinetic contributions amount to less than 1% of \( C_{11}^T (U_o) \). The fluctuation term is generally much smaller than the Born term. Since \( U_2', U_3 \) and \( U_Q \) contribute only small amounts to the elastic constants we do not consider their fluctuation terms. This approximation was employed by Squire et al. (1969) for \( U_Q \) and found to be satisfactory.

We will now consider the contribution of \( U_2 \).

\[
\frac{1}{V} \left( \frac{\partial}{\partial \eta_{ij}} U_2 \right) T = \frac{1}{kT} \left[ \frac{< U_2 >}{E} \right] < a_{ijk} a_{jlk} >_0 - \frac{< U_2 >}{E} \left( \sum \frac{u'}{r} a_{ijk} a_{jlk} > \right)
\]

Dropping the variance term we obtain

\[
\frac{1}{V} \left( \frac{\partial^2}{\partial \eta_{ij} \partial \eta_{mn}} U_2 \right) T = \frac{1}{V} \left( \sum \frac{u''}{r^2} - \frac{u'}{r^3} \right) a_{ikl} a_{jkl} a_{mk} a_{nk} >_0
\]

Further variance terms arising from taking the second derivative have also been dropped. We now have

\[
C_{11}^T (U_2') = \frac{1}{V} \left( \sum \frac{u''}{r^2} - \frac{u'}{r^3} \right) a_{ikl} a_{jkl} >_0 r > R \quad 5:38
\]

\[
C_{12}^T (U_2') = C_{44}^T (U_2') = \frac{1}{V} \left( \sum \frac{u''}{r^2} - \frac{u'}{r^3} \right) a_{ikl} a_{jkl} >_0 r > R \quad 5:39
\]

Similarly for \( U_Q \) we have

\[
< U_Q > = - \frac{\hbar^2}{48 \pi^2 mkT} = \frac{\hbar^2}{48 \pi^2 mkT} < \Sigma \nu^2 u >_0 
\]

\[
= - \frac{\hbar^2}{48 \pi^2 mkT} < \Sigma \left( \frac{u'' + 2u'}{r} \right) >_0 r < R \quad 5:40
\]
and as a result
\[
C_{11}^T (U_3) = \frac{h^2}{4\pi^2 \tau} < \Sigma \left( \frac{u(4)}{r^2} + \frac{u(3)}{r^3} - \frac{6u''}{r^4} + \frac{6u'}{r^5} \right) a_{ikl}^4 >_0 \\
r < R 
\]
and
\[
C_{12}^T (U_3) = C_{44}^T (U_3) = \frac{h^2}{4\pi^2 \tau} \times \\
< \Sigma \left( \frac{u(4)}{r^2} + \frac{u(3)}{r^3} - \frac{6u''}{r^4} + \frac{6u'}{r^5} \right) a_{ikl}^2 a_{jkl}^2 >_0 \\
i \neq j, r < R
\]
Equations 5.41 and 5.42 were published by Squire et al. (1969) when discussing their work on the Lennard-Jones potential.

Long-range corrections to these terms can be calculated using the static lattice approximation and performing the required lattice sums. The expectation values are replaced by the value for a face-centred cubic lattice at the same density as the argon being studied.

We now consider \(C_{11}^T (U_3), C_{12}^T (U_3), C_{44}^T (U_3)\)

We have
\[
V \frac{C_{11}^T (U_3)}{\eta_{ij} \eta_{pg}} = \frac{\phi^2 <U_3>}{\eta_{ij} \eta_{pg}}
\]
Consider three atoms at \((x_i, y_i, z_i), (x_j, y_j, z_j)\) and \((x_k, y_k, z_k)\).

Let
\[
\begin{align*}
    r_{ij} &= r \\
    r_{ik} &= s \\
    U_{ijk} &= \phi \\
    r_{jk} &= t \\
    \Delta R_r &= R_i - R_k \\
    \Delta R_s &= R_i - R_j \\
    \Delta R_t &= R_k - R_j
\end{align*}
\]
where
\[
R_i = (x_i, y_i, z_i)
\]
Then
\[
V \mathcal{C}_{11}^{T}(U_3) = \frac{2}{\partial \eta_{ij}} < \Sigma \left[ \frac{3 \phi}{\partial r} \frac{(\Delta x_r)^2}{r^2} + \frac{3 \phi}{\partial s} \frac{(\Delta x_s)^2}{s^2} + \frac{3 \phi}{\partial t} \frac{(\Delta x_t)^2}{t^2} \right] > 0
\]

= \Sigma \left[ \frac{3 \phi}{\partial r} \frac{(\Delta x_r)^4}{r^2} + \frac{3 \phi}{\partial s} \frac{(\Delta x_s)^4}{s^2} + \frac{3 \phi}{\partial t} \frac{(\Delta x_t)^4}{t^2} \right] + 2 \frac{3 \phi}{\partial r} \frac{(\Delta x_r \Delta x_s)^2}{rs} + 2 \frac{3 \phi}{\partial r} \frac{(\Delta x_r \Delta x_t)^2}{rt} + 2 \frac{3 \phi}{\partial s} \frac{(\Delta x_s \Delta x_t)^2}{st}

= \frac{3 \phi}{\partial r} \frac{(\Delta x_r)^4}{r^3} - \frac{3 \phi}{\partial s} \frac{(\Delta x_s)^4}{s^3} - \frac{3 \phi}{\partial t} \frac{(\Delta x_t)^4}{t^3} > 0

Also

\[
V \mathcal{C}_{12}^{T}(U_3) = \frac{2}{\partial \eta_{ij}} < \Sigma \left[ \frac{3 \phi}{\partial r} \frac{\Delta x_r \Delta y_r}{r} + \frac{3 \phi}{\partial s} \frac{\Delta x_s \Delta y_s}{s} + \frac{3 \phi}{\partial t} \frac{\Delta x_t \Delta y_t}{t} \right] > 0
\]

= \Sigma \left[ \frac{3 \phi}{\partial r} \frac{(\Delta x_r \Delta y_r)^2}{r^2} + \frac{3 \phi}{\partial s} \frac{(\Delta x_s \Delta y_s)^2}{s^2} \right] + \frac{3 \phi}{\partial t} \frac{(\Delta x_t \Delta y_t)^2}{t^2} + \frac{3 \phi}{\partial r} \frac{(\Delta x_r \Delta y_t)^2}{rt} + \frac{3 \phi}{\partial s} \frac{(\Delta x_s \Delta y_t)^2}{st}

= \frac{3 \phi}{\partial r} \frac{(\Delta x_r \Delta y_r)^2}{r^3} - \frac{3 \phi}{\partial s} \frac{(\Delta x_s \Delta y_s)^2}{s^3} - \frac{3 \phi}{\partial t} \frac{(\Delta x_t \Delta y_t)^2}{t^3} > 0

and

\[
V \mathcal{C}_{44}^{T}(U_3) = \frac{2}{\partial \eta_{ij}} < \Sigma \left[ \frac{3 \phi}{\partial r} \frac{\Delta x_r \Delta y_r}{r} + \frac{3 \phi}{\partial s} \frac{\Delta x_s \Delta y_s}{s} + \frac{3 \phi}{\partial t} \frac{\Delta x_t \Delta y_t}{t} \right] > 0
\]

= \Sigma \left[ \frac{3 \phi}{\partial r} \frac{(\Delta x_r \Delta y_r)^2}{r^2} + \frac{3 \phi}{\partial s} \frac{(\Delta x_s \Delta y_s)^2}{s^2} \right] + \frac{3 \phi}{\partial t} \frac{(\Delta x_t \Delta y_t)^2}{t^2} + \frac{3 \phi}{\partial r} \frac{(\Delta x_r \Delta y_t)^2}{rt} + \frac{3 \phi}{\partial s} \frac{(\Delta x_s \Delta y_t)^2}{st}

= \frac{3 \phi}{\partial r} \frac{(\Delta x_r \Delta y_r)^2}{r^3} - \frac{3 \phi}{\partial s} \frac{(\Delta x_s \Delta y_s)^2}{s^3} - \frac{3 \phi}{\partial t} \frac{(\Delta x_t \Delta y_t)^2}{t^3} > 0
This completes the derivation of the isothermal elastic constants of argon in terms of configurations generated using the truncated Barker-Bobetic two-body potential. Equations 5.43, 5.44 and 5.45 involve the most time consuming averages to calculate proposed in this work. The fluctuation terms which have been ignored are even more complex. As a consequence, values of the contributions $C_{11}^T(U_3)$, $C_{12}^T(U_3)$ and $C_{44}^T(U_3)$ have been used that were calculated using the static lattice approximation throughout. This approximation allows the symmetry of the lattice to be used to reduce the computation considerably. The results used here are those of Barker, Bobetic and Klein (1971). Zucker and Chell (1968) developed expressions for three-body contributions to the static lattice using the method of homogeneous deformations. Their results were not in agreement with others of Hüller et al. (1970). They also disagreed with results of Barker et al. (1971a) who used the method of long waves. The cause of this discrepancy was the omission of a non-zero lattice sum in the work of Zucker and Chell. Barker et al. (1971b) recalculated the sums correctly and extrapolated their results to give values for the infinite lattice. Their results for the various elastic constants are

\[
\begin{align*}
C_{11}^T(U_3) &= 9.93 \frac{\nu}{2a^{12}} \\
C_{12}^T(U_3) &= 10.30 \frac{\nu}{2a^{12}} \\
C_{44}^T(U_3) &= 0.035 \frac{\nu}{2a^{12}}
\end{align*}
\]

If the nearest neighbour distance in lattice is $d$ then $a = d/\sqrt{2}$. These results are independent of temperature and the two-body potential used. We used the value of $\nu$ from Chapter 2 and calculated the value of a corresponding to the densities used in our Monte Carlo calculations.

The final result which we need is the expression for $\frac{\partial P}{\partial T}$ to enable us to calculate $\Delta C = C^S - C^T$.
From Chapter 2

\[ PV = NkT + \langle P_2 \rangle_0 + \langle P_3 \rangle_0 + \langle P_Q \rangle_0 + \langle P_o \rangle_o \]

\[ \frac{1}{kT} \left[ \langle U_3 P_o \rangle_0 - \langle U_3 \rangle_0 \langle P_o \rangle_o \right] \]

\[ + \langle U_2 P_o \rangle_0 - \langle U_2 \rangle_0 \langle P_o \rangle_o \]

\[ + \langle U_Q P_o \rangle_0 - \langle U_Q \rangle_0 \langle P_o \rangle_o \]

\[ \left( \frac{\partial P}{\partial T} \right)_V = \frac{NK}{V} - \frac{1}{Vkt^2} \left[ \langle (P_T + P_o) U_o \rangle_0 - \langle U_o \rangle_0 \langle P_T + P_o \rangle_o \right] \]

Where we have used \( \langle A + B \rangle = \langle A \rangle + \langle B \rangle \) and defined \( P_T = P_2 + P_3 + P_Q \). The derivatives of the variance terms have been ignored in consistency with equation 5:38 and later similar expressions. The expression for \( C_V \) was derived in Chapter 2. We now can calculate

\[ \Delta C = C_{11}^S - C_{11}^T = C_{12}^S - C_{12}^T \]

from

\[ \Delta C = \frac{\Delta T}{C_V} \left( \frac{\partial P}{\partial T} \right)_V^2 \]

\[ \frac{kT}{V} \left[ N - \frac{1}{(kT)^2} \left\{ \langle (P_T + P_o) U_o \rangle_0 - \langle P_T + P_o \rangle_o \langle U_o \rangle_0 \right\} \right]^2 \]

\[ = \frac{3}{2} N + \frac{1}{(kT)^2} \left[ \langle (U_o + U_T) U_o \rangle_0 - \langle U_o \rangle_0 \langle U_o + U_T \rangle_o \right] \]

The results of using the expressions derived here in conjunction with Monte Carlo calculations are discussed in section 5:5.

5:4 The Internal Energy and Equation of State of Solid Argon

Using Monte Carlo methods, solid argon has been modelled along the solid-vapour coexistence line at five temperatures, from 40 to 80°K. The density, molar volume, and lattice constant of argon at the temperatures studied appear in Table 5:1. The experimental values used were measured by Peterson, Batchelder, and Simmons (1966) using X-ray diffraction methods. The values of the lattice constant are
close to the earlier results reported by Barrett and Meyer (1964) but are believed to be more accurate.

Table 5.1

Temperature, Density, Molar Volume, and Lattice constants of solid argon.

<table>
<thead>
<tr>
<th>( T^\circ K )</th>
<th>( \rho ) ( \text{gm/cm}^3 )</th>
<th>( V_M ) ( \text{cm}^3/\text{mole} )</th>
<th>Lattice Constant ( \times 10^8 \text{cm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.7322</td>
<td>23.06</td>
<td>5.35048</td>
</tr>
<tr>
<td>50</td>
<td>1.7149</td>
<td>23.29</td>
<td>5.36839</td>
</tr>
<tr>
<td>60</td>
<td>1.6919</td>
<td>23.61</td>
<td>5.39262</td>
</tr>
<tr>
<td>70</td>
<td>1.6656</td>
<td>23.98</td>
<td>5.42087</td>
</tr>
<tr>
<td>80</td>
<td>1.6350</td>
<td>24.43</td>
<td>5.45454</td>
</tr>
</tbody>
</table>

In this work the present Barker potential was used. This potential was developed in conjunction with the liquid state studies discussed in Chapter 3. In the Monte Carlo work the two-body potential, truncated at \( 4L \) was used to generate at least 250,000 configurations. The initial configuration at 40\(^\circ\) consisted of a face-centred cubic lattice at the appropriate density. Some of the higher temperature runs used an equilibrium configuration of a lower temperature run, suitably expanded, for the initial configuration. The thermodynamic pressure and the internal energy were then calculated using the perturbation expansion described in Chapter 2. The statistical error in the pressure and internal energy was estimated to be \( \sqrt{1.5} \) that given for the Monte Carlo work reported in Barker, Fisher, and Watts, (1971) since 200,000 rather than 300,000 configurations have been used in the averages. The statistical error is thus estimated at \( \pm 2.5 \text{ cal./mole in } U \) and \( \pm 19 \text{ atm. in } P \). The calculated values of \( U \) and \( P \) at every 20,000th configuration appear in Table 5.3. The kinetic energy contribution to the pressure has been included in the tabulated values.
The long range two-body contributions to the pressure and energy have been calculated using 10 configurations. For one point 42 configurations were used to calculate the perturbation terms $U_2$ and $P_2$. $U_2$ and $P_2$ as a function of the number of configurations appear in Table 5:2. From the table, it appears that $P_2$ is accurate to ± 5 atm., and $U_2$ to ± 2 cal./mole when only 10 configurations are considered. Contributions from atoms separated by more than 1.5 L have been estimated by using the static lattice approximation from this distance out to 65 nearest neighbour shells. This contribution has not been added to the values appearing in Table 5:2 but is included in subsequent tables. The static lattice values corresponding to $U_2$ and $P_2$ have also been calculated. Pressures evaluated using the static lattice approximation were consistently 5 to 10 atm. higher than those calculated using the perturbation theory. Thus the error has been reduced even when only 10 configurations have been used in the perturbation estimates.

Short range three-body and quantum corrections were calculated using 200 configurations generated during the Monte Carlo run, using the perturbation expansion derived in Chapter 2. $U_3$, $P_3$, $U_3^Q$ and $P_3^Q$ are presented as a function of the number of configurations used in Table 5:3. Long range corrections have been made using the static lattice approximation and these corrections are incorporated in later tables. The static lattice contributions to $U_3$ and $P_3$ have been calculated by subtracting the equivalent short range static lattice result from the extrapolated value of the three-body static lattice energy reported by Zucker and Chell (1968), and confirmed by Barker, Klein and Bobetic (1971b). The error introduced by this method should not be significant. The error is difficult to estimate since it depends on the accuracy of the extrapolation used.

At low temperatures a major source of error can arise in our work. The perturbation theory used was developed originally as a high temperature expansion of the free energy for a material in which quantum effects are small. At low
TABLE 5.2
Long-range contributions to the two-body pressure and internal energy, as a function of the number of configurations used

\[
T = 80^\circ K \quad \quad V_m = 24.43 \text{ cm}^3/\text{mole}
\]

<table>
<thead>
<tr>
<th>No.</th>
<th>(U_2)</th>
<th>(P_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-81.64</td>
<td>-279.83</td>
</tr>
<tr>
<td>4</td>
<td>-85.21</td>
<td>-291.095</td>
</tr>
<tr>
<td>6</td>
<td>-84.54</td>
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</tr>
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STATIC
LATTICE  | -83.1  | -285.1
## Table 5.3

Contributions to the Pressure and Internal Energy as Functions of the Number of Configurations

\( U \) and \( P \) every 2000 configurations. All others every 20 configurations.

\[ T = 60^\circ K \quad V_M = 23.61 \text{ cm}^3/\text{mole} \]

<table>
<thead>
<tr>
<th>( U_0 )</th>
<th>( P_0 )</th>
<th>( U_3 )</th>
<th>( P_3 )</th>
<th>( U_Q )</th>
<th>( P_Q )</th>
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\[ \text{Page 116} \]
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<tr>
<th>T°K</th>
<th>No.</th>
<th>Vₘ</th>
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<td>23.98</td>
<td>-1806.6</td>
<td>-87.8</td>
<td>122.6</td>
<td>24.4</td>
<td>-1747.4</td>
</tr>
<tr>
<td>70(b)</td>
<td>297</td>
<td>23.98</td>
<td>-1808.2</td>
<td>-87.8</td>
<td>122.6</td>
<td>24.4</td>
<td>-1745.8</td>
</tr>
<tr>
<td>80</td>
<td>200</td>
<td>24.43</td>
<td>-1757.7</td>
<td>-86.5</td>
<td>115.1</td>
<td>19.2</td>
<td>-1709.9</td>
</tr>
</tbody>
</table>
temperatures terms of higher order in $T$ will become important. The quantum effects are also larger in this region. Finally there is the related problem arising since we have used the classical rather than the quantum statistical expression for the partition function in our Monte Carlo work. This is not really distinct from the use of the Wigner-Kirkwood expansion at low temperatures. Because of this we have not undertaken calculations at temperatures below 40°.

**Table 5:5**

Comparison of calculated and experimental internal energies of solid argon. Values in units of cal./mole. $U_i(0) = -1846$.

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>$U_i$ (calc.)</th>
<th>$U_i$ (expt.)</th>
<th>$\int C_{Sat} dT$</th>
<th>$-3/2 NkT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>-1849</td>
<td>-1856</td>
<td>109</td>
<td>-119</td>
</tr>
<tr>
<td>50</td>
<td>-1822</td>
<td>-1829</td>
<td>166</td>
<td>-149</td>
</tr>
<tr>
<td>60</td>
<td>-1790</td>
<td>-1797</td>
<td>228</td>
<td>-179</td>
</tr>
<tr>
<td>70</td>
<td>-1746</td>
<td>-1758</td>
<td>296</td>
<td>-208</td>
</tr>
<tr>
<td>80</td>
<td>-1710</td>
<td>-1715</td>
<td>371</td>
<td>-238</td>
</tr>
</tbody>
</table>

The various contributions to the internal energy appear in Table 5:4. In Table 5:5 these are compared with experimental values. In this work we have used the value of the heat of sublimation at $0^\circ K$ calculated by Beaumont, Chihara and Morrison (1961) from their experimental results. Their specific heat data (Flubacher, Leadbetter and Morrison, 1961) was then used to calculate the internal energy by means of the thermodynamic equation

$$U_i(T) = U(0) + \int_0^T C_{Sat} dT - \frac{3}{2} NkT \quad 5:51$$

The estimated error in the experimental values of $U_i$ is ± 8 cal./mole. The maximum difference between the
experimental and calculated values of the internal energy is 11 cal./mole. This agreement is even better than that found in the liquid state investigations. There is no apparent increase in error at lower temperatures either which might at first indicate that the Monte Carlo procedure could be extended to even lower temperatures. This will be discussed further in conjunction with the specific heat calculations. The calculated pressures in Table 5:6 are all reasonably close to the experimental value. The agreement is not within our expected total error of ± 25 atm. however. It appears that the calculated pressures are about 25 atm. high on average. The results can be considered quite pleasing however, in view of the large contributions added together in its calculation. Three of our points give pressures within the expected error of the experimental value. The value at 70° is less satisfactory; however, when the Monte Carlo run at this temperature was extended to 290,000 configurations, the pressure was reduced by 16.5 atm. This significantly improves our results. The extended run appears in the tables as 70(b). The point labelled 60(a) was formed by extending the Monte Carlo run to 400,000 configurations with 400 configurations being used in the calculation of the three-body and quantum perturbation terms. No error due to using classical rather than quantum statistics in our calculations at low temperatures is apparent in these results. The calculations of energy and pressure have been very successful.

Barker (1971) has reported a calculated pressure of + 8 atm. for the Barker-Bobetic potential at 60° using Monte Carlo methods. It appears that the Barker-Bobetic and present Barker potentials give essentially the same results for the solid state pressures. This is shown more clearly in Table 5:7 where our results are compared with Monte Carlo results of Barker and Klein (Barker, 1971) calculated using the Barker-Bobetic potential. Experimental data below 80°
### TABLE 5:6

CONTRIBUTIONS TO THE PRESSURE OF SOLID ARGON

<table>
<thead>
<tr>
<th>$T^0K$</th>
<th>$V_m$</th>
<th>$P_0$</th>
<th>$P_2$</th>
<th>$P_3$</th>
<th>$P_Q$</th>
<th>$P_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>23.06</td>
<td>-609.2</td>
<td>-354.9</td>
<td>693.0</td>
<td>238.6</td>
<td>32.5</td>
</tr>
<tr>
<td>50</td>
<td>23.29</td>
<td>-458.3</td>
<td>-351.0</td>
<td>656.4</td>
<td>168.3</td>
<td>15.3</td>
</tr>
<tr>
<td>60</td>
<td>23.61</td>
<td>-410.3</td>
<td>-330.6</td>
<td>621.4</td>
<td>131.4</td>
<td>11.7</td>
</tr>
<tr>
<td>60(a)</td>
<td>23.61</td>
<td>-405.5</td>
<td>-330.6</td>
<td>621.4</td>
<td>131.4</td>
<td>15.2</td>
</tr>
<tr>
<td>70</td>
<td>23.98</td>
<td>-327.3</td>
<td>-311.8</td>
<td>590.2</td>
<td>103.0</td>
<td>54.1</td>
</tr>
<tr>
<td>70(b)</td>
<td>23.98</td>
<td>-343.8</td>
<td>-311.8</td>
<td>590.2</td>
<td>103.0</td>
<td>37.6</td>
</tr>
<tr>
<td>80</td>
<td>24.43</td>
<td>-312.8</td>
<td>-314.8</td>
<td>535.7</td>
<td>70.6</td>
<td>21.3</td>
</tr>
</tbody>
</table>
are from Peterson et al (1966). At higher temperatures the data were obtained from Crawford and Daniels (1968). This table also shows that the Barker-Bobetic potential gives good values for the solid state pressure at temperatures above the normal boiling point.

<table>
<thead>
<tr>
<th>T&lt;sub&gt;K&lt;/sub&gt;</th>
<th>V&lt;sub&gt;M&lt;/sub&gt; cm&lt;sup&gt;3&lt;/sup&gt;/mole</th>
<th>P&lt;sub&gt;calc.&lt;/sub&gt; atm.</th>
<th>P&lt;sub&gt;expt&lt;/sub&gt; atm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>60*</td>
<td>23.61</td>
<td>11.71</td>
<td>0.0</td>
</tr>
<tr>
<td>60(a)*</td>
<td>23.61</td>
<td>15.16</td>
<td>0.0</td>
</tr>
<tr>
<td>63.10†</td>
<td>23.75</td>
<td>1.2</td>
<td>0.0</td>
</tr>
<tr>
<td>63.10†</td>
<td>23.75</td>
<td>.6</td>
<td>0.0</td>
</tr>
<tr>
<td>77.13†</td>
<td>24.30</td>
<td>28.0</td>
<td>0.0</td>
</tr>
<tr>
<td>77.13†</td>
<td>24.30</td>
<td>28.5</td>
<td>0.0</td>
</tr>
<tr>
<td>80. *</td>
<td>24.43</td>
<td>21.28</td>
<td>0.0</td>
</tr>
<tr>
<td>108.12†</td>
<td>24.03</td>
<td>1014.</td>
<td>1037.</td>
</tr>
<tr>
<td>160.40†</td>
<td>22.55</td>
<td>3758.</td>
<td>3755.</td>
</tr>
<tr>
<td>180.15†</td>
<td>22.09</td>
<td>4892.</td>
<td>4934.</td>
</tr>
<tr>
<td>201.32†</td>
<td>21.70</td>
<td>6118.</td>
<td>6252.</td>
</tr>
</tbody>
</table>

In summary our calculations have resulted in excellent agreement with the experimental values of the pressure and internal energy. The values reported here are very near those calculated elsewhere using the Barker-Bobetic potential, showing that the two potentials give similar solid state results. The anticipated increase in error due to quantum effects at low temperatures has not become apparent, since the agreement with experiment is uniformly good. In the following section we discuss the calculation of the elastic constants of argon.

* This work.
† Barker.
5.5 The Elastic Constants of Argon

The elastic constants for argon have been investigated at the same temperatures for which the internal energy and equation of state have been investigated. The various contributions to the isothermal elastic constants $C_{11}^T$, $C_{12}^T$ and $C_{44}^T$ are listed in Table 5:8 in units of $10^{10}$ dynes/cm$^2$. Table 5:9 contains the value of $\Delta C$, $C_{11}^S$, $C_{12}^S$ and $C_{44}^S$, as well as the corresponding experimental values as measured by Keeler and Batchelder (1970). Our elastic constants are consistent with the lattice dynamics results of Barker, Klein and Bobetic (1971a) at low temperatures, calculated using the Barker-Bobetic potential, which show similar deviations from the experimental values. The results of Barker et al (1971a) appear with ours and the experimental points in figure 5:1.

The effect of pressures on the elastic constants has been considered as well. Barron and Klein (1965) showed that for a cubic solid under a pressure $P$ the following relations hold

$$c_{11}^S = C_{11}^S - P$$
$$c_{12}^S = C_{12}^S + P$$
$$c_{44}^S = C_{44}^S - P$$

Here the $C_{ij}^S$ are the elastic constants defined previously and the $c_{ij}^S$ are the corresponding adiabatic elastic constants as determined from sound velocity measurements in a solid under an external pressure $P$. This correction amounts to less than 4% at the pressures considered in this work. Therefore no correction for this effect has been made.
### TABLE 5:8

CONTRIBUTIONS TO THE ISOTHERMAL ELASTIC CONSTANTS OF ARGON  
(values in units of $10^{10}$ dynes cm$^{-2}$)

<table>
<thead>
<tr>
<th>$T^{\circ}K$</th>
<th>$C_{11}^{T}(U_0)$</th>
<th>$C_{11}^{T}(U_2)$</th>
<th>$C_{11}^{T}(U_3)$</th>
<th>$C_{11}^{T}(U_Q)$</th>
<th>$C_{11}^{T}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>2.8966</td>
<td>-.1849</td>
<td>.2705</td>
<td>.2219</td>
<td>3.204</td>
</tr>
<tr>
<td>50</td>
<td>2.4401</td>
<td>-.1784</td>
<td>.2598</td>
<td>.1725</td>
<td>2.694</td>
</tr>
<tr>
<td>60</td>
<td>2.4270</td>
<td>-.1699</td>
<td>.2462</td>
<td>.1380</td>
<td>2.641</td>
</tr>
<tr>
<td>60(a)</td>
<td>2.3654</td>
<td>-.1699</td>
<td>.2462</td>
<td>.1380</td>
<td>2.579</td>
</tr>
<tr>
<td>70</td>
<td>2.008</td>
<td>-.1593</td>
<td>.2312</td>
<td>.1130</td>
<td>2.193</td>
</tr>
<tr>
<td>70(b)</td>
<td>1.962</td>
<td>-.1593</td>
<td>.2312</td>
<td>.1130</td>
<td>2.189</td>
</tr>
<tr>
<td>80</td>
<td>1.5637</td>
<td>-.1491</td>
<td>.2146</td>
<td>.0932</td>
<td>1.722</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$C_{12}^{T}(U_0)$</th>
<th>$C_{12}^{T}(U_2)$</th>
<th>$C_{12}^{T}(U_3)$</th>
<th>$C_{12}^{T}(U_Q)$</th>
<th>$C_{12}^{T}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1.6026</td>
<td>-.0503</td>
<td>.2805</td>
<td>.1100</td>
</tr>
<tr>
<td>50</td>
<td>1.2681</td>
<td>-.0489</td>
<td>.2695</td>
<td>.0852</td>
</tr>
<tr>
<td>60</td>
<td>1.3188</td>
<td>-.0471</td>
<td>.2553</td>
<td>.0679</td>
</tr>
<tr>
<td>60(a)</td>
<td>1.2684</td>
<td>-.0471</td>
<td>.2553</td>
<td>.0679</td>
</tr>
<tr>
<td>70</td>
<td>1.105</td>
<td>-.0450</td>
<td>.2398</td>
<td>.0551</td>
</tr>
<tr>
<td>70(b)</td>
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<td>.2398</td>
<td>.0551</td>
</tr>
<tr>
<td>80</td>
<td>.7770</td>
<td>-.0425</td>
<td>.2226</td>
<td>.0452</td>
</tr>
<tr>
<td>$T^0 \text{K}$</td>
<td>$C_{44}^T (U_0)$</td>
<td>$C_{44}^T (U_2)$</td>
<td>$C_{44}^T (U_3)$</td>
<td>$C_{44}^T (U_Q)$</td>
</tr>
<tr>
<td>-------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>40</td>
<td>1.7064</td>
<td>-.0503</td>
<td>.0010</td>
<td>.1100</td>
</tr>
<tr>
<td>50</td>
<td>1.5656</td>
<td>-.0489</td>
<td>.0009</td>
<td>.0852</td>
</tr>
<tr>
<td>60</td>
<td>1.4565</td>
<td>-.0471</td>
<td>.0009</td>
<td>.0679</td>
</tr>
<tr>
<td>60(a)</td>
<td>1.4513</td>
<td>-.0471</td>
<td>.0009</td>
<td>.0679</td>
</tr>
<tr>
<td>70</td>
<td>1.278</td>
<td>-.0450</td>
<td>.0008</td>
<td>.0551</td>
</tr>
<tr>
<td>80</td>
<td>1.0618</td>
<td>-.0425</td>
<td>.0008</td>
<td>.0452</td>
</tr>
</tbody>
</table>
The contributions \( c_{ij}^S(U_3) \) were obtained using the static lattice approximation. Therefore we have used the value of \( P_3 \) as calculated using the same approximation in the relation (Barker, Klein and Bobetic, 1971b).

\[
\begin{align*}
c_{11}^S(U_3) &= c_{11}^S(U_3) - P_3 \\
c_{12}^S(U_3) &= c_{12}^S(U_3) + P_3 \\
c_{44}^S(U_3) &= c_{44}^S(U_3) - P_3
\end{align*}
\]

These were used to correct for the effect of pressure on these contributions.

In an attempt to measure the statistical error in our expressions for the elastic constants we have applied the statistical test used in Chapter 3 to the various contributions appearing in eqns. 5:35, 5:36 and 5:37. Subaverages were formed over groups of 2000 configurations and eqn. 3:11 was applied to the results. We found that the standard error in the Born terms is about 1%. The error in the fluctuation terms is estimated at about 4%. The errors in the terms

\[
< \sum \frac{u_i'}{r} (\Delta x)^2 >
\]

and

\[
< \sum \frac{u_i'}{r} (\Delta x)^2 \cdot \sum \frac{u_j'}{r} (\Delta y)^2 >
\]

are about 1.5% and 2% respectively. The overall statistical error should then be about 3%, considering the relative magnitudes of the Born and fluctuation terms. However, examining the results for 60° over configurations 200,000 to 400,000, the maximum and minimum values of \( C_{11}^T(U_0) \) are 2.46 and \( 2.36 \times 10^{10} \) dynes/cm\(^2\) respectively. The corresponding values for \( C_{12}^T(U_0) \) are 1.38 and 1.27. For \( C_{44}^T(U_0) \)
Figure 5:1

Adiabatic elastic constants of argon.
they are 1.459 and 1.445. These variations amount to 4%, 10%, and 1% of $C_{11}^{T}$, $C_{12}^{T}$, and $C_{44}^{T}$ respectively. As a result the error bounds on $C_{11}^{T}$, $C_{12}^{T}$, and $C_{44}^{T}$ have been taken to be $\pm 4\%$, $\pm 10\%$ and $\pm 2\%$ respectively. It is interesting to note that the uncertainties in the experimental results have similar relative uncertainties (Keeler and Batchelder, 1970). Since the isothermal elastic constants have not been measured directly we have compared our results for the adiabatic elastic constants with experiment. Estimates of the experimental values of $\Delta C$ have also been made.

Before discussing these results we will consider the self-consistency of our calculated values of $C_{ij}^{T}$ appearing in Table 5:8. In general, the results are quite reasonable however the magnitudes of $C_{11}^{T}$ and $C_{12}^{T}$ at 50° are low relative to the values at 40° and 60°. Consistency can be achieved however using values within our stated error bounds. Further discussion of this temperature will appear in the following section.

In Table 5:9 we have compared the calculated values of the adiabatic elastic constants with the experimental results of Keeler and Batchelder (1970). A further comparison appears as figure 5:1. It can be seen from these results that the calculated values of $C_{11}^{S}$ are consistently lower than experiment. The values of $C_{12}^{S}$ and $C_{44}^{S}$ are consistently high. Similar results were obtained at 0°K by Barker et al (1971a) using lattice dynamics methods. In fact our results are in better agreement with the Lennard-Jones Monte Carlo calculations as can be seen from Table 5:10. These values have been calculated using the published results for the isothermal elastic constants, (Squire et al (1969) along with the values of $\Delta C$ calculated later (Hoover et al (1969)). Quantum corrections have been made using the percentages quoted in the second paper. Our overall agreement with experiment appears to be only slightly better.
### TABLE 5:9

ADIABATIC ELASTIC CONSTANTS OF ARGON

(values in $10^{10}$ dynes cm$^{-2}$)

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>$\Delta C$</th>
<th>$C_{11}^S$</th>
<th>$C_{11}^S$(expt)</th>
<th>$C_{12}^S$</th>
<th>$C_{12}^S$(expt)</th>
<th>$C_{44}^S$</th>
<th>$C_{44}^S$(expt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>.328</td>
<td>3.532</td>
<td>3.766</td>
<td>2.271</td>
<td>1.766</td>
<td>1.767</td>
<td>1.345</td>
</tr>
<tr>
<td>50</td>
<td>.576</td>
<td>3.270</td>
<td>3.507</td>
<td>2.150</td>
<td>1.712</td>
<td>1.603</td>
<td>1.234</td>
</tr>
<tr>
<td>60</td>
<td>.442</td>
<td>3.083</td>
<td>3.240</td>
<td>2.037</td>
<td>1.628</td>
<td>1.478</td>
<td>1.121</td>
</tr>
<tr>
<td>60(a)</td>
<td>.484</td>
<td>3.064</td>
<td>3.240</td>
<td>2.029</td>
<td>1.628</td>
<td>1.473</td>
<td>1.121</td>
</tr>
<tr>
<td>70</td>
<td>.557</td>
<td>2.750</td>
<td>2.972</td>
<td>1.912</td>
<td>1.516</td>
<td>1.289</td>
<td>1.005</td>
</tr>
<tr>
<td>70(b)</td>
<td>.578</td>
<td>2.767</td>
<td>2.972</td>
<td>1.898</td>
<td>1.516</td>
<td>1.306</td>
<td>0.887</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>$C_{11B}^S$</th>
<th>$C_{11LJ}^S$</th>
<th>$C_{12B}^S$</th>
<th>$C_{12LJ}^S$</th>
<th>$C_{11B}^S$</th>
<th>$C_{12LJ}^S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>3.532</td>
<td>3.41</td>
<td>2.271</td>
<td>2.07</td>
<td>1.767</td>
<td>1.81</td>
</tr>
<tr>
<td>60</td>
<td>3.064</td>
<td>2.91</td>
<td>2.029</td>
<td>1.86</td>
<td>1.473</td>
<td>1.52</td>
</tr>
<tr>
<td>80</td>
<td>2.424</td>
<td>2.40</td>
<td>1.704</td>
<td>1.61</td>
<td>1.065</td>
<td>1.21</td>
</tr>
</tbody>
</table>

### TABLE 5:10

COMPARISON OF ELASTIC CONSTANTS CALCULATED USING THE PRESENT BARKER AND LENNARD-JONES POTENTIALS.

(Values in units of $10^{10}$ dynes cm$^{-2}$)
In Table 5:11 the ΔC calculated here has been compared with experimental values derived using the expression.

$$ΔC = γ^2 T \frac{C_V}{V}.$$  

The experimental values of $C_V$ and $γ$ are described in the next section. The values labelled ΔC (pert) were calculated using the quantum and three-body perturbation terms in eqn. 5:50. The others included only terms related to the short range two-body results. These latter values have been used in the development of Table 5:9 since the perturbation terms are not calculated with any accuracy using only 200 configurations. This can be seen clearly from the scatter in the perturbation values appearing in the table. The estimated error in the calculated values of ΔC is ± 10% when perturbation terms are ignored. It is apparent that the calculated values of ΔC are consistently higher than those derived from experimental data. The error seems to increase with decreasing temperatures. This may be evidence that quantum effects are more important at low temperatures but considering the large statistical error in these quantities this can only be a tentative conclusion. One interesting feature is the value of ΔC at 50°. This very high value compensates for the low values of $C_{11}^T$ and $C_{12}^T$ mentioned earlier. It should be noted that the adiabatic elastic constants at 50° all lie nicely between the values at 40° and 60°. There appears to be a correlation between ΔC and the fluctuation terms in the elastic constants. Thus might tend to reduce the statistical error in the calculated adiabatic elastic constants, rather than increase it as you would expect from adding two terms with uncorrelated statistical errors. This would add more weight to the suggestion that there is a real difference between the calculated values and the experimental ones.
Table 5:11

Comparison of experimental and calculated values of $\Delta C$

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>$\Delta C$ (expt)</th>
<th>$\Delta C$</th>
<th>$\Delta C$ (pert)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.246</td>
<td>0.328</td>
<td>0.345</td>
</tr>
<tr>
<td>50</td>
<td>0.326</td>
<td>0.576</td>
<td>0.557</td>
</tr>
<tr>
<td>60</td>
<td>0.399</td>
<td>0.442</td>
<td>0.413</td>
</tr>
<tr>
<td>60(a)</td>
<td>0.399</td>
<td>0.484</td>
<td>0.532</td>
</tr>
<tr>
<td>70</td>
<td>0.460</td>
<td>0.557</td>
<td>0.627</td>
</tr>
<tr>
<td>70(b)</td>
<td>0.460</td>
<td>0.578</td>
<td>-</td>
</tr>
<tr>
<td>80</td>
<td>0.512</td>
<td>0.702</td>
<td>0.761</td>
</tr>
</tbody>
</table>

Several possible sources of the discrepancy between experimental and calculated values have been considered. The experimental measurements of Keeler and Batchelder (1970) appear to be soundly based. There is a good knowledge of the crystal orientation that was missing in the earlier measurements of Moeller and Squire (1966). The values of the elastic constants derived from the experimental velocities have been checked by recalculating them and are correct.

The potential function used does not appear to be a difficulty since the results for the Barker and Lennard-Jones potentials are so similar. The fluctuation terms used in the expressions for the elastic constants should be accurate since they are directly related to the pressure which is in agreement with the experimental results. When we consider the terms

$$<r \frac{\partial u}{\partial r} > = < \frac{1}{r} \frac{\partial u}{\partial r} (x^2 + y^2 + z^2)$$

the first expression occurs in the equation for the pressure and the second appears in the fluctuation terms
of $C_{11}^T$ and $C_{12}^T$. The Born terms cannot be altered to improve
agreement since they are connected and must be raised for
$C_{11}^T$ and lowered for $C_{12}^T$ if we wish to obtain agreement
with experimental results. The value of $\Delta C$ cannot be
improved for the same reason. The accuracy of the potential
has been established but the Lennard-Jones results indicate
the elastic constants are not sensitive to the particular
potential used.

A further error lies in the fluctuation terms that
have been neglected in the perturbation corrections. Since
these corrections are small it seems unlikely that their
fluctuation terms are important.

We are thus left with a definite discrepancy between
theoretical and experimental elastic constants. It seems
that this can only be remedied by further developments in
the theory of elastic media. Perhaps the energy can only
be adequately described using higher order terms in its
their error to uncertainties in the potential used but
this no longer seems to be the case.

As a final point we note a difference between the
freedom of movement allowed the atoms in our work and in
that of Squire et al (1969). One restriction on the
allowed moves for the atoms in our solid has been
considered. It is discussed here since it only affects
the elastic constants. In their work Squire et al (1969)
restricted their atoms to lie within one half of the
nearest neighbour distance from their lattice sites. If
this restriction is not made then the most probable
change in the lattice structure would be an interchange
of two atoms, or possibly a change to a different form
of close packing. Under the interchange of two atoms
eqns. 5:35, 5:36 and 5:37 are unchanged and so the
calculated elastic constants remain the same. However,
this would not be a homogeneous deformation such as was assumed initially in the theoretical development. After the calculations were made the positions of all the atoms were compared with their initial lattice sites and it was found that their positions lay nearer the original lattice sites than to other sites. This indicates that in fact no interchanges had taken place, that the structure had not changed and that the orientation of the lattice remained the same in all cases. It seems then that the only effect of restricting atoms to cells in solid calculations using 108 particles is to increase the necessary calculations. There does not seem to be enough freedom in a periodic system of this size to allow interchanges at solid densities, because of the great amount of co-operative motion necessary. With larger systems interchanges might be possible and the theoretical development of expressions for the elastic constants would then need modification if atoms were not restricted to cells of some form. However with 108 particles this restriction does not seem to be necessary.

5.6 Other Thermodynamic Properties of Solid Argon

Several additional properties of solid argon have also been calculated in this work. These are the anharmonicity, bulk moduli, specific heat at constant volume and Gruneisen constant. The anharmonicity $A$ is defined by

$$A = \frac{2 \, C_{44}}{C_{11} - C_{12}}$$

The bulk modulus $B$ at zero pressure may be related to the elastic constants by the relation

$$B = \frac{C_{11} + 2C_{12}}{3}$$
Both isothermal and adiabatic values of these properties may be calculated by using the appropriate elastic constants. The adiabatic and isothermal bulk moduli and the adiabatic anharmonicity appear as $B_{SB}$, $B_{TB}$ and $A_{SB}$ respectively in Table 5:12. They are compared with experimental values of $B_S$ and $B_T$ derived from the compressibilities of Peterson, Batchelder, and Simmons (1966). The experimental values of $A_S$ were calculated, from the elastic constants of Keeler and Batchelder (1970). In addition the Lennard-Jones values for $B_T$ calculated by Squire et al (1969) and values of $B_S$ and $A_S$ derived from the results of Hoover et al (1969) appear for comparison. The experimental values of the $B_S$ are close to those calculated by Keeler and Batchelder (1970) from their elastic constants, however the accuracy of the earlier work should be greater (Bobetic and Barker (1970). The values of $B_T$ were calculated using the relation

$$B_T = \frac{B_S}{1 + \alpha T \gamma}$$

where $\alpha$ is the coefficient of thermal expansion and $\gamma$ is Gruneisen's constant to be discussed shortly. The values of $B_{TB}$ and $B_{SB}$ appear to be 10 - 11% higher than the experimental results. This is approximately the magnitude of the experimental uncertainty. Bobetic and Barker (1971) found that their value of the bulk modulus at 0°C was 9% higher than experiment. It has been inferred from this that the high value of the bulk modulus is found over the whole range of solid temperatures when the Barker potentials are used. Including quantum corrections in $B_{TLJ}$ would raise those values a few percent giving reasonable agreement with experiment. The values of $B_{SLJ}$ lie between $B_{SB}$ and the experimental values.
TABLE 5:12

THE ISOTHERMAL AND ADIABATIC BULK MODULI AND ANISOTROPY OF SOLID ARGON

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>$B_{TB}$</th>
<th>$B_T$(expt)</th>
<th>$B_{TLJ}$</th>
<th>$B_{SB}$</th>
<th>$B_S$(expt)</th>
<th>$B_{SLJ}$</th>
<th>$A_{SB}$</th>
<th>$A_{SLJ}$</th>
<th>$A_S$(expt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>2.36</td>
<td>2.17</td>
<td>2.04</td>
<td>2.69</td>
<td>2.43</td>
<td>2.52</td>
<td>2.80</td>
<td>2.70</td>
<td>1.35</td>
</tr>
<tr>
<td>50</td>
<td>1.95</td>
<td>1.96</td>
<td>2.52</td>
<td>2.29</td>
<td>2.86</td>
<td></td>
<td></td>
<td></td>
<td>1.37</td>
</tr>
<tr>
<td>60</td>
<td>1.94</td>
<td>1.72</td>
<td>1.64</td>
<td>2.39</td>
<td>2.12</td>
<td>2.21</td>
<td>2.83</td>
<td>2.90</td>
<td>1.39</td>
</tr>
<tr>
<td>60(a)</td>
<td>1.89</td>
<td>1.72</td>
<td>2.37</td>
<td>2.12</td>
<td>2.85</td>
<td></td>
<td></td>
<td></td>
<td>1.39</td>
</tr>
<tr>
<td>70</td>
<td>1.63</td>
<td>1.47</td>
<td>2.19</td>
<td>1.93</td>
<td>3.08</td>
<td></td>
<td></td>
<td></td>
<td>1.38</td>
</tr>
<tr>
<td>70(b)</td>
<td>1.61</td>
<td>1.47</td>
<td>2.19</td>
<td>1.93</td>
<td>3.08</td>
<td></td>
<td></td>
<td></td>
<td>1.38</td>
</tr>
<tr>
<td>80</td>
<td>1.24</td>
<td>1.21</td>
<td>1.12</td>
<td>1.94</td>
<td>1.72</td>
<td>1.87</td>
<td>2.96</td>
<td>3.06</td>
<td>1.35</td>
</tr>
</tbody>
</table>

TABLE 5:13

COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES
OF THE SPECIFIC HEAT AND GRUNEISEN $\gamma$ OF ARGON

(C$_V$ in units of cal./mol/$^\circ$K)

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>C$_V$</th>
<th>C$_V$(pert)</th>
<th>C$_V$(expt)</th>
<th>$\gamma$</th>
<th>$\gamma$(pert)</th>
<th>$\gamma$(expt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>5.48</td>
<td>5.79</td>
<td>4.83</td>
<td>2.87</td>
<td>2.87</td>
<td>2.65</td>
</tr>
<tr>
<td>50</td>
<td>6.28</td>
<td>6.47</td>
<td>5.14</td>
<td>3.19</td>
<td>3.10</td>
<td>2.66</td>
</tr>
<tr>
<td>60</td>
<td>5.33</td>
<td>5.56</td>
<td>5.30</td>
<td>2.79</td>
<td>2.69</td>
<td>2.66</td>
</tr>
<tr>
<td>60(a)</td>
<td>5.49</td>
<td>5.83</td>
<td>5.30</td>
<td>2.88</td>
<td>2.93</td>
<td>2.66</td>
</tr>
<tr>
<td>70</td>
<td>5.50</td>
<td>5.90</td>
<td>5.40</td>
<td>3.00</td>
<td>2.95</td>
<td>2.64</td>
</tr>
<tr>
<td>70(b)</td>
<td>5.54</td>
<td>5.57</td>
<td>2.92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>5.70</td>
<td>6.00</td>
<td>5.57</td>
<td>2.89</td>
<td>3.04</td>
<td>2.59</td>
</tr>
</tbody>
</table>
In the case of the anisotropy the Lennard-Jones and Barker potentials have given essentially the same values. These are consistently more than twice the experimental anharmonicity. All of these results are consistent with the relative magnitudes of the various calculated and experimental elastic constants. It is the anharmonicity that most clearly shows the similarity of the Lennard-Jones and Barker potential results.

In Table 5.13 the experimental specific heat at constant volume $C_V$ and Gruneisen constant $\gamma$ are compared with the calculated values. The first point is that the perturbation corrections to $C_V$ are very unreliable as can be seen from the scatter in these values. The perturbation corrections to $\gamma$ must also be discounted since they depend on those related to $C_V$ and $\Delta C$ as mentioned earlier. Therefore, these values have not been used in the following discussion. The experimental values of $\gamma$ are those calculated by Peterson et al (1966) in their figure 5. We have also used their values of $C_V$ which were derived from the $C_p$ measurements of Flubacher et al (1961). All of these values are similar to but not in strong agreement with earlier results appearing in the review articles of Dobbs and Jones (1957) and Pollack (1964).

The calculated values of the specific heat are subject to large statistical errors and therefore comments based on these results are only advisory. This is most apparent from the calculated value at 50°K. Although the experimental values of $C_V$ begin to fall fairly rapidly at lower temperatures this is not apparent in our results. This could be expected since quantum mechanical effects are important in the specific heat of solid argon. It is also true that the specific heat of a solid at 0°K is zero, whereas the classical expression used would result in a value of 2.98 cal./mole. Thus quantum effects must become important, certainly at 20° and possibly at 30°K.
Combining this with the fact that $\Delta C$ was not going to zero quickly enough at low temperatures it seems that large quantum effects may be important in our fluctuation terms although they were not observed in the values of the pressure and internal energy.

The calculated value of $\gamma$ is also subject to a large statistical error. It does appear to be closer to the earlier estimates of Dobbs and Jones (1957) than the later work of Peterson et al (1966). The calculated values are slightly higher than any earlier experimental work has indicated, but lie nearly within the experimental uncertainty of $\pm 10\%$ (Peterson et al, 1966). $\gamma$ has only been calculated here as an adjunct to the calculation of $\Delta C$. It comes from the Gruneisen equation of state for the solid which assumes that $\gamma$ is a constant defined by

$$\gamma = \frac{\alpha V B_T}{C_V}$$

Its current usefulness seems to be in combining the quantities in calculations of various thermodynamic properties from each other.

5:7 Summary of the Solid State Results

Properties of solid argon have been calculated using Monte Carlo methods at temperatures from 40° upwards. The calculated values of the energy and pressure are in very good agreement with experimental values. There are systematic differences between measured and experimental values of the same order as the combined error. The same is true of several other properties such as the bulk moduli and Gruneisen $\gamma$.

The elastic constants of argon have also been calculated and reasonable agreement with experiment was obtained. However systematic differences were observed and the
calculated values were actually closer to values calculated previously using the Lennard-Jones potential. This has suggested that further theoretical developments may be necessary before better agreement can be achieved. The largest difference appears in the anisotropy, where the calculated value is more than twice the experimental one. Values depending on the energy and pressure fluctuations appear to be too large at 40°K indicating that the Monte Carlo method may not be useful for argon at lower temperatures. The evidence for this is tenuous, however theoretical considerations indicate that it cannot adequately represent the specific heat at 20°K.

Argon has been successfully simulated at temperatures between 40 and 80°K. The overall agreement with experiment has been quite pleasing. It also appears that the Barker-Bobetic and present Barker potentials give essentially the same results in contrast to the earlier study of liquid argon.
CHAPTER 6

DISTRIBUTION FUNCTIONS

In the previous chapter the solid was described in terms of a lattice structure. In the solid, systematic ordering of atoms persisted for distances of macroscopic length. This order can be studied experimentally using X-ray diffraction (Barrett and Meyer, 1964). The liquid state also shows a definite structure when investigated using this technique (Egelstaff, 1967). However, the ordering is not as strong or persistent as in the solid. Liquids have been studied using lattice theory (Barker, 1963) in an attempt to use the order present but this was not very satisfactory. A more successful technique uses a probabilistic approach. The structure of the liquid is expressed in terms of molecular distribution functions. The n-particle distribution function for a fluid of N identical particles is

\[ f^{(n)}_N (x_1, \ldots, x_n) \, dx_1 \ldots dx_n \]

This function is defined so that it equals the probability of finding one of the n particles in each of n volume elements \( dx_1, \ldots, dx_n \). In this chapter we will investigate the one and two-particle distribution functions \( f^{(1)}_N \) and \( f^{(2)}_N \). Distribution functions will be calculated for a liquid interacting through the truncated Barker-Bobetic potential. From the results the pressure and internal energy are calculated. These will be compared with the equivalent values from Chapter 2. We begin by describing the theory of distribution functions.

6.1 One and Two-Body Distribution Functions

From Chapter 2 we have the function \( Z \) for a canonical ensemble of N identical particles contained in a volume \( V \)

\[ Z = \int \ldots \int e^{-U/kT} \, d^{3N} x \]

The probability that particle 1 will be in \( dx_1 \), particle 2 in \( dx_2 \), \ldots, and particle N in \( dx_N \) is given by (Hill, 1956)

\[ \frac{e^{-U/kT} \, dx_1 \ldots dx_N}{Z} \]

6.1
To find the probability of particles 1 through n being in 
\(dr_1 \ldots dr_n\) respectively, we integrate over the possible 
positions of particles n + 1 to N. One each of particles 
1 through N may be placed in \(dr_1 \ldots dr_n\). \(\frac{N!}{(N-n)!}\) ways. 
The probability of finding one particle in each of the volume 
elements \(dr_1 \ldots dr_n\) is then 
\[
\frac{f^{(n)}_N(x_1 \ldots x_n) \, dr_1 \ldots dr_n}{\frac{N!}{(N-n)!} \, \frac{1}{Z} \int \ldots \int e^{-U/kT} \, dr_{n+1} \ldots dr_N}
\]
This is the required n-particle distribution function.

For a uniform fluid \(f^{(1)}_N\) is independent of \(dr_1\) and is equal 
to the number density.

\[
f^{(1)}_N(x_1) = \frac{N}{V} = \rho
\]

It is now convenient to define the radial distribution 
function of a uniform fluid

\[
g_N(r) = \frac{f^{(2)}_N(r)}{f^{(1)}_N(r) \, f^{(1)}_N(r)} = \frac{f^{(2)}_N(r)}{\rho^2}
\]

We have used the fact that the fluid is uniform to reduce 
g_N(r) to a function of the distance

\[r = |x_1 - x_2|
\]
The general form of \(g_N(r)\) for a simple liquid is well known, 
and is described by Egelstaff (1967). An example appears 
in figure 6:1.

6:2 Thermodynamic Properties in Terms of \(g(r)\)

From Chapter 2 the internal energy of a system is given 
by

\[
E = \frac{3}{2} N kT + <U>
\]

\[
E = \frac{3}{2} N kT + \frac{1}{2} \int \int \int U \, e^{-U/kT} \, dr_1 \ldots dr_N.
\]

We now assume that \(U\) depends only on the distances separating 
pairs of particles

\[
U = \sum_{i<j=1}^{N} u(r_{ij})
\]
Figure 6:1
High and low density radial distribution functions.
Then
\[ <U> = \frac{1}{Z} \int \ldots \int \sum_{ij} u(r_{ij}) \ e^{-U/kT} \ d^{3N} r \]

In a uniform fluid \( U \) is the sum of \( \frac{N(N-1)}{2} \) terms which will give the same result when the integration is carried out. (Hill, 1956)

\[ <U> = \frac{1}{Z} \int \ldots \int \frac{u(r)}{2} \left( \frac{N(N-1)}{Z} e^{-U/kT} \ dr_3 \ldots \ dr_N \right) \ dr_1 \ dr_2 \]

\[ = \frac{1}{2} \int \ldots \int u(r) f^{(2)}_{N}(r_1, r_2) \ dr_1 \ dr_2 \]

\[ = \frac{\rho^2}{2} \int \ u(r) g(r) \ dr \]

Therefore

\[ <U> = 2\pi \ N \ \rho \int_0^\infty r^2 \ u(r) \ g(r) \ dr \]

6:7

here we have assumed that \( u(r) \) and \( g(r) \) are both radially symmetric.

The pressure is given in Chapter 2 as

\[ PV = N \ kT - \frac{1}{3} < \sum_{i<j} r_{ij} \ \frac{\partial u}{\partial r_{ij}} > \]

6:8

From the development of equation 6:7 it is apparent that

\[ \frac{1}{3} < \sum_{i<j} r_{ij} \ \frac{\partial u}{\partial r_{ij}} > = \frac{2\pi \ N \rho}{3} \int_0^\infty r^3 \ \frac{\partial u}{\partial r} \ g(r) \ dr \]

6:9

and as a result

\[ \frac{PV}{N \ kT} = 1 - \frac{2\pi \ \rho}{3kT} \int_0^\infty r^3 \ \frac{\partial u}{\partial r} \ g(r) \ dr \]

6:10

Three further properties of interest may be calculated using the radial distribution function. Their derivation is rather complicated and will not be included here.

The first of these is the isothermal compressibility \( K_T \). It is derived using the grand canonical ensemble in which the energy and number of particles both fluctuate (Egelstaff, 1967). The result is
Expressions for the high frequency shear and bulk moduli were derived by Zwanzig and Mountain (1965) starting from the time-correlation expressions for the frequency dependent shear and bulk viscosities.

\[ \eta(\omega) = \frac{1}{\nu kT} \int_0^\infty dt \, e^{-i\omega t} <J^{XY}(0) J^{XY}(t)> \quad 6:12 \]

\[ \eta_V(\omega) = \frac{1}{9\nu kT} \sum_{a,b} \int_0^\infty dt \, e^{-i\omega t} <J^{aa}(0) J^{bb}(t)> \quad 6:13 \]

\[ J^{ab} = \sum_{j=1}^N \left[ \frac{\mathbf{p}_j \cdot \mathbf{p}_j}{m} + \frac{\mathbf{F}_j \cdot \mathbf{R}_j}{m} \right] \]

\[ \delta_{ab} [FV + \frac{3}{8}(PV) \left( E - <E> \right)] \quad 6:14 \]

Here the shear and bulk viscosities \( \eta \) and \( \eta_V \) depend on the frequency \( \omega \) of the sound being propagated. The equations are similar in form to those used in Chapter 4 for the frequency independent coefficients. Zwanzig and Mountain then showed that the high frequency bulk modulus is given by

\[ K_\infty = \frac{2}{3} \rho kT + P + \frac{2\pi}{9} \rho^2 \int_0^\infty g(r) \, r^3 \frac{\partial}{\partial r} \left[ \frac{3u}{r^2} \right] \, dr \quad 6:15 \]

and the high-frequency shear modulus by

\[ G_\infty = \rho kT + \frac{2\pi}{15} \rho^2 \int_0^\infty g(r) \, \frac{\partial}{\partial r} \left( r^4 \frac{3u}{r^2} \right) \, dr \quad 6:16 \]

Similar expressions for \( K_\infty \) and \( G_\infty \), derived previously by Green (1952) are shown to treat the \( kT \) term incorrectly.

It must be emphasised that these expressions are only correct for a potential depending on two-body interactions. Where \( U \) is a function of three-body interactions as well, Rushbrook and Silbert (1965) have expressed the contributions to the pressure and energy as

\[ \frac{P_3}{NkT} = - \frac{\rho^2}{18kT} \int \left[ \left( r \frac{\partial}{\partial r} + s \frac{\partial}{\partial s} + t \frac{\partial}{\partial t} \right) u(r,s,t) \right] \]

\[ g^3(r,s,t) \, dr_2 \, dr_3 \quad 6:17 \]

\[ E_3 = \frac{N \rho^2}{6} \int \int u(r,s,t) \, g^3(r,s,t) \, dr_2 \, dr_3 \quad 6:18 \]
where \( g^{(3)}(r,s,t) \) is the three-body correlation function
\[
g^{(3)}(r,s,t) = \frac{f^{(3)}_N(r,s,t)}{\rho^3}
\]

This function has been investigated experimentally (Egelstaff, Page and Heard, 1969) and theoretically (Raveche and Mountain, 1970), but not to the extent of \( g(r) \). When it is needed to calculate thermodynamic properties it is commonly approximated by using the superposition principle (Kirkwood, 1935).

\[
g^{(3)}(x_1, x_2, x_3) = g(r) \cdot g(s) \cdot g(t)
\]

This approximation is valid in the low density limit where the distribution of pairs of particles becomes independent of the positions of the other particles in the system.

We mentioned earlier that the radial distribution function has been studied experimentally. In fact the structure factor \( S(k) \) is studied directly. \( S(k) \) is defined by (Egelstaff, 1967).

\[
S(k) = 1 + \int \frac{e^{ik \cdot r}}{\rho} [g(r) - 1] \, dr \quad 6:20
\]

and is shown there to be proportional to the cross-section in neutron scattering for \( k = 0 \). In a liquid \( S(k) \) is a function of the magnitude of \( k \) since the scattering is independent of the orientation of the liquid sample. \( S(k) \) may also be derived from X-ray scattering experiments (Egelstaff, 1967).

Comparing equation 6:11 and 6:20 we relate \( S(0) \) to \( K_T \)

\[
S(0) = K_T \rho kT
\]

The next section describes the calculation of the radial distribution function of a liquid using molecular dynamics configurations.

6:3 Calculation of \( g(r) \)

The radial distribution function of a system gives the relative probability of finding two atoms in the fluid, separated by a distance \( r \). It is essentially a fluid concept since the analagous distribution function in a
crystal is strongly dependent on the crystal orientation. For this reason we have not calculated distribution functions for the solid.

The molecular dynamics calculations used the truncated Barker-Bobetic potential. While generating each configuration the distances separating pairs of atoms were calculated. A histogram was then formed of the number of pairs of atoms found at separations between \( r \) and \( r + d(r^2) \). The interval from \( r = 0.8\sigma \) to \( r = R \), the point at which the potential was truncated, was separated into 200 intervals equidistant in \( r^2 \). This formed the base of the histogram. The expected number of atoms at a particular separation \( <M> \) is then the number of pairs in the histogram \( M_H(r) \) divided by the product of the number of atoms in the system \( N \) and the number of configurations \( C \) chosen.

\[
<M> = \frac{M_H(r)}{NC}
\]

\( <M> \) was plotted by Eisenstein and Gingrich (1942). The number of particles lying between \( r \) and \( r + d(r^2) \) is given by

\[
4\pi r^2 dr \rho g(r)
\]

Therefore

\[
g(r) = \frac{<M>}{2\pi rd(r^2)\rho}
\]  

6:4 Calculation of Thermodynamic Properties Using \( g(r) \)

The equation for the pressure, energy and other thermodynamic properties of a liquid were given in an earlier section. They include integrals of the form

\[
I = \int_0^\infty g(r) \frac{\partial u}{\partial r^n} r^m dr
\]

\( g(r) \) has been calculated in the manner described in the previous section. \( u \) and its derivatives are analytic functions previously described in Chapter 2. Since \( g(r) \) is a tabulated function a numerical quadrature method must be used to evaluate 6:23. Several difficulties arise immediately.

\( g(r) \) is known at 200 points only and these points are not equidistant. If we wish to use Simpson's rule for the quadrature or to use more than 200 grid points we must therefore interpolate to find \( g(r) \) at some of these grid points.
For values of \( r^* \) near 1, \( g(r) \) varies rapidly and interpolation is therefore unlikely to be accurate. \( u(r) \) and its derivatives vary rapidly in this region as well. Simple interpolation is thus likely to give inaccurate results in this region which contributes a great deal to the integrals being studied.

In order to surmount this difficulty we consider the function

\[
p(r) = e^{u(r)/kT} g(r) \quad 6:24
\]

This is a smooth function of \( r \) in the region of interest near \( r=1 \). (Watts, 1968). \( p(r) \) is therefore calculated for each point at which \( g(r) \) is known. Accurate values of \( g(r) \) can now be calculated by interpolating to find \( p(r) \) at the point of interest and calculating

\[
g(r) = e^{-u(r)/kT} p(r)
\]

Since \( p(r) \) is a smooth function we can be confident of accurate interpolation for the required values of \( p \) and therefore the values of \( g(r) \) calculated by this method should be accurate. For \( r < .9\sigma \) \( p(r) \) was calculated by extrapolation of the values of \( p(r) \) for \( r > .9\sigma \) to \( r = .8\sigma \).

Using this procedure to obtain \( g(r) \) the values of \( U_0 \) and \( P_0 \) were calculated by integrating equations 6:7 and 6:9 from \( r = .8\sigma \) to \( r = R \).

This is equivalent to the integral from 0 to \( R \) since \( g(r) \) is effectively zero for \( r < .8\sigma \). \( R \) is again the distance at which the potential is truncated.

In Table 6:1 we have presented values of \( U_0 \) and \( P_0 \) as defined in Chapter 2 calculated by using \( g(r) \). We used Simpson's rule at 2000 points in the numerical integration, together with the interpolation scheme just discussed. All values in the table are given in reduced units since the radical distribution function is that of the truncated Barker-Bobetic fluid. Values of \( U_0 \) and \( P_0 \) calculated directly from the configurations generated using molecular dynamics are also included for comparison. The histogram used to calculate \( g(r) \) resulted from the analysis of 4500 molecular dynamics configurations.
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Quantum corrections to the internal energy and pressure may also be calculated using $g(r)$. The results of such calculations also appear in table 6:1, and were obtained using the formulae

$$U^{QGR} = 2 \langle U'^{Q} \rangle$$

$$= \frac{\hbar^2 Np}{48 \pi mkT} \int_0^R g(r) \nabla^2 u(r) r^2 dr$$

$$P^{QGR} = \langle P'^{Q} \rangle$$

$$= -\frac{\hbar^2 Np}{144 \pi mkT} \int_0^R g(r) r^3 \frac{\partial}{\partial r} (\nabla^2 u(r)) dr$$

These formulae follow directly from the previous development, of eqn. 6:7. In this case the integral is from 0 to $R$ rather than to $\infty$ since we are comparing the results with values calculated using only interactions with $r_{ij} < R$. This is consistent with the calculation of $U^{G}_{GR}$ and $P^{G}_{GR}$.

The agreement between the molecular dynamics and radial distribution function calculations is quite satisfactory. The results lie within the statistical error of the molecular dynamics calculations. It is thus possible to perform molecular dynamics calculations without evaluating $P^{o}$ for each configuration thus saving computational time. Subsequently $P^{o}$ can be evaluated using the function $g(r)$ obtained from the molecular dynamics. This would however make a statistical analysis more difficult. The same approach could not be used in evaluating the perturbation terms however and in addition $g(r)$ gives us no information about corrections for interactions beyond $R$. Thus we cannot obtain an exact value for $g(r)$ for the range $r > R$. For large enough values of $R$ we can adequately approximate $g(r)$ by 1. Three-body contributions also cannot be evaluated exactly in terms of $g(r)$, since the three-body distribution function $g^{(3)}(r,s,t)$ is not known. We may use the superposition approximation (Kirkwood, 1935)

$$g^{(3)}(r,s,t) = g(r) g(s) g(t).$$

Some error will be introduced however especially if we integrate over the region where $r, s$ and $t$ are all small. The correction introduced in Chapter 2 for contributions where we consider only $t > R$ should not introduce a significant error however.
We may calculate $U_Q$ and $P_Q$ for interactions with $r \leq R$ using $g(r)$. Contributions for $r > R$ may be estimated by setting $g(r) = 1$ in this region. As we saw in Chapter 2 this does not present any difficulty because of the small contribution from this region.

The real difficulty arises when we try to evaluate the fluctuation terms in the perturbation expansion. The problem centres on the calculation of the expressions $<U_O U_Q>$ and others of a similar form. This may be expressed as the total of three sums

$$<U_O U_Q> = \Sigma <\Sigma_{i<j} u_{ij} \nabla^2 u_{ij}> + \Sigma_{i<j<k} u_{ij} \nabla^2 u_{ik} >$$

$$+ \Sigma_{i<j<k<l} u_{kl} \nabla^2 u_{kl} >$$

The first term may be calculated using $g(r)$. However the other two sums require a knowledge of the three and four-body distribution functions respectively. The accuracy of approximating these functions using the superposition approximation in the region $(0, R)$ is very suspect. Evaluating these distribution functions accurately from the molecular dynamics calculations would be very time consuming. For this reason the radial distribution function approach is not adequate for these terms. The approach developed in Chapter 2 is more economic in this case.

In Table 6:2 values of the isothermal compressibility $K_T$ and the high-frequency shear and bulk elastic moduli, $G_\infty$ and $K_\infty$ are given. The tabulated values are all expressed in reduced units and apply only to the truncated Barker-Bobetic liquid. It should also be noted that no corrections for long-range interactions have been made. $G_\infty$ and $K_\infty$ have been calculated previously for the Lennard-Jones potential (Verlet, 1967) Zwanzig and Mountain (1965) have also prepared tables of $G_\infty$ and $K_\infty$ specifically for the case of the Lennard-Jones potential, using the tabulated argon energies and PVT data of Levelt (1960). This approach was made possible only by the simple mathematical form of the potential used.

The ratio $K_\infty/G_\infty$ has also been tabulated. For an isotropic solid composed of molecules interacting with a two-body central
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</table>
potential Cauchy's identity states that

\[ K_\infty = \frac{5}{3} G_\infty \]

This relation was generalised by Zwanzig and Mountain (1965) to give

\[ K_\infty = \frac{5}{3} G_\infty + 2 (P - \rho k T) \]

for liquids.

From the table it is apparent that the ratio \( \frac{K_\infty}{G_\infty} \) lies near the value \( \frac{5}{3} \) in the liquid region. It is somewhat smaller in the dense gas phase. This behaviour is similar to that found by Verlet (1967) for the Lennard-Jones liquid.

In Appendix C we list \( g(r) \) as a function of \( r \) at intervals of 0.01 for all the points studied. Verlet (1968) has tabulated \( g(r) \) for the Lennard-Jones potential at \( T^* = .614 \) and \( \rho^* = .822 \) in our reduced units, which is very close to our point at \( T^* = .596, \rho^* = .825 \). In figure 6:2 these radial distribution functions are compared. The plots are very similar. The main difference occurs at the first peak in \( g(r) \). Verlet's function peaks at 3.00 whereas ours peaks at 3.13. The depth of the first minimum is slightly greater for the Lennard-Jones potential, \( .566 \) in comparison to our value of \( .575 \). These differences lie outside the estimated error of 1% given by Verlet (1968). It appears that our values lie a little above Verlet's for \( r < 1.14 \) and a little below his values for \( 1.14 < r < 1.3 \). Thus the Barker-Bobetic \( g(r) \) has its first peak at a slightly smaller value of \( r \) than the Lennard-Jones potential. For \( r > 1.7 \) the differences are barely significant. This comparison reinforces our earlier comment on the importance of using accurate values of \( g(r) \) near \( r = 1 \). It is remarkable that significant differences in the calculated pressures can arise from two such similar distribution functions. The main difference occurs near \( r = \sigma \) and it is for this reason that so much care was then taken in developing the interpolation formulae described earlier.

6:5 Time Dependent Distribution Functions

In the derivation of the high frequency elastic moduli, the frequency dependent viscosity was introduced. This is a generalisation of the viscosity to time dependent phenomena.
Figure 6:2

Comparison of Barker-Bobetic and Lennard-Jones $g(r)$. 
A time dependent generalization of the radial distribution function has also been studied in connection with transport and scattering. The van Hove correlation function $G(r,t)$ (van Hove, 1954) describes the time decay of the radial distribution function $g(r)$. It is defined so as to be proportional to the probability of finding a particle separated by a distance $r$ from the position of the particular particle under consideration, at a time $t$ later. It is normalised so that $G(\infty,t) = \rho$. From this definition it is apparent that

$$G(r,0) = \rho g(r) + \delta(r)$$  \hspace{1cm} 6:28

where $\delta(r)$ is again a delta function. An additional property is that

$$G(r,\infty) = \rho$$  \hspace{1cm} 6:29

$G(r,t)$ may be determined experimentally using neutron scattering (Lomer and Low, 1965). Since it is a time dependent function, it cannot be studied using Monte Carlo techniques. Rahman (1964) has studied one part of this using molecular dynamics. This is $G_D(r,t)$, the probability of finding two different particles separated by a distance $r$ at a time $t$. In this discussion we are assuming that the distributions depend only on distance and not on orientation. This is consistent with the earlier discussion of $g(r)$. In order to calculate $G(r,t)$ using molecular dynamics we first define:

$$G_s(r,t) = G(r,t) - G_D(r,t)$$  \hspace{1cm} 6:30

Pairs of configurations separated by a time $t$ are then selected, and histograms formed describing the separations of pairs of atoms. One atom in each pair is selected from each of the two configurations and their separation calculated. One histogram is formed using the time separation of a particular atom. This is used to calculate $G_s(r,t)$. Another is formed using the separations of distinct atoms and is used to form $G_D(r,t)$. Using many pairs of configurations and all possible combinations of atoms, the histograms are completed.
The correlation functions are then calculated by the same method used to calculate \( g(r) \) from its related histogram.

We have

\[
G_D(r,t) = \frac{M_D(r,t)}{2\pi r d(r^2)} \quad \ldots \quad 6:31
\]

\[
G_S(r,t) = \frac{M_S(r,t)}{2\pi r d(r^2)} \quad \ldots \quad 6:32
\]

As before \( d(r^2) \) is the spacing along the base of the histogram. \( M_D \) and \( M_S \) are the number of atoms per configuration studied in the histograms for \( G_D \) and \( G_S \) respectively. In figure 6:3 \( G_D(r,t) \) and \( G_S(r,t) \) are plotted for \( t = 10^{-12} \) secs. and \( t = 2.5 \times 10^{-12} \) secs. The temperature and density are .7484 and .85 respectively in reduced units. 1900 configurations were used in forming the histograms. The form and decay of the function \( G_D(r,t) \) show the same behaviour as that reported by Rahman (1964) for a temperature of 94.4° and density of 1.374 gm./cm.³. Comparing figure 6:3 with 6:1 which in effect gives \( G_D(r,0) \) for the same density and temperature, it can be seen that as \( t \) increases the form of \( G_D \) becomes smoother and smoother, with both peaks and minima becoming less pronounced. In addition the value of \( G_D \) increases steadily in the region \( r < \sigma \), and the region excluded by the earlier presence of a particle at \( r = 0 \) becomes smaller and smaller. To make the comparison simpler, figure 6:3 is plotted with the ordinate in units of \( \rho \). The function \( G(r,t) \) is used a great deal in the study of light scattering (Egelstaff, 1967; Mountain, 1970) as well as neutron scattering. It can be related to the frequency dependent structure factor \( S(k,\omega) \) by Fourier transformation in both \( r \) and \( t \). In addition \( G_S(r,t) \) is related to transport by the diffusion equation (Egelstaff, 1967)

\[
\nabla^2 G_S(r,t) = \frac{\partial G_S(r,t)}{\partial t} \quad 6:33
\]
Figure 6.3

The time-dependant distribution function $G(r,t)$.
While the diffusion coefficient can be calculated in principle by numerical differentiation of calculated values of $G_S(r,t)$, it is not feasible to perform this calculation using molecular dynamics with any accuracy due again to the excessive amount of computation involved. Calculating the values presented in figure 6:3 involved 3 hours of computer time. Also the scheme used in the generation of the histogram did not give fine resolution in the range of small $r$. Thus $G_S(r,t)$ has not been calculated as accurately as $G_D(r,t)$ by this scheme. However the spreading and decay of $G_S(r,t)$ are apparent from the results plotted in figure 6:3, although the magnitudes plotted have large error bounds. The procedure used in Chapter 4 to calculate the diffusion coefficient is more straightforward than the use of eqn. 6:33 in conjunction with molecular dynamics results.

In an attempt to calculate $G_S(r,t)$ with more precision another program was developed. In this case the base of the histogram was formed by dividing the range of $r$ from 0 to 1 into 200 intervals equidistant in $r$. If we consider the interval between $r$ and $r + 2dr$, eqn. 6:32 becomes,

$$G_S(r + dr, t) = \frac{M_S(r, t)}{4/3 \pi ((r + 2dr)^3 - r^3)}$$

This equation is much more accurate than eqn. 6:32 when $r$ is small. The two equations are equivalent when $r >> dr$. The results of analysing 3500 configurations in order to form the histogram appear in figures 6:5 and 6:6 for values of $t = 10^{-12}$, $2 \times 10^{-12}$ and $3 \times 10^{-12}$ secs. For comparison, values are also plotted using the Gaussian approximation to $G_S(r,t)$.

$$G_S(r,t) \approx \frac{1}{(4\pi Dt)^{3/2}} \exp \left( \frac{-r^2}{4Dt} \right)$$

6:34
The time-dependant distribution function $G_S(r,t)$.

$T = 94^\circ \text{K. } V_M = 27.04 \text{ cm}^3/\text{mole.} \bullet \bullet$ as calculated.

--- Gaussian, $D=1.28$. --- Gaussian, $D=1.37$. 

Figure 6:4
The decay of $G_s(r,t)$. See fig. 6:4 for legend.
Here D is the diffusion coefficient calculated in Chapter 4 using the mean square fluctuation of r. Figure 6:4 and 6:5 give the results for T = 94°K, V_M = 27.04. The values of D used in eqn. 6:34 were 1.28 and 1.37 x 10^-5 cm^2/sec. corresponding to the calculated values of D using the velocity autocorrelation function and mean square fluctuation approaches respectively. The decay of G^S(r,t) and its near Gaussian form can be seen in figure 6:4 and 6:5. It is also apparent that the Gaussian approximation leads to a G^S(r,t) that is too large at small r, and too small at large values of r. This can be observed at all three values of t. Better agreement could result from using a larger value of D but this would not be consistent with the calculations of Chapter 4. The difference must arise from the fact that G^S(r,t) is not a true Gaussian.

Experimental measurements of D using nuclear magnetic resonance are now common (Abragam, 1961). The relation between D and the diffusion of nuclear spins are described using the Fourier transform of eqn. 6:33. A general description of diffusion including relations between G^S(r,t) and the velocity autocorrelation function described in Chapter 4, is given by (Egelstaff, 1967).

6:6 Summary

In conclusion g(r) has been calculated accurately for values of r less than R using the method of molecular dynamics and tabulated using an appropriate interpolation formula. Various properties of the Barker-Bobetic liquid have then been calculated and the results tabulated. Comparison with thermodynamic values calculated directly from the molecular dynamics configurations shows that both approaches give essentially the same results for several contributions. However, it has not proved possible to recast our perturbation expansion of the internal energy into the form of an integral involving only g(r). Finally the radial distribution functions and G^D(r,t) for the Lennard-Jones and Barker-Bobetic fluids have been shown to be very similar. Tables of g(r) have also been made available to other workers in Appendix C. Finally G^S(r,t) has been recalculated but it is apparent that the procedure used in Chapter 4 is a more useful method for calculating the diffusion coefficient.
CHAPTER 7
DISCUSSION AND CONCLUSIONS

The results discussed in the previous chapters are most encouraging. It is now possible to calculate accurately the thermodynamic properties of argon using classical statistical mechanics and a model involving only 108 particles. It is convenient to divide the discussion into sections on solid and liquid regions.

7:1 The Study of Liquids

The success of the calculations of the equation of state and internal energy reported here indicates that the potential function for argon developed by Barker and co-workers adequately represents argon throughout the liquid and dense gaseous states. The development of the present Barker potential from the Barker-Bobetic potential indicates that present experimental values of argon are consistent with a family of very similar pair potential functions. Further improvement by checking other members of this group of potentials may be possible. However the pressures calculated using the present Barker potential indicate that sensitive tests are needed to find a more accurate potential. This makes further developments in the area unlikely. The potential function of argon is now known with sufficient accuracy to perform calculations of many properties of interest.

Several difficulties have presented themselves in the study of transport however. The diffusion coefficient can be calculated with a statistical error of one percent for a liquid interacting through a truncated two-body potential. It does not provide a sensitive test of the accuracy of the potential used. Before tests of the accuracy of the values for argon can be undertaken, further experimental measurements at different temperatures and pressures and of high accuracy must be made. A computationally useful and accurate perturbation theory is also needed in order to show the effects of long range and three-body interactions.
Theoretical developments are also needed in the study of transport generally. Only the theory of diffusion appears to be reasonably well treated at the microscopic level. The two general theories of transport, due to Kubo and Kirkwood, both give results in serious disagreement with experiment. The most attractive approach still seems to be that of Kubo. However, computational difficulties prevented us from obtaining useful values of the shear and bulk viscosities, and the thermal conductivity. The Kirkwood approach when applied to argon does not appear to be internally consistent. Successful calculations based on this approach and using a plausible form of the potential function appear unlikely. Thus the whole microscopic theory of liquid transport with the possible exception of diffusion appears in need of further development.

In the case of diffusion a new perturbation theory must be developed. This theory must be both correct, and computationally useful. When it is possible to correct for both long-range and three-body interactions, then diffusion in argon can be studied in detail with great accuracy.

These studies of transport has been considerably advanced by two studies using simple systems. The implications of this work of Fehder (1969); Fehder, Emeis, and Futrelle (1971) using Lennard-Jones disks and of Alder, Gass and Wainwright (1970) using hard spheres are quite extensive. Both papers demonstrate the existence of correlations in the motions of groups of atoms. The vortex motion used by Alder et al to describe their results seems consistent with the work of Fehder. In spite of their simple potential, the results quoted by Alder et al show that they have done a considerably larger amount of calculation than that reported here. The extra calculation has been necessary to reduce the statistical errors. The dependence of various transport coefficients on the number of particles has also been studied in their work. Sufficient accuracy has been achieved to show that correction of order \( \frac{1}{N} \) should be made the calculated transport coefficients. Achieving the same statistical accuracy for our potential would
require about 800 hours per point on the /360-50 in contrast to the 12 hours used in this work. Using these results the theory of transport may be advanced significantly. The treatment of the approximations used may well be possible. The difficulty may lie in reducing the formulae to a convenient computational form.

Investigations of argon involving the present Barker potential and using larger numbers of particles could be undertaken for several thousand timesteps. While the current computing facilities at The Australian National University do not justify such work, the most recently developed equipment would allow such calculations to be performed in a reasonable amount of time. Modelling very large systems would allow some investigation of phase changes to be undertaken. The separation of a system of Lennard-Jones particles into two phases has already been observed (Watts, 1970).

Calculations such as those outlined above could be undertaken using either molecular dynamics of Monte Carlo techniques. The main consideration involved is whether or not time dependent phenomena are to be studied. Molecular dynamics calculations are known to give some redundant information when only equilibrium properties are to be considered. In this case Monte Carlo calculations would be more efficient. If transport studies are envisaged however, only molecular dynamics calculations provide the required information.

Finally it appears that a system of 108 particles in conjunction with the perturbation theory used to include long-range and three-body effects is adequate for calculations outside the region of a phase change. Near phase changes or the critical point more particles may be necessary because of possible large fluctuations in the real system that cannot be observed in small model system.
Liquid argon has now been successfully simulated. The development of potentials for the other heavy rare gases should now be straightforward providing accurate experimental data is available. More interesting developments would evolve from the development of potential functions for other molecules. Some work has already been undertaken for carbon monoxide and oxygen mixtures using the Stockmayer potential (Harp and Berne, 1970). This is basically a Lennard-Jones potential with additional terms to deal with the angular dependence of the interaction between polar molecules. Several potential functions intended to model the interactions between water molecules have already been reported (Rowlinson, 1951; Ben-Naim and Stillinger, 1971) and some Monte Carlo work on these have been reported (Barker and Watts, 1969). Water is of course one of the most interesting systems to study. The difficulty lies mainly in the treatment of its strong hydrogen bonding. Potentials for simple organic molecules are also of interest and two obvious choices for study are carbon tetrachloride, a simple near spherical molecule, and benzene the simplest carbon ring compound. These studies will be more expensive in terms of computer time than the work on argon. The results however should be more productive than a simple extension of the present work to the heavier rare gases. Machines currently in use are capable of handling the three molecules mentioned. The allocation of computing resources to this work may have to wait for further technical developments before a full scale attack becomes possible. The quality of the argon results indicates however, that machine simulation methods may be more productive than approximate methods. In the latter case there is always the difficulty of separating the effects of approximations used from the inaccuracies in the potential function used. The study of liquids should remain an area of productive research for some time, with experimental, computational and theoretical work necessary in several areas.
The results of the solid state calculations reported here have established several important points. The first of these is that Monte Carlo calculations for argon are presently limited to temperatures above $30^\circ K$. Providing an adequate expression for the quantum contribution to the Helmholtz free energy is developed, calculations at lower temperatures may be possible. However, it is apparent that classical statistical mechanics cannot deal adequately with properties dependent on fluctuations even at temperatures as high as $50^\circ K$, as we see from the specific heat studies. It is probable that more useful results will arise from applying self-consistent phonon calculations (Koehler, 1968) at temperatures from $0^\circ K$ to $40^\circ K$ if not higher. Since the Monte Carlo work cannot be readily extended to lower temperatures, self consistent phonon calculations of high accuracy should be performed to cover the region from $12^\circ K$ to $40^\circ K$. Then the adequacy of the present Barker potential will be known over the full range of solid temperatures.

This research has also established that there are systematic differences between experimental values for the elastic constants and their values calculated using the present Barker potential. Some of these were suggested previously by the work of Barker, Klein and Bobetic (1971a). Differences between the values of the calculated and experimental values of the bulk modulus and anisotropy are a consequence of the fact that the calculated values of $C_{11}$ are low and those of $C_{12}$ are high by a similar amount. In this work we have established that this behaviour is observed at all temperatures above $40^\circ K$ and there is a strong inference that this behaviour also occurs at lower temperatures. It is quite surprising that this behaviour is observed at all solid temperatures, considering the success of the liquid state calculations. It should be remembered that the high temperature results reported here are generally as good or better than previous results using other methods or potentials.
Since the Lennard-Jones and present Barker potentials give similar results for the elastic constants, it seems that a real discrepancy exists here between theory and experiment. Experimental confirmation of the elastic constants measured by Keeler and Batchelder (1970) would eliminate one possible source of the discrepancy between theory and experiment. Extensive self consistent phonon calculations (Koehler, 1968) using the present Barker potential should also be useful.

As a final consideration, a study of vacancies in the Lennard-Jones solid has already been undertaken (Squire and Hoover, 1969). Vacancies have also been studied using molecular dynamics with a hard sphere potential (Bennett and Alder, 1971). These and other defects in solid argon using the present Barker potential could be studied at high temperatures using Monte Carlo methods.

7:3 Summary

Extensive calculations of the properties of solid and fluid argon have been undertaken using the Barker-Bobetic and present Barker potential. The results indicate that the present Barker potential adequately represents the potential function of argon for many properties of interest. It has been shown that further improvement may still be possible as more properties of argon are investigated. The approach to the optimum potential has become an iterative procedure. The potential has been developed by consideration of gas phase data first. Then it was modified to represent the solid at low temperatures as well. Finally it has been modified to improve agreement with liquid state pressures. Possibly the study of the solid at high
temperature may lead to a further modification. Each time
the necessary change has been smaller than the previous
adjustment. The potential is now known accurately enough
to show real differences between theoretical and experimental
values of some solid state properties. Careful consideration
should be undertaken before further extensive calculations
are undertaken. The present potential is the best available
however and since it is possible to use this potential rather
than a simpler one without excessively increasing the time
needed for computation, it is reasonable to suggest that
future calculations of the properties of argon should use
this potential. The equilibrium properties of solid liquid
and gaseous argon can now be calculated accurately using the
same potential for all three phases.

A further conclusion from this work is that considerable
theoretical investigations are needed on the theory to
transport. Full information concerning a system of particles
behaving in a similar manner to argon atoms is now available.
However the present theories of transport have not allowed
us to calculate the viscosity of the liquid from this record.
Studies of hard spheres (Wainwright, 1964; Alder, Gass and
Wainwright, 1970) have resulted in reasonable values of the
viscosity being calculated and as a result it is believed
that the difficulty lies in the amount of computation needed.

Finally it has been shown that molecular dynamics and
Monte Carlo calculations involving small numbers of particles
and a realistic potential function can provide results of
the desired statistical accuracy. When the same potential is
used with the same number of particles the two methods do not
give systematically different results. It is also believed
that the effects of the small number of particles considered
are adequately corrected for by means of the perturbation
expansion used, when temperatures above 40°K are considered.
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APPENDIX A

LIQUID ARGON: MONTE CARLO AND MOLECULAR DYNAMICS CALCULATIONS

by

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ABSTRACT: Thermodynamic properties of liquid argon are calculated by Monte Carlo and molecular dynamics techniques, using accurate pair potential functions determined from the properties of solid and gaseous argon, together with the Axilrod-Teller three-body interaction. Satisfactory techniques for evaluating three-body contributions to thermodynamic properties without excessive requirements of computer time are described. Quantum corrections are included. Agreement with experiment is excellent: the best pair and triplet potentials give an excellent description of the properties of solid, gaseous and liquid argon.
I. INTRODUCTION

The determination of interatomic forces in the inert gases is of lasting interest. Once the forces are known they may be used to calculate the thermodynamic and transport properties of the solid, liquid and gaseous states, thus providing a stringent test of present theories of these states. As the quantum effects in argon are relatively small it has been widely studied as the prototype of a classical system.

In the theory of classical fluids computer simulation techniques [1-8] have provided exceedingly valuable insights, and stimulated rapid development in more conventional theories. These methods are the Monte Carlo method, based on ensemble averaging, and due originally to Metropolis et al. [1]; and the method of molecular dynamics, due to Alder and Wainwright [2]. Most of these studies have used simple model potentials, in particular the Lennard-Jones 6:12 potential. The results of these calculations have been used to guide and test the development of conventional theories, and they have also been compared with experimental data, usually for argon, with fair quantitative agreement. In this latter quantitative aspect the success of calculations using the 6:12 potential function must be regarded as largely fortuitous. The work of Guggenheim and McGlashan [9,10] showed clearly that the actual interactions of argon atoms are considerably different from those described by the 6:12 potential.

Previous attempts to use more realistic potentials led to worse agreement with experiment [5]. The actual interactions may differ from the 6:12 model in two ways, firstly in the form of the two-body potential, and secondly in the presence of many-body interactions. There have been many studies of these problems [11-22]. Dymond and Alder [12,13] made a thorough study of the consequences of the approximation of neglecting all many-body interactions. Recent spectroscopic and molecular beam evidence has shown that the pair potential function to which they were led is unsatisfactory, so that their approximation must now be regarded as inadequate. Others [14-22] have considered the next simplest assumption, that the dominant three-body interaction (the
Axilrod-Teller triple-dipole interaction \([23,24]\) should be included, but that other many-body interactions may be neglected. Bobetic and Barker \([16]\) found that, with this approximation, a pair potential function could be determined giving excellent agreement with experiment for the thermodynamic properties of solid argon at low temperatures, and for the thermodynamic and transport properties of dilute gaseous argon \([18]\). This pair potential proved to be in good (though not quite perfect) agreement with the spectroscopic data of Tanaka and Yoshino \([18,25,26]\), and with the molecular beam differential scattering measurements of Lee and Parson \([27]\).

This is strong evidence for the accuracy of the approximation of neglecting many-body interactions other than the triple-dipole interaction. A further stringent test can be made by using the pair and triplet interactions to compute properties of liquid argon. Results of such calculations, using both Monte Carlo and molecular dynamics techniques, are described in this paper.

We assume that the potential energy of a set of argon atoms is a function of the nuclear positions alone (Born-Oppenheimer approximation) and is given by

\[
U = \sum_{k<\ell=1}^N u(k\ell) + \sum_{k<\ell<m=1}^N u(k\ell m) = U_2 + U_3
\]

The triplet potential \(u(k\ell m)\) is assumed to have the Axilrod-Teller form,

\[
u(1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3) / (R_1 R_2 R_3) \quad (2)
\]

in which \(R_1 R_2 R_3\) and \(\theta_1 \theta_2 \theta_3\) are the sides and angles of the triangle formed by the three atoms. For the coefficient \(\nu\) we used the value \(73.2 \times 10^{-84}\) erg cm\(^9\) due to Leonard \([28]\) which is very close to the value given by Bell and Kingston \([29]\).

For the pair-potential \(u(k\ell)\) we have used the potentials due to Bobetic and Barker \([16]\) and to Barker and Pompe \([14]\), and also a third potential which is a linear combination of
these two potentials with coefficients .75 and .25 respectively. The first two potentials have the analytic form

\[ u(k, l) = \varepsilon \left[ \sum_{i=0}^{5} A_i (r-1)^i e^{a(1-r)} - \sum_{j=0}^{2} \frac{C_{2j+6}}{(r^2 + r^2j + 6)} \right] \] (3)

with \( r = R_{kl}/R_m \) where \( R_{kl} \) is the separation of the atoms and \( R_m \) is the separation at the minimum of the potential. The constants corresponding to the three potentials are listed in Table 1.

II. COMPUTER SIMULATION METHODS

The Monte Carlo and molecular dynamics techniques for the case of two-body interactions are now well-known [1-8]. One considers a fixed number of molecules (10^8 in our calculations) in a cubic box with periodic boundary conditions. For the Monte Carlo calculations one performs a biased random walk which generates configurations of the molecules with probability proportional to \( e^{-U/kT} \). The thermodynamic properties are then obtained as configurational averages. Molecular dynamics calculations involve solving the equations of motion of the system,

\[ m \frac{d^2 r_i}{dt^2} = -\nabla_i U \]

Positions and momenta are then recorded at successive instances of time (10^-14 sec) and thermodynamic properties obtained as time averages (over about 5000 time steps in our calculations).

In principle these procedures would be equally satisfactory in the presence of three-body interactions, but in practise the computer time requirements would be very large, since for two-body interactions the time per step is in part proportional to the number of molecules, while for three-body interactions it is in part proportional to the square of that number. For that reason we have included three-body effects by using a perturbative technique involving an expansion in powers of the three-body coefficient \( v \) with neglect of terms beyond that of degree 1. It is known from the work of Barker et al. [15], and is reconfirmed by the present calculations, that this leads to negligible error in the case of liquid argon, because the triple-dipole interaction is (a) relatively weak and (b) only slightly dependent
on configuration for the relevant configurations at high densities. For example at \( T = 100^\circ K \) and \( V = 35.36 \text{ cm}^3/\text{mole} \) the term of order \( v^2 \) contributes only \(-0.25 \text{ cal/mole} \) to the Helmholtz free energy.

We have also included quantum corrections using the well-known expansion of the partition function in powers of \( h^2 \); effects of statistics are negligible at all temperatures for liquid argon. Hansen and Verlet [30] showed that it is sufficient to include the first quantum correction (order \( h^2 \)), and to neglect terms of order \( h^4 \), in liquid neon; this is a fortiori true for liquid argon, in which the quantum effects are relatively smaller by a factor of about 10.

According to the Wigner-Kirkwood expansion [31] the Helmholtz free energy of the system is given by

\[
A = -kT \ln \left[ \frac{\lambda^{-3N}}{N!} \int \cdots \int e^{-\beta U} \, dr_1 \cdots dr_N \right]
+ \frac{8h^2}{96\pi^2m} \int \cdots \int \left( \sum_i \nabla_i^2 U \right) e^{-\beta U} \, dr_1 \cdots dr_N / \cdots e^{-\beta U} \, dr_1 \cdots dr_N + o(h^4)
\]

(4)

in which \( \lambda = (\frac{h^2}{2\pi mkT})^{1/2} \), \( \beta = 1/(kT) \) and \( \nabla_i^2 \) is the Laplacian with respect to the coordinates of the \( i \)th atom. We now make a double Taylor series expansion in \( v \) and \( h^2 \) and neglect terms of order \( v^2, \sqrt{v}h \) and \( h^4 \); the result is

\[
A = -kT \ln \left[ \frac{\lambda^{-3N}}{N!} \int \cdots \int e^{-\beta U_2} \, dr_1 \cdots dr_N \right] + <U_3> + \\
+ \frac{8h^2}{48\pi^2m} \sum_{i<j} \nabla^2_i u(ij)
\]

(5)

in which the notation \( <>_o \) implies canonical averaging for the classical system with only two-body interactions:

\[
<X>_o = \int \cdots \int e^{-\beta U_2} x \, dr_1 \cdots dr \int \cdots \int e^{-\beta U_2} \, dr_1 \cdots dr_N
\]

(6)

The thermodynamic internal energy \( U_1 \) and pressure \( p \) can now be calculated by differentiating (5) with respect to temperature and volume. The 'scaling' procedure for differentiating with respect to volume is described by Born and Green [32]. The results are
\[ U_i = \beta \frac{\partial A}{\partial \beta} - \frac{3}{2} NkT \]

\[ = <U_2>_o + <U_3>_o - \beta [<U_2 U_3>_o - <U_2>_o <U_3>_o] \]

\[ + 2 <U_2>_o - \beta [<U_Q U_2>_o - <U_Q>_o <U_2>_o] \]

\[ pV = - V \frac{\partial A}{\partial V} \]

\[ = NkT + <P_2>_o + <P_3>_o - \beta [<U_3 P_2>_o - <U_3>_o <P_2>_o] \]

\[ + <P_Q>_o - \beta [<U_Q F_2>_o - <U_Q>_o <P_2>_o] \]

in which we define

\[ P_3 = - \frac{1}{3} \sum_{i < j < k} (R_{ij} \frac{\partial}{\partial R_{ij}} + R_{ik} \frac{\partial}{\partial R_{ik}} + R_{jk} \frac{\partial}{\partial R_{jk}}) u(ijk) \]

\[ = 3U_3 \]

\[ U_Q = \frac{\hbar^2}{48 \pi \hbar m} \sum_{i < j} \nabla_i^2 u(ij) \]

\[ P_Q = -\frac{\hbar^2}{48 \pi \hbar m} \sum_{i < j} \frac{1}{3} (R_{ij} \frac{\partial}{\partial R_{ij}}) \nabla_i^2 u(ij) \]

\[ P_2 = - \sum_{i < j} \frac{1}{3} (R_{ij} \frac{\partial}{\partial R_{ij}}) u(ij) \]

The second form of (9) follows [33,34] from Euler's theorem on homogeneous functions, since \( u(ijk) \) is a homogeneous function of degree -9 in the variables \( R_{ij} \), \( R_{jk} \) and \( R_{ik} \).

We have now expressed correctly to first order in \( v \) and \( h^2 \) the three-body and quantum corrections to energy and pressure in terms of canonical averages over the configurations of a classical system with only two-body interactions; these averages are readily evaluated by the Monte Carlo procedure. As in previous work it was found sufficient to average the three-body terms over a subset of the Monte Carlo chain; we used a subset consisting of every 1000th configuration. We also calculated some of the correction terms directly from the molecular dynamics calculations, evaluating the three-body term after every 25 time-steps. The results were essentially the same as those obtained from the Monte Carlo calculations.
In the Monte Carlo calculations we truncated the potentials at a distance \( R_{\text{max}} \) equal to half the edge of our basic cube, and given by

\[
R_{\text{max}} = \frac{1}{2} (108/\rho^*)^{1/3}
\]  

in which \( \rho^* \) is \( N\sigma^3/V \) and \( \sigma \) is the separation at the zero of the pair potential. In the molecular dynamics calculations we chose \( R_{\text{max}} = 2.5\sigma \). To correct for these truncations we added terms to the energy and pressure respectively given by

\[
\begin{align*}
\Delta_2 U_i &= \frac{N\rho^* 2\pi}{\sigma^3} \int_{R_{\text{max}}}^{\infty} u(R) R^2 dR \\
\Delta_2 (pV) &= \frac{N\rho^* 2\pi}{\sigma^3} \int_{R_{\text{max}}}^{\infty} -\frac{1}{3} R \frac{d}{dR} (R^3 R^2) dR
\end{align*}
\]

McDonald and Singer [5] showed that this led to errors less than 2 cal/mole in energy and 10 atm. in pressure for the case of the 6:12 potential. Since for our potentials the long-range tail is relatively weaker by a factor of about two, these errors should be roughly halved in our calculation.

We also added long-range three-body corrections calculated according to the equations

\[
\begin{align*}
\Delta_3 U_i &= N\rho^2 \int \cdots \int_{R_{12} < R_{13} < R_{23}} \int_{R_{\text{max}} < R_{23}} g_2(R_{12}) g_2(R_{13}) u(123) dr_2 dr_3 \\
\Delta_3 (pV) &= 3\Delta_3 U_i
\end{align*}
\]

Thus we assumed that the three-body distribution function \( g_3(R_{12}, R_{13}, R_{23}) \) could be approximated for \( R_{23} > R_{\text{max}} \) by the superposition approximation value \( g_2(R_{12}) g_2(R_{13}) g_2(R_{23}) \) with \( g_2(R_{23}) \) set equal to unity. For \( g_2(R) \) we used values computed from the machine calculations, with \( g_2(R) \) set equal to unity for \( R > R_{\text{max}} \). The equations (16) and (17) involve a further approximation in that contributions from the fluctuation terms in (7) and (8) are neglected; the error due to this must be very small. Preliminary calculations indicated that long-range contributions from \( U_Q \) and \( P_Q \) were negligible and no correction was made for these.
On the basis of the results of McDonald and Singer [5] we estimate the statistical error (standard deviation) in our Monte Carlo results as ±15 atm. in pressure and ±2 cal/mole in energy for runs of 300,000 configurations; for runs of 900,000 configurations the corresponding numbers are ±9 atm. and ±1.2 cal/mole.

III. RESULTS

The results of our calculations with the three potentials are given in Tables 2-4, with experimental data for comparison. In the temperature range 96 - 140°K we give two different 'experimental' values for the energy of which the 'present' values are to be preferred on the basis of existing data [35-48]; these values are discussed in Appendix 1.

We note first the excellent agreement between the Monte Carlo and molecular dynamics results. There is no evidence of a systematic difference between the results from the two methods such as was suggested by comparison of the results of McDonald and Singer [5] and Verlet [6-8] for the 6:12 potential.

Considering now the Bobetic-Barker potential, which gives better agreement with solid-state and gas-state data than other potentials so far proposed, we note that the calculated and experimental energies are in excellent agreement. The differences are almost within experimental error, which is probably about ±15 cal/mole (see Appendix 1). This is an improvement on the 6:12 potential for which the computed energies were more negative than those of Streett and Staveley [35] by up to 50 cal/mole (this is not affected by the correction of Streett and Staveley's data in Appendix 1, but if the alternative energy values of Appendix 1 are used the 6:12 discrepancy is reduced to about 30 cal/mole. The calculated pressures are also in very good agreement with experiment [35,46,48]. The largest discrepancy within the range of reliable measurements is at \( T = 100°K \) and \( V = 27.04 \text{ cm}^3/\text{mole} \), where the calculated pressure is about 70 atm. too high. The calculations of McDonald and Singer [5] using the 6:12 potential showed a discrepancy of 68 atm. (in the opposite sense) at \( T = 127°K, V = 33.51 \text{ cm}^3/\text{mole} \).
Thus considering both pressures and energies the Bobetic-Barker potential (with the Axilrod-Teller interaction) gives somewhat better agreement with experiment than does the 6:12 potential. We make this point not to show that the 6:12 potential is incorrect as a pair potential for argon; that is shown most clearly by comparing the experimental [49-52] and calculated second virial coefficients of gaseous argon, as in Figure 1. However the present results show that even as an 'effective potential' for dense liquid argon the Bobetic-Barker potential with Axilrod-Teller interaction is somewhat superior to the 6:12 potential; it has the further advantage that it is also consistent with solid state and gas state data and spectroscopic and molecular beam data (see below).

Having said this one must note that the agreement with experiment for the Bobetic-Barker potential is not perfect; the calculated pressures are a little too high, and increase too rapidly with increasing density at high densities. The Barker-Pompe potential on the other hand gives pressures which are too low (Table 4). We therefore experimented with interpolated functions of the form

$$u_x(R) = xU_{BP}(R) + (1 - x) u_{BB}(R)$$  \hspace{1cm} (18)

and found that such a potential with $x = .25$ gave excellent agreement with the experimental liquid pressures at high densities. This is the third potential for which results are given in Table 4; the agreement with experiment is indeed excellent.

It is interesting to note that the agreement remains good on the critical isotherm ($T = 150.87^\circ K$), in spite of the known singular character of the critical point, which is presumably not reproduced by our calculations with a relatively small number of molecules. Evidently the contributions of the singular terms to energy and pressure are relatively small.

In Tables 5 and 6 we show for some selected thermodynamic states the separate two-body, three-body and quantum correction contributions to the energy and pressure, as well as the long-range corrections given by (14) - (17). The long-range two-body corrections are relatively large. However because
the deviation of $g_2(R)$ from unity amounts to only a few percent for $R>R_{\text{max}}$ (and fluctuates in sign) while $u(R)$ and $u'(R)$ vary relatively slowly, these terms are given with sufficient accuracy by (14) and (15) (as shown by McDonald and Singer [5]). The three-body contributions are quite large, and must clearly be included in a realistic calculation. The possibility that these contributions are to an appreciable extent cancelled by other many-body interactions now seems remote. The quantum corrections are relatively small, as expected, but not negligible at the level of accuracy to which we are working here.

There is independent evidence from the spectroscopic data of Tanaka and Yoshino [25,26] (Fig. 3) and the molecular beam differential scattering intensities of Lee and Parson [27] (Fig. 2) that our third potential is more accurate than either the Bobetic-Barker or Barker-Pompe potentials; it gives almost perfect agreement with both these sets of data. Cavallini et al [53] have also made differential scattering measurements, from which they estimate that $R u'(R)/k$ at the inflexion point of the potential has the value $440^\circ K$. For this quantity the Bobetic-Barker potential gives $440^\circ K$, the 'present' potential gives $458^\circ K$, the Barker-Pompe potential gives $510^\circ K$, the Dymond-Alder potential gives $495^\circ K$ and the 6:12 potential gives $360^\circ K$. There is a little uncertainty in the experimental number since the 6:12 potential was used in its determination, and the agreement with the present potential may be regarded as satisfactory. The scattering measurements of Mueller et al [54] were consistent with a sufficiently wide range of potentials to include the present potential, except perhaps for a slight discrepancy beyond $5 \AA$.

Thus our assumption that many-body interactions other than the Axilrod-Teller interaction may be neglected has led us to a pair-potential which is very accurate. By contrast the assumption that all many-body interactions could be neglected led Dymond and Alder [12,13] to a pair-potential in much worse agreement with both the spectroscopic and molecular beam data (Figs. 2 and 3).

The Bobetic-Barker potential has been shown to give good agreement with the properties of gaseous and solid argon, while the Barker-Pompe potential gives fair agreement;
it is therefore necessary to consider the consequences for these properties of changing from the Bobetic-Barker potential to our third potential. On the reasonable assumption (which we have checked in several cases) that all quantities would vary linearly with the parameter $x$, the following conclusions can be drawn. The repulsive potential near $2\hbar$, the long-range coefficients of $R^{-6}$, $R^{-8}$ and $R^{-10}$, the second and third virial coefficients and the lattice spacing of crystalline argon at $0^\circ K$ would be unchanged, and in excellent agreement with experiment. The cohesive energy at $0^\circ K$ would change from $-1844$ cal/mole to about $-1850$ cal/mole, still within experimental error (Flubacher et al. [41] give $-1846\pm7$ cal/mole). The low-temperature Debye theta values would be reduced by about $0.4^\circ K$, leading to slightly worse agreement with experiment at $0^\circ K$ but slightly better agreement on the average over the range $0-12^\circ K$. The calculated thermal expansion in the range $0-12^\circ K$ would be reduced slightly [16], leading to even closer agreement with the results of Tilford and Swenson [55]. The calculated gas viscosities would be raised [18] by a fraction of a percent at temperatures below $400^\circ K$, improving slightly the already excellent agreement with experiment; at temperatures above $1000^\circ K$ they would be raised by $0.5\%$, leading to a better compromise between the modern measurements of Guevara et al. [56] and of Dawe and Smith [57]. The agreement with experiment for other gas transport properties would be essentially unchanged, and excellent. The agreement with measured elastic constants of crystalline argon would be essentially unchanged [17], and rather poor. It was suggested [16,17] that this discrepancy may be due to experimental problems, and the good agreement which we find for liquid properties perhaps adds some weight to that possibility. The agreement with experimental phonon dispersion curves would be essentially unchanged [17], and good.

Overall then the new potential gives excellent agreement with thermodynamic properties of solid, liquid and gaseous argon, and with transport properties of gaseous argon. Further, the resulting pair potential is in good agreement with molecular beam differential scattering cross-sections and spectroscopic data on the $\operatorname{Ar}_2$ molecule, indicating that it is very close.
to the true pair potential. Evidently our approximation of neglecting many-body interactions other than the Axilrod-Teller interaction is an excellent one.

It is interesting to note that the internal energies calculated with the present potential (Table 4) are in considerably better agreement with the revised experimental energies derived in Appendix 1 than with the older values based on the analysis of Din, and it was the discrepancies with the older data which led us to reanalyse the experimental data. This may perhaps be taken as evidence that the study of intermolecular forces has attained a certain maturity. Theory and "computer experiments" provide a way of comparing and cross-checking different kinds of experiments in a manner similar to but more far-reaching than that provided by thermodynamics.

In Figure 4 we compare our final potential with the 6:12 potential most commonly used for argon. Considering that the quite similar Bobetic-Barker and Barker-Pompe potentials gave calculated liquid pressures differing by as much as 250 atm., it must be regarded as remarkable that the quite different 6:12 potential gave such good quantitative agreement with experiment.

IV. ACKNOWLEDGEMENTS

We are grateful to Dr. Y. T. Lee for communicating the scattering data and the calculated results for two potentials. This work was supported in part by the U.S. Department of the Interior, Office of Saline Water. One of us (RAF) thanks the Australian National University for the award of a Research Scholarship.
REFERENCES


Here we discuss existing experimental evidence on the internal energy of liquid argon. Streett and Staveley [35] recently used their pVT data and energies on the liquid-vapor equilibrium line derived from the results of Din [37] to calculate the internal energy of argon in the range 100-140°K. Their calculations contain a slight error, amounting to as much as 20 cal/mole at $T = 140°K$, $p = 50$ atm. In the values given in the text we have corrected the error, following the procedure described by Streett and Staveley.

The energies on the saturation line were derived by Din from the vapor pressure data of Clark et al. [42] and the vapor densities of Mathias et al. [57] using the Clausius-Clapeyron equation; this led to a discrepancy of about 140 cal/mole with the calorimetrically measured latent heat of Frank and Clusius [39] at the normal boiling point. Din ascribed this discrepancy to errors in the vapor density results at low pressures, and therefore extrapolated the latent heat from temperatures above 110°K in such a way as to agree with the result of Clusius and Frank. Experimental results published since the work of Din indicate that the energies derived in this way are not altogether satisfactory. In particular there is a serious disagreement with the measurements of the specific heat along the saturation curve made by Walker and Jones and Walker [43,44]; this is shown in Table A1, where the values in the second column were calculated from the energies listed by Streett and Staveley according to the equation

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v + 1.5 R + p \left(\frac{\partial V}{\partial T}\right)_v$$

(A1)

Since it seems very unlikely that the measured specific heats are in error by as much as 22%, we have made a new analysis of the experimental data, seeking the best compromise between existing experiments.

There are several measurements of the latent heat of argon at the normal boiling point, which we list in Table A2. The value of Eucken and Hauck is clearly too low and the values of Clusius and Frank and especially of Flubacher et al. are presumably to be preferred. However the values derived from
the independent and careful London and Amsterdam vapor pressure measurements of Clark et al. [42] must also be given some weight; in calculating the latent heat the vapor density was determined using accurate modern second virial coefficients [49]. In the case of the Amsterdam measurements a short extrapolation (about 1°K) was involved.

We calculated values of $U_1$ using the calorimetric latent heat value of Flubacher et al. and the measured specific heats in the integrated form of (Al). At 138.16°K the calculated value was about 41 cal/mole more negative than the value derived from pVT and vapor pressure data by Michels et al. [58]. This is a real discrepancy between different experiments. In the absence of further information we sought a compromise by distributing this in the proportion of 10 cal/mole to the latent heat of Flubacher et al., 21 cal/mole to the specific heat data, and 10 cal/mole to the results of Michels et al. [58]. Thus we adopted a latent heat at the boiling point of 1545 cal/mole (this is about half way between the value of Flubacher et al. and the London value of Clark et al.). We increased the values of $C_v$ uniformly by 4.5% and repeated the calculation of $U_1$. The resulting value of $U_1$ at 138.16°K was -932 cal/mole, compared with the value -923 cal/mole found by Michels et al. [58].

The resulting values of $U_1$ are shown in Table A3, with the values of Streett and Staveley [35] and those listed by Rowlinson [45], also derived from Din's results, for comparison. We believe that the present results are probably the best estimates that can be formed with existing experimental data, and that the experimental error should be estimated as about ±15 cal/mole.

The values called "present" in the tables in the text were calculated using these values together with the procedure of Streett and Staveley [35] and their pVT data.
Fig. 1. Second virial coefficients; deviations from values calculated with quantum correction for the 6:12 potential with $\varepsilon/k = 119.8^\circ K, \sigma = 3.405 \text{ Å}$. The solid curve is computed for the present potential (with quantum correction). Experimental data: o Weir et al. [49]; Byrne et al. [50]; $\Delta$ Fender and Halsey [51]; $\nabla$ Michels et al. [52]; o Whalley et al. [53].

Fig. 2. Molecular beam differential scattering intensities of Lee and Parson [27]. In the upper set of curves the points are experimental, the solid and dashed curves were calculated for the Bobetic-Barker and Barker-Pompe potentials respectively by Lee and Parson while the dash-dotted curve represents interpolated values for the present potential. The lower curve was calculated for the potential of Dymond and Alder [13] by Lee and Parson.

Fig. 3. Vibrational level spacings of argon. Experimental data of Tanaka and Yoshino [25] (with error bars set by Bruch and McGee [26]) are shown thus I; calculated values are shown for the present potential ($\nabla$) and those of Bobetic and Barker (o), Barker and Pompe (x) and Dymond and Alder (□). For all potentials except the present these results are due to Bruch and McGee [26].

Fig. 4. Comparison of the 6:12 potential (with $\varepsilon/k = 119.8^\circ K, \sigma = 3.405 \text{ Å}$) with the present potential.
Figure 1
Figure 2
Figure 3
Figure 4
<table>
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TABLE A2. Latent heat of argon at normal boiling point

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<td>1555.0±4.6</td>
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TABLE A3. The internal energy of liquid argon on the saturation line; $U_i$, cal/mole.

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(a) All Monte Carlo calculations in this table had 300,000 configurations.
TABLE 3. Pressures and internal energies for Bobetic-Barker potential.

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a. MC represents Monte Carlo, with the following digit giving the number of configurations in hundreds of thousands; MD represents Molecular Dynamics.

b. Unless otherwise indicated, from Streett and Staveley [35].
TABLE 3 - (cont'd).

c. Unless otherwise indicated, from Streett and Staveley [35], corrected as discussed in Appendix 1.

d. Unless otherwise indicated present values as discussed in Appendix 1.

e. Extrapolated.

f. Interpolated from the tables of Levelt [36].

g. Van Itterbeek and Verbeke [46].
in Table 3. The quantity $x$ is that appearing in eqn. (18); $x = 1.0$ is the Barker-Pompe
meaning as in Table 3. The quantity $x$ is that
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| TABLE 4. Pressures and internal energies for Barker-Pompe and "present" potentials.

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TABLE 4. Pressures and internal energies for Barker-Pompe and "present" potentials.
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**TABLE 5.** Contributions to the internal energy, "present" potential.
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TABLE 6. Contributions to the pressure, "present" potential.
APPENDIX B

THE FRICTION COEFFICIENT FORMALISM IN THE
STATISTICAL MECHANICS OF TRANSPORT PROCESSES

BY

R. A. Fisher and R. O. Watts,

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

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

In this paper the method of molecular dynamics (Rahman, 1964) is used to test the assumptions implicit in Kirkwood's theory. Rahman used his results to calculate the velocity autocorrelation function and compared this with the exponential form predicted by the Langevin equation. In the liquid region it was found that the machine result gave a negation region, which contradicts the Langevin result. This was evidence for the conclusion that Kirkwood's theory was not exact. However no test of the range of validity of the assumptions in the friction coefficient theory was carried out and it has generally been assumed that the theory gives good results (see for example Cole, 1970). We begin in section 2 by outlining the assumptions inherent in the friction coefficient theory. A brief discussion of the relation between the friction coefficient and the intermolecular forces is also
given. The next section gives a short outline of the molecular dynamics calculations, with particular emphasis given to the accuracy of the calculations. In section 4 the results of the study are presented again with some emphasis on possible sources of error. Finally the results are summarised and some discussion of their implications given.

2. Friction Coefficient Theory

Suppose that the forces acting upon a particle can be written as the sum of two terms. The first term is proportional to the momentum of the particle, whilst the second term corresponds to microscopic fluctuating force. Then we may write the force in the form

$$F_i = \frac{dp_i}{dt} = -\zeta \frac{p_i}{M} + X(t)$$  \hspace{1cm} (1)

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

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

where $\langle \rangle$ represents an average over an equilibrium ensemble. The autocorrelation function for the fluctuating term is given by

$$\langle X_1(t) X_1(t+\tau) \rangle_1 = \phi(\tau)$$  \hspace{1cm} (2)

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

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

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

\[ \langle p_1(t) X_1(t+\tau) \rangle_1 = 0 \]  

(3)

and that

\[ \langle X_1(t)p_1(t+\tau) \rangle_1 = 2\zeta kT e^{-\zeta \tau / M} \]  

(4)

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

\[ \zeta = \frac{1}{kT} \int_{0}^{\tau_1} \langle F(t)F(t+\tau) \rangle \, d\tau \]  

(5)

where the average is now over a full equilibrium ensemble. Equation (5) is Kirkwood's expression for the friction coefficient. Provided the conditions on \( \phi(\tau) \) are satisfied then Suddaby and Gray (1960) showed that Kirkwood's friction coefficient could be used to calculate the self diffusion coefficient through Einstein's equation

\[ D = kT / \zeta. \]  

(6)

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

\[ \langle F(t) F(t+\tau) \rangle = \phi(\tau) - \frac{\zeta^2 kT}{M} \exp(-\zeta \tau / M) \]  

(7)

During the period \( \tau < \tau_1 \) the function \( \phi(\tau) \) is the dominant contributor to the autocorrelation function. However \( \phi(\tau) \) is supposed to be essentially zero when \( \tau = \tau_1 \), and the exponential term will take over. Thus \( \langle F(t) F(t+\tau) \rangle \) will reach a minimum value at the plateau time \( \tau_1 \), and then rise slowly to zero. As the results should be relatively insensitive to \( \tau_1 \) to be acceptable, again we would expect \( \tau_1 \) to be of the order of \( 10^{-11} \) secs.
There exists (in principle) a method of calculating the self-diffusion coefficient corresponding to that measured experimentally. This is the Linear Response Theory of Green (1952) and Kubo (1957). If we assume that the non-equilibrium distribution function can be expanded linearly about its equilibrium value, and define the self-diffusion coefficient as the coefficient of proportionality when writing the mass flux in terms of a chemical potential gradient then the Linear Response theory gives

\[ D = \frac{1}{Mz} \int_{0}^{\infty} < p(t) p(t+\tau) > \, d\tau \]  

(8)

an equation originally derived by Einstein in his theory of Brownian motion. By calculating the momentum autocorrelation function and carrying out the required integral we can obtain D. If Kirkwood's theory is valid we would expect the D obtained from equ. (8) to agree with that obtained from equs. (5) and (6). In order to determine D from molecular dynamics calculations we need to truncate the infinite integral in equ. (8) at some time \( \tau_D \). We might expect that if Kirkwood's theory is valid \( \tau_1 < \tau_D \). Again this question is examined in Section 4.

3. Molecular Dynamics Calculations

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

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

\[ u(r) = \varepsilon \left[ e^{\alpha(1-r)} \sum_{i=0}^{L} A_i (r-1)^i - \frac{2}{3} \sum_{i=0}^{\infty} \frac{C_{2i+6}}{(\delta + r)^{2i+6}} \right] \]
together with the Axilrod-Teller triplet potential. Details may be found in the paper by Barker and Pompe (1968). In the results reported here the pair potential was truncated at 2.5\(\sigma\), where \(\sigma\) is the position of the zero in the potential. It was not possible to perform the calculations with the three-body potential included. As no satisfactory perturbation theory exists for including such terms no attempt was made to include the long-range and three-body terms. Consequently the results given here are not strictly applicable to argon, although our self-diffusion coefficients are close to the experimental values. However the truncated potential is at least as realistic as the Lennard-Jones potential, for example, and we believe our conclusions are generally valid. In order to facilitate the comparisons the reduced variables given in table 1 will be used in the rest of this paper.

The molecular dynamics calculations were similar to those described for the Lennard-Jones potential by Rahman (1964) and Verlet (1968). The equations of motion were solved for a system of 108 particles in steps of \(\delta t^* = 0.00506\) for about 5000 time steps. This corresponds to about \(5 \times 10^{-11}\) secs. in real time. During this time the total momentum of, and force on, the system remained essentially zero. The average total energy of the system was constant to about 1% throughout the run. Around 500 time steps were discarded at the beginning of each run to allow the system to reach equilibrium. The agreement with Monte Carlo results reported earlier (Barker, Fisher and Watts, 1971) along with the good agreement with experiment indicates that equilibrium had been reached. To show the accuracy of the calculations, in fig. 1 we have compared the values of \(PV/NkT\) and \(U/NkT\) obtained from the molecular dynamics with the results of the Monte Carlo calculations. The agreement is very satisfactory. It is possible that the diffusion coefficient calculation may depend upon the size of the system. Calculations for the Barker-Bobetic potential using more than 108 particles have not been performed. Consequently we cannot directly test this effect. However in table 2 some values of \(D\) calculated by us are given. For the liquid state point the value of 0.026 has been reported by Levesque and Verlet (1971) for 864 particles interacting
through the Lennard-Jones (12,6) potential. The values are in good agreement considering the different potential functions, and so it seems reasonable to suppose that any effect due to the number of particles is small.

4. Results

If we introduce reduced variables into the equations given in Section 2 we obtain the following results:

Langevin equation

\[ F^* = \frac{dv^*}{d\tau^*} = -\zeta^* v^* + X^* \]  

(9)

Einstein equation

\[ \zeta^* = \frac{T^*}{D^*} \]  

(10)

Kirkwood equation

\[ \zeta^* = \frac{1}{T^*} \int_{0}^{\tau^*} <F^*(0) F^*(\tau^*)> d\tau^* \]  

(11)

The correlation between initial momentum and the later fluctuating force becomes

\[ <v^*(0) X^*(\tau^*)>_1 = <v^*(0) X^*(\tau^*)> = 0 \]  

(12)

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

\[ <X^*(0) v^*(\tau^*)>_1 = <X^*(0)v^*(\tau^*)> = 2\zeta^* T^* e^{-\zeta^* \tau^*} \]  

(13)

In equs. (11)-(13) we have used the fact that the autocorrelation functions depend only upon the difference of time to put \( t = 0 \). Also as the results given in equs. (3) and (4) are independent of the initial momentum \( p^* \) we have integrated over this co-ordinate to get the second parts of equs. (12) and (13). Finally, the Kubo-Green equation for the self-diffusion coefficient can be written

\[ D^* = \int_{0}^{\infty} <v^*(0) v^*(\tau)> d\tau^* \]  

(14)

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

Suddaby and Gray (1960) show that if $\mathcal{O}^*(\tau^*)$ is sufficiently sharp then in reduced units
\begin{equation}
< F^* (0) F^* (0) > = \xi^* T^* / \tau^* \quad (15)
\end{equation}
In addition this autocorrelation function will reach a minimum at the plateau time $\tau^*_1$, this minimum being $-\xi^* T^*$. We can now obtain the predicted graph of $< F^* (0) F^* (\tau^*) >$. From the molecular dynamics calculations we obtain $< F^* (0) F^* (0) >$. Then using the Kubo-Green equation and Einstein's relation we can obtain the macroscopic friction coefficient. Rearranging equ. (15) gives an estimate of the plateau time $\tau^*_1$. Finally we can write equ. (7) in terms of reduced variables to give
\begin{equation}
< F^* (0) F^* (\tau^*_1) > = \mathcal{O}^*(\tau^*_1) - \xi^* T^* e^{-\xi^* \tau^*_1} \quad (16)
\end{equation}
At times such that $\tau^* < \tau^*_1$ the first term in equ. (16) is supposed to be dominant. This conclusion arose from the assumptions that $\mathcal{O}^*(\tau^*)$ is sharply peaked and that $\xi^* \tau^*_1 << 1$. The curve resulting from equ. (16) is also shown in fig. 2, together with the function $\mathcal{O}^*(\tau^*)$. There are many features of interest in fig. 2. Perhaps the most surprising is the time-scale over which $< F^* (0) F^* (\tau^*) >$ is significant. In comparison with the first peak the function is small beyond $\tau^* = .2$. In real time units this interval corresponds to about $4 \times 10^{-13}$ secs. Remembering that Suddaby and Gray (1960) showed the plateau time to be in the region of the minimum, it is obvious that $\tau^*_1$ is not microscopically long. In fact the minimum occurs after only two or three molecular collisions. The next most obvious result is that the predicted autocorrelation function, from equ. (16), is in very poor agreement with the machine results. The friction coefficient used in the calculation was obtained from the self-diffusion coefficient through Einstein's equation.
Notice that the maximum is very high. For $\tau^* = 0.01$ it was found that the predicted curve had a value greater than 1200. The minimum is far more pronounced than the machine minimum, although it occurs at nearly the same time. It is interesting that the minimum of Suddaby and Gray's conjectured curve, at -1611, is very much deeper than that of equ. (16). However, it occurs at essentially the same time, $\tau_1^* = .18$. The function $\phi^* (\tau^*)$ also shown in fig. 2 is definitely sharply peaked. However, the minimum in this curve accounts for nearly all the depth in equ. (16). It is not, as was conjectured, effectively zero. We can also comment on the restriction that $\zeta^* \tau_1^* << 1$. If we estimated $\tau_1^*$ using the self-diffusion coefficient and $<F^* (0) F^* (0)>$ from eq. (15) we find $\zeta^* \tau_1^* = 8.92$. Thus the restriction on $\tau_1^*$ necessary for Kirkwood's theory to be valid is not satisfied at all. In fact the supposedly sharply peaked function $\phi^* (\tau^*)$ is dominant at all times greater than about $\tau^* = .01$. We can conclude from this that at least in the liquid region the concept of a plateau time, in Kirwood's sense, has no meaning. There is one other comparison of interest before leaving the liquid state calculations. We can calculate $\tau^*$ from the self-diffusion coefficient and Einstein's relations, and directly from Kirkwood's equation. The required integrations must be truncated at some point. The resulting coefficients as a function of the upper limit on the integration, are given in table 2. It is at once obvious that the Kubo-Einstein coefficient is much different from the Kirkwood estimate. In particular the Kirkwood estimate is negative and does not appear to have stabilised. As the negative friction coefficient leads to a negative self-diffusion coefficient, it is obviously unphysical. To test for any evidence of a plateau value in the region of the minimum the Kirkwood friction coefficient is given for three times near the minimum. Although the results are all positive they are changing rapidly. We can only conclude that at least in the liquid region Kirkwood's theory of the friction coefficient is not valid.

We continue by examining the Kirkwood theory at a density corresponding to the critical density of argon. The results are given in Fig. 3. It is at once apparent that the Suddaby-Gray result, equ. (16) is in excellent agreement with the
machine results. The violent disagreement found for the liquid state no longer exists. However this agreement is about the only satisfactory observation at this density. Again the position of the minimum gives a meaningless plateau time. In addition the function \( \phi^*(\tau^*) \) is not particularly sharply peaked, and is obviously the dominant contributor to \( \langle F^*(0)F^*(\tau^*) \rangle \) throughout the complete time of interest. The Suddaby-Gray estimate for the plateau time, equ. (15), gives \( \tau_1^* = 0.0033 \), which is much too small to have any macroscopic interpretation. In fact this is less than the time needed for one collision to take place. Also the Suddaby-Gray guess at the value of the minimum, \( -\zeta^* T^* \), gives -2.37, which is too small by a factor of five or six. The value of \( \zeta^* T^* \) is 0.0061, which is much less than one. However as \( T^* \) itself is so short, this result is of little interest. Finally we can compare the Kirkwood friction coefficient obtained from equ. (11), with that obtained from the Kubo-Green equation and Einstein's relation. The relevant results are presented in table 2. Again the Kirkwood values are negative and show no real sign of a plateau value existing. Integrating out to the minimum in the autocorrelation function gives results that are close to the macroscopic results, but as with the liquid state results there is no reason to prefer the very short time results over any other. We can only conclude that although the gas phase results are better than the liquid phase results, there is no evidence to suggest that Kirkwood's theory is valid in this region.

5. Discussion

We have shown that the force autocorrelation function approach to the friction coefficient is not valid at dense gas and liquid densities. However, this does not imply that the macroscopic friction coefficient, connecting diffusion with viscosity, is a meaningless concept. It is well known (see for example Edward, 1970), that the diffusion coefficients and shear viscosities of simple non-electrolytes are quite strongly correlated through the Einstein equation and the equation

\[
\eta = \text{const} \, \zeta \rho \tag{17}
\]
where \( \rho \) is the density. What must now be questioned is the concept of Brownian Motion being the dominating influence on transport phenomena in dense fluids. One of the most popular theories of transport in simple liquids is due to Rice and Allnatt (1961). This theory is essentially an attempt to obtain the friction coefficient from Kirkwood's equation. In this theory the intermolecular potential is assumed to consist of a rigid core repulsion superimposed on an arbitrary soft potential. On the basis of this separation the forces are treated on two time scales. The hard core collisions are treated using the Enskog approach (Chapman and Cowling, 1939) and the soft potential is dealt with using a quasi-brownian motion approach. Early work on this theory suggested that Rice and Allnatt's approach gave good results for the liquid (Rice and Gray, 1965). However despite its modification this theory represents an approximate attempt to evaluate the friction coefficient. Consequently there must be some explanation for the apparently good results. The most obvious is that the accumulation of errors was such that accidental agreement with experiment was obtained. In particular a hard-sphere modified pair-potential was used in conjunction with an approximate radial distribution function for that potential (Kirkwood et al, 1952). When Monte-Carlo calculations using the pair-potential were used to test the Rice-Allnatt theory the agreement with experiment was much less impressive, although a positive friction coefficient was found (Collings et al, 1971). In addition it was shown that the pair potential itself leads to very poor predictions of the thermodynamic properties of the inert gases. Obviously there is room for extensive cancellation of errors here. Given the poor agreement between the Rice-Allnatt results for the friction coefficient and the results given here - particularly \( \zeta < 0 \) - it would seem that this theory is not as useful as it was first considered.

The Kirkwood approach to a theory of transport is based on the extension of hydrodynamic equations to microscopic phenomena. This approach would be acceptable if the fluctuating forces \( X(t) \) were small. In fact it would appear that the fluctuating terms are at least as important as the strongly repulsive forces caused by 'hard-core' collisions.
These 'soft' forces appear to swamp the correlations between collisions. This can be seen clearly in fig. 4. Here the force autocorrelation functions given in figs. 2 and 3 are shown over a longer time. It is obvious that the forces acting on a particle become essentially random within about two or three collision times. If the fluctuating terms were small one would expect the autocorrelation function to be of longer range. Notice that the ratio $\frac{\langle F^*(0)F^*(0) \rangle}{\langle F^*(0)F^*(\tau) \rangle}$ is greater for the gas than for the liquid. There is also a small positive peak after the minimum on the liquid curve. These observations can be correlated with those of Fehder (1969) on the behaviour of a two-dimensional system of discs. He found that for quite long times a particle tends to stay in a cage formed by its neighbours. The force autocorrelation function can be interpreted in a similar way. The strong negative well would represent the particle reaching the end of its 'cage', and the small positive peak the time at which it returned to the beginning. This effect is not obvious in the more dilute gaseous system.

These effects also show up in the velocity autocorrelation functions given in fig. 5. Here the liquid curve shows the negative regions first observed by Rahman (1964). These regions would correspond to the particle returning along its 'cage'. Also shown in fig. 5 are the Langevin equation results for the autocorrelation function

$$\langle v^*(0) v^*(\tau) \rangle = T^* \exp \left( - \frac{T^* \tau^*}{D^*} \right)$$

This is of course also the form predicted by Kirkwood's theory. Notice that for the gas the agreement with our results is good. This is expected as Suddaby and Gray's (1960) conjectured force autocorrelation function agrees with our results. The Langevin result for the liquid is in poor agreement with the machine results, confirming the findings of Rahman. It is of interest that the gas-phase results are of much longer range than the liquid-phase result. This is in agreement with the much weaker minimum in the gas force autocorrelation function. It would appear that although after a short time the forces are opposed to the initial forces, this opposition is not sufficient to reverse the velocity of the particle.
6. Conclusions

We have used the method of molecular dynamics to examine the friction coefficient approach to transport phenomena. It appears that the concept of a plateau value for the friction coefficient, as proposed by Kirkwood (1946) is invalid. Using the machine results to calculate the plateau time $\tau^*$ using results due to Suddaby and Gray (1960), it was found that $\tau^*$ was less than $2 \times 10^{-13}$ secs. Thus it cannot be termed microscopically long. When the friction coefficient was calculated by integrating the force autocorrelation function to fairly long times it was found to be negative. As this leads to a negative self-diffusion coefficient we concluded that Kirkwood's approach is not useful. Finally we examined the meaning of our results for the force and velocity autocorrelation functions. We concluded that the behaviour of these functions confirmed the findings of Fehder (1969) that particles in liquid systems tend to stay in 'cages' formed by their neighbours for quite long times.

7. Acknowledgement

One of us (R.A.F.) is grateful to the Australian National University for the award of a Postgraduate Scholarship.
REFERENCES


Kubo, R., 1959, Lectures in Theoretical Physics 1, 120.


### TABLE 1
Reduced variables used, along with MKS equivalents for value of 1.

<table>
<thead>
<tr>
<th>Reduced Variable</th>
<th>Real Variable</th>
<th>MKS for $R^* = 1$</th>
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<tr>
<td>$T^*$</td>
<td>$T = \frac{E}{K}$ $T^*$</td>
<td>140.2°K</td>
</tr>
<tr>
<td>$r^*$</td>
<td>$r = \sigma r^*$</td>
<td>$3.367 \times 10^{-10}$ m</td>
</tr>
<tr>
<td>$v^*$</td>
<td>$v = \frac{1}{2} \frac{E}{M} v^*$</td>
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<tr>
<td>$\tau^*$</td>
<td>$\tau = \frac{1}{2} \frac{\sigma}{\rho} \tau^*$</td>
<td>$1.96 \times 10^{-12}$ s.</td>
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<tr>
<td>$F^*$</td>
<td>$F = \frac{E}{\sigma}$ $F^*$</td>
<td>$5.746 \times 10^{-12}$ N</td>
</tr>
<tr>
<td>$D^*$</td>
<td>$D = \frac{1}{2} \frac{\sigma}{\rho} D^*$</td>
<td>$5.778 \times 10^{-9}$ m.$^2$s.$^{-1}$</td>
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<tr>
<td>$\zeta^*$</td>
<td>$\zeta = \frac{(\rho \varepsilon)^{1/2}}{\sigma} \zeta^*$</td>
<td>$3.379 \times 10^{-14}$ kg.s.$^{-1}$.</td>
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TABLE 2
Reduced diffusion coefficients and friction coefficients from Kubo-Green theory and Kirkwood theory as a function of the upper limit in the time integration

<table>
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<tr>
<th>( \tau_1^* )</th>
<th>( D^* )</th>
<th>( \zeta^E )</th>
<th>( \zeta^K )</th>
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<td>0.020</td>
<td>48.9</td>
<td>-2.43</td>
</tr>
</tbody>
</table>
Legends for Figures

**Figure 1:**

- **Molecular dynamics results** for internal energy.
- **Monte Carlo results** for internal energy.
- **Molecular dynamics results** for equation of state.
- **Monte Carlo results** for equation of state.

The lines are to give some indication of the agreement.

**Figure 2:** Short time behaviour of the force autocorrelation function for the liquid phase.

**Figure 3:** Short time behaviour of the force autocorrelation function for the gas phase.

**Figure 4:** Long time behaviour of the force autocorrelation function.

**Figure 5:** Velocity autocorrelation function.
Figure 1
M.D. results from 3 runs
Suddaby-Gray
\( \phi^* (\tau^*) \)

10^{-13} \text{ secs.}

Figure 2
Figure 3

\[ \langle F^*(0), F^*(\tau^*) \rangle \]

- M.D. results
- Suddaby-Gray
- \[ \phi^*(\tau^*) \]

10^{-13} secs.
Figure 4
Figure 5
Temperature $T^*$ and density $p^*$ are given in reduced units.

Values are tabulated according to the following format.

$r$, $g(r)$, $g(r+.01)$, $g(r+.02)$ etc.

$r+.1$, $g(r+.1)$, ... etc.

$r+.2$, $g(r+.2)$ etc.

etc.
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<td>2.4</td>
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<td>G(R) AT RHO=0.825 AND T*= 0.59643</td>
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<tr>
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</tr>
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<tr>
<td>G(R) AT RHOD=0.300 AND T*= 0.65047</td>
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\[
G(R) \text{ AT } \rho = 0.800 \text{ AND } T^* = 0.68819
\]

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<tr>
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<tr>
<td>0.9</td>
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</tr>
<tr>
<td>1.0</td>
<td></td>
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</tbody>
</table>

\[
\text{Note: } G(R) \text{ is given in units of } \text{m}^2/\text{kg} \cdot \text{s}^{-1/2}
\]
| G(R) AT \( \rho = 0.400 \) AND \( T^* = 1.19093 \) |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| \( \theta \)   | \( 0.00000 \) | \( 0.00000 \) | \( 0.00000 \) | \( 0.00000 \) | \( 0.00002 \) | \( 0.00007 \) |
| \( 0.9 \)     | \( 0.00005 \) | \( 0.01877 \) | \( 0.03942 \) | \( 0.07543 \) | \( 0.13306 \) | \( 0.21713 \) |
| \( 1.0 \)     | \( 1.02257 \) | \( 1.22986 \) | \( 1.42326 \) | \( 1.59940 \) | \( 1.75614 \) | \( 1.88669 \) |
| \( 1.1 \)     | \( 2.16921 \) | \( 2.16498 \) | \( 2.13874 \) | \( 2.08543 \) | \( 2.02280 \) | \( 1.98651 \) |
| \( 1.2 \)     | \( 1.73419 \) | \( 1.68294 \) | \( 1.63726 \) | \( 1.59316 \) | \( 1.55006 \) | \( 1.50834 \) |
| \( 1.3 \)     | \( 1.34247 \) | \( 1.31430 \) | \( 1.29116 \) | \( 1.25897 \) | \( 1.23305 \) | \( 1.22635 \) |
| \( 1.4 \)     | \( 1.12296 \) | \( 1.10863 \) | \( 1.08948 \) | \( 1.06811 \) | \( 1.04960 \) | \( 1.03498 \) |
| \( 1.5 \)     | \( 0.96641 \) | \( 0.96156 \) | \( 0.94766 \) | \( 0.94127 \) | \( 0.95125 \) | \( 0.95193 \) |
| \( 1.6 \)     | \( 0.91434 \) | \( 0.91698 \) | \( 0.90230 \) | \( 0.89465 \) | \( 0.89314 \) | \( 0.89135 \) |
| \( 1.7 \)     | \( 0.88314 \) | \( 0.89647 \) | \( 0.89672 \) | \( 0.88933 \) | \( 0.88415 \) | \( 0.88105 \) |
| \( 1.8 \)     | \( 0.89330 \) | \( 0.90058 \) | \( 0.91039 \) | \( 0.91748 \) | \( 0.92394 \) | \( 0.92938 \) |
| \( 1.9 \)     | \( 0.97057 \) | \( 0.96948 \) | \( 0.95993 \) | \( 0.95741 \) | \( 0.95466 \) | \( 0.95882 \) |
| \( 2.0 \)     | \( 1.00332 \) | \( 1.00282 \) | \( 1.00718 \) | \( 1.00822 \) | \( 1.01387 \) | \( 1.02900 \) |
| \( 2.1 \)     | \( 1.04771 \) | \( 1.04750 \) | \( 1.04507 \) | \( 1.05227 \) | \( 1.05898 \) | \( 1.06924 \) |
| \( 2.2 \)     | \( 1.05194 \) | \( 1.05064 \) | \( 1.05493 \) | \( 1.06206 \) | \( 1.06595 \) | \( 1.06472 \) |
| \( 2.3 \)     | \( 1.04100 \) | \( 1.04476 \) | \( 1.05852 \) | \( 1.07113 \) | \( 1.08408 \) | \( 1.10431 \) |
| \( 2.4 \)     | \( 1.03282 \) | \( 1.02498 \) | \( 1.01362 \) | \( 1.00514 \) | \( 1.00527 \) | \( 1.00525 \) |
| \( 2.5 \)     | \( 1.00207 \) | \( 0.98853 \) | \( 0.99843 \) | \( 0.99450 \) | \( 0.98338 \) | \( 0.98771 \) |
| \( 2.6 \)     | \( 0.97907 \) | \( 0.97577 \) | \( 0.98174 \) | \( 0.97835 \) | \( 0.98266 \) | \( 0.99194 \) |
| \( 2.7 \)     | \( 0.98786 \) | \( 0.98184 \) | \( 0.97386 \) | \( 0.97466 \) | \( 0.96049 \) | \( 0.96304 \) |
| \( 2.8 \)     | \( 0.98886 \) | \( 0.97315 \) | \( 0.96990 \) | \( 0.97383 \) | \( 0.97865 \) | \( 0.98392 \) |
| \( 2.9 \)     | \( 0.98762 \) | \( 0.97854 \) | \( 0.97620 \) | \( 0.97973 \) | \( 0.98737 \) | \( 0.98782 \) |
| \( 3.0 \)     | \( 0.99348 \) | \( 0.99444 \) | \( 0.99008 \) | \( 0.97953 \) | \( 0.97864 \) | \( 0.97812 \) |
| \( 3.1 \)     | \( 0.97768 \) | \( 0.98034 \) | \( 0.98217 \) | \( 0.97699 \) | \( 0.97573 \) | \( 0.96344 \) |
| \( 3.2 \)     | \( 0.97215 \) | \( 0.97604 \) | \( 0.97888 \) | \( 0.97878 \) | \( 0.97859 \) | \( 0.97760 \) |
\[
\begin{align*}
G(K) \text{ at } R\nu = 0.350 \text{ and } T^* = 1.20419
\end{align*}
\]
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<td>G(R) AT RHO=0.250 AND T*= 1.13450</td>
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