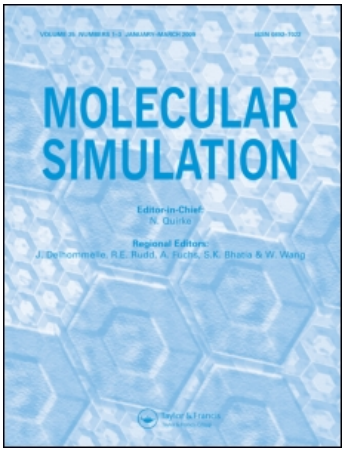


Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

The Investigation of Spatial Correlations in Liquid Phosphorus by Reverse Monte Carlo Calculations

M. Scheidler[ab]; A. N. North[a]; J. C. Dore[a]
[a] Physics Laboratory, University of Kent, Canterbury, Kent., UK [b] Erasmus student from Fachbereich Physik, Universitat Marburg, Germany

To cite this Article Scheidler, M. , North, A. N. and Dore, J. C.(1993) 'The Investigation of Spatial Correlations in Liquid Phosphorus by Reverse Monte Carlo Calculations', Molecular Simulation, 11: 6, 345 — 363
To link to this Article: DOI: 10.1080/08927029308022519
URL: http://dx.doi.org/10.1080/08927029308022519

Molecular Simulation, 1993, Vol. 11, pp. 345-363
Reprints available directly from the publisher
Photocopying permitted by license only Printed in the United States of America

THE INVESTIGATION OF SPATIAL CORRELATIONS IN LIQUID PHOSPHORUS BY REVERSE MONTE CARLO CALCULATIONS

M. SCHEIDLER†, A.N. NORTH and J.C. DORE

Physics Laboratory, University of Kent, Canterbury, Kent. CT2 7NR, UK.

(Received September 1992, accepted April 1993)

The RMC method is used to model neutron diffraction results for liquid phosphorus. The adaptation of the basic routine for the treatment of molecular systems is described and the consequent changes in producing an initial configuration and achieving satisfactory convergence are critically examined. The programme is based on a structural unit of tetrahedral symmetry (P_4) and random moves involving both translation and rotation of the molecule are introduced and selected on the usual χ^2 probability criteria. The resultant configuration is found to have a relatively simple centre-centre correlation function resembling that of an atomic liquid or a close-packed disordered array of spheres. The relative orientation of molecules within the first neighbour shell has been investigated and is found to differ from that proposed earlier from a simple consideration of geometrical anisotropy. The general use of RMC for molecular systems is discussed in relation to future work.

1 INTRODUCTION

The structural study of liquids by neutron or X-ray diffraction is based on the experimental measurement of the liquid structure factor S(Q) and the conversion to a pair-correlation function, g(r) in real-space by Fourier transform relationships. The resulting information is effectively angle-averaged and therefore gives only partial information about the spatial relations between the molecules. Frequently the data are used as a means of checking the effectiveness of various forms of interaction potential in computer simulation predictions through Molecular Dynamics (MD) or Monte Carlo (MC) routines. In some cases there is little knowledge from other thermo-physical data about the acceptable parameters required to define an appropriate potential but the structural data are rarely of sufficient precision to allow direct inversion.

The situation with molecular liquids is particularly interesting since the interaction potential is influenced by various angle-dependent forces arising from electrostatic (e.g. multipole) effects or specific angle-dependent interactions (e.g. hydrogen-bonding) as well as the overall contours of the molecules. These effects contribute to a local ordering of molecular axes which leads to orientational correlations. However, the diffraction measurements yield information about atom-atom correlations so that the extraction of this information is dependent on other assumptions in the analysis [1, 2]. Even for the simplest case of diatomic molecules (e.g. N_2, Cl_2 etc,) it is not possible to convert the measured data to a correlation function for

† Erasmus student from Fachbereich Physik, Universitat Marburg, Germany.

molecular centres without making some assumptions about the orientation correlations [3]. The recent introduction of the Reverse Monte Carlo (RMC) method by McGreevy and colleagues [4] has created new opportunities for investigating this problem although very little work has yet been done with molecular systems other than that of Howe [5] for diatomic systems. In the present paper, we consider how the RMC method can be used for this type of study and present some preliminary data for liquid phosphorus.

2 THEORETICAL PRINCIPLES

a) *Molecular Geometry*

The structural characteristics of molecular liquids are defined in terms of pair correlation functions which can be written in several different forms. If the reference unit is the molecule itself, the most general form of the correlation function is given by the expression $G(\mathbf{R}, \omega_1, \omega_2)$ where $\mathbf{R}$ is a vector between molecular centres and ω_1, ω_2 define the relative orientation of the molecular axes; the function defines the probability of finding two molecules at a certain separation and relative orientation. In practice, it is found that this complete description is rarely attainable and some simplifying approximations must be made. In the case of monatomic liquids the formalism reduces to the single pair correlation function g(r) which represents the probability of finding any two atoms separated by a distance, r. This formalism contains no angle-dependent features so that the structure factor and correlation function are represented by the simple transform relation

$$S(Q) = 1 + \frac{1}{4\pi r^2 \rho_N} \int_0^\infty [g(r) - 1] \sin Qr \, dr$$

where ρ_N is the atomic number density. A measured structure factor can therefore be converted directly to a spatial representation by the inverse transform which is frequently written as

$$d(r) = 4\pi r \rho_N [g(r) - 1] = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin Qr \, dQ$$

In practice there is an upper limit to the integral, Q_{max}, due to experimental limitations but the integral can still be evaluated to give an appropriate $d(r)$ function. These relations still apply in the case of partial structure factors $S_{\alpha\beta}(Q)$ for multicomponent liquids containing atoms or ions of type α and β involving correlations $g_{\alpha\beta}(r)$ between specific labelled species [2].

The complexity arises when the reference unit itself has some structure features which causes the spherical symmetry to be broken. The structure factor for a molecular liquid, $S_M(Q)$, is conventionally written in the form [2]:

$$S_M(Q) = f_1(Q) + D_M(Q)$$

where $f_1(Q)$ is the molecular form-factor that depends only on the geometrical characteristics of the molecule (intra-molecular correlations) and $D_M(Q)$ defines the spatial relations between molecules (inter-molecular correlations). The liquid structure, as distinct from the molecular structure is contained within the $D_M(Q)$

function which can be transformed to give a composite pair correlation function containing only inter-molecular contributions, i.e.

$$d_L(r) = 4\pi r\pi\rho m\left[\bar{g}(r) - 1\right] = \frac{2}{\pi}\int_0^\infty QD_M(Q)\sin\, Qr\, dQ$$

where ρ_M is the molecular number density and $\bar{g}(r)$ is a composite function incorporating all partial functions with appropriate weighting functions dependent on relative concentration and scattering amplitudes [6]. For homonuclear systems such as N_2, Cl_2 and P_4 there is only one observable correlation function, $g(r)$ which represents the atom-atom correlations. Since there is no atom at the molecular centre it is impossible to determine either $g_C(r)$ or $S_C(Q)$ representing the correlation of molecular centres by any direct experimental measurement. In effect the information on centres correlation and local orientation are linked together in the only observable function and cannot, in principle, be separated.

b) *The RMC approach*

The use of Monte Carlo methods is well established in computer simulations. An assembly of 'particles' (i.e. atoms, molecules, ions) are located within a specified volume and interact through a given interaction potential. The assembly is allowed to evolve towards a minimum energy configuration by choosing random moves of individual particles. When convergence is achieved, various properties of the assembly can be evaluated. The results are obviously dependent on the interaction potential used but the predicted structure may be compared with experimental data to check the efficacy of the chosen values.

The reverse Monte Carlo (RMC) routine uses a similar principle in a different procedure by evaluating the pair correlation function from the assembly and comparing it directly with the experimental data. In this case, there is no need to define an interaction potential as the moves are determined entirely by reference to the structural features contained within the experimental data. The RMC routine [4, 5] introduced by McGreevy and colleagues, has been applied primarily to atomic and ionic systems but the principles allow the method to be used for any assembly of scattering centres for which experimental data are available either as single measurements or as a combined set of partial functions. The advantage of this approach is that structural features which are present in the original data can possibly be revealed by a detailed analysis of the co-ordinates of the particles produced by the programme without reference to other information. However, there are further questions relating to the information content of the derived function because there is no guarantee that the extracted characteristics correspond to an optimised distribution of scattering centres. The original dataset is essentially one-dimensional, dependent on the single variable, Q, but is represented by a characteristic distribution dependent on **r** (or possibly **Q**), which is three-dimensional. There cannot therefore be a unique relation between the original dataset and the derived spatial correlations but in practice this does not seem to be a major difficulty [5]. Further studies with different types of experimental data and varied initial conditions are required to fully explore these features. Furthermore it is already apparent that the final results are critically dependent on the precision of the experimental data. Current experience suggests that the RMC method is a very

valuable aid to the interpretation of diffraction measurements but that the limitations should be carefully assessed to avoid over-interpretation of the data.

c) *Angular correlations*

A recent review [3] has emphasised the importance of orientational correlations in the structural properties of diatomic fluids. There appear to be weak effects in the case of nitrogen, oxygen and fluorine but very marked effects for chlorine, bromine and iodine. The hydrogen halides (HF, HCl, HBr) show even more complex behaviour due to the effects of hydrogen-bonding. Another interesting case is that of molecular liquids formed by molecules with tetrahedral symmetry (CCl_4, $TiCl_4$, $GeBr_4$ etc.) which have been reviewed in earlier papers [7, 8]. The series of tetrachloride and tetrabromide liquids presents a particularly rich area for study since the anisotropic contours of the molecules and the overall number density show significant variation. It has been recognised for some time that there is substantial interlocking of adjacent molecules leading to strong orientational correlations. Within this series, the tetrahedral molecules, P_4 and As_4 are special cases in which it would seem that the overall contours are not strongly deformed from spherical symmetry. However, the experimental data suggest that these materials exhibit stronger orientational correlations than would initially be expected and this effect is presumably related to the strained bond-angles (60° instead of 100°) which are responsible for deforming the electron density distribution of the individual atoms in the molecule. Neutron diffraction data for liquid phosphorus were obtained several years ago [9, 10] and have not been fully interpreted so they provide an excellent basis for use of the RMC procedure, particularly in relation to molecular systems where the interaction potential has not been determined.

3 THE RMC PROGRAMME AND FITTING PROCEDURE

a) *Adaptation for molecular liquids*

The current version of the RMC programme [11] which is available for general use is based on an assembly of atomic (or ionic) scattering centres. The first step is to create a box of size L and to insert N atoms such that the number density (N/L^3) is equivalent to that of the liquid being studied. The initial configuration is based on a random choice of co-ordinates with the additional constraint that atoms are not closer than a specified distance which acts as an effective hard core diameter, σ. The box is surrounded by equivalent boxes following normal procedures to eliminate edge effects and a pair correlation function, $g(r)$, is evaluated by counting the number of pairs of atoms separated by a distance r (up to a limiting value of L/2).

Having evaluated a histogram (for incremental steps Δr over the index i) which represents the g_i^{comp} (r) function corresponding to the given configuration there are several different procedures for comparison with the experimental data. The simplest method concerns the real-space behaviour in which a standard χ^2 routine is used to determine the goodness of fit i.e.

$$\chi^2_G = \sum_{i=1}^{N} w_i(r) \left[g_i^{exp}(r) - g_i^{comp}(r) \right]^2$$

where $g_i^{exp}(r)$ and $w_i(r)$ are the experimental value and chosen weighting factor for each datapoint and the summation is made over the N datapoints in the range chosen.

The programme then generates a move for one of the particles using standard Monte Carlo techniques and the χ^2 value is re-evaluated for the new configuration. If the new χ^2 value is lower, the move is accepted, if it is higher the move is possibly accepted on the basis of a conventional probability criterion. The programme repeats these moves on an iterative basis until a defined level of convergence is achieved. An alternative procedure which is sometimes preferable is to evaluate the structure factor, $S_i^{comp}(Q)$ from the given configuration by Fourier transformation of the $g_i^{comp}(r)$ distribution and to evaluate the χ_S^2-value by

$$\chi_S^2 = \sum_{i=1}^{N_S} w_i \left[S_i^{exp}(Q) - S_i^{comp}(Q) \right]^2$$

where the summation runs over the N_S datapoints of the experimental measurement. This approach has some advantages in the sense that it provides a direct comparison with the observations and therefore avoids the problem of error evaluation and statistical noise in the transformed function, $g^{exp}(r)$ but it can also produce difficulties in the sharpness of peaks in $S^{comp}(Q)$ arising from the finite box size; these points are discussed in Section 3d.

The measured structure factor for molecular liquids is $S_M(Q)$ and it is possible to adopt a similar approach in which individual atoms are moved as single entities. Since the total $g(r)$ function contains a sharp peak for the intra-molecular configuration it might be assumed that the basic programme would determine that molecules are present. Unfortunately, this is not so because there is no way of knowing on *a priori* grounds that each atom must have identical local correlations. Thus for a diatomic fluid, it is possible to obtain good agreement with the data for a mixture containing some isolated atoms and others with two neighbours at the appropriate bondlength. In the case of a P_4 molecule with three equivalent intra-molecular neighbours the simulation is even more complex and the normal program [11] produces a distribution in which many atoms are connected in a polymeric type of structure [12]. It is clear that knowledge of the molecular characteristics is an important piece of information which must be included in the routine as a constraint on acceptable solutions. It is consequently necessary to specify the molecular structure and to define the assembly in terms of molecular units. The simplest way of achieving this is to define the atom co-ordinates in such a way that they are labelled according to their assigned molecule number and that any moves chosen by the routine ensure that the co-ordinates of all atoms are changed together in a way that maintains the correct conformation of the molecular unit. The principles of the RMC approach are retained but the routine for obtaining satisfactory solutions is significantly changed.

b) *Setting the initial distribution*

The tetrahedral P_4 molecule has a high degree of symmetry in which all the atoms are equidistant from the molecular centre; this distance is $(\sqrt{3}/2\sqrt{2})r_p$ where r_p is the PP bondlength (2.21 Å). The most convenient way to define the molecular co-ordinates within the box is therefore to specify the (x,y,z) values of the molecular centre and two angles (θ,ϕ) defining the direction of the molecular axis, which

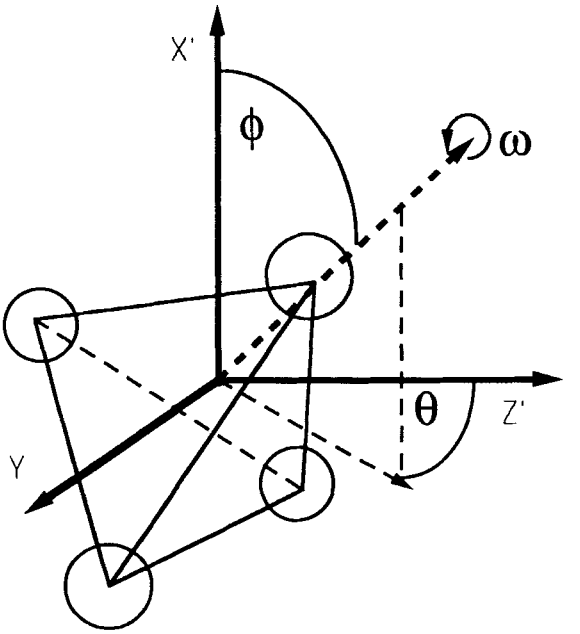


Figure 1 The general co-ordinate system for aphosphorus molecule.

in this case corresponds to one of the centre-atom (C-P) directions. The Cartesian co-ordinates of the four phosphorus atoms, which can be evaluated by the use of rotation matrices, are therefore defined by five geometric co-ordinates plus one bondlength instead of the twelve required for four independent atoms. The features are illustrated in Figure 1 and the method chosen here can be generalised to any molecular geometry.

The creation of an initial distribution of phosphorus molecules with the required number density using the standard procedure proved to be quite difficult. The problem arises because as more molecules are introduced into the box, the probability of locating a suitable space for the insertion of a correlated four-atom molecule becomes very small. This feature is itself an indication that the packing density is high and both translational and orientational correlations must be imposed in order to satisfy the physical conditions. Two approaches may be used to solve this problem. The first method is to reduce the hard-core parameter σ so that sufficient molecules can be introduced and then to gradually increase the value to its correct magnitude in the convergence routine. This method has not been adopted in the present situation as there is no guarantee that the required conditions can be achieved and it leads to a further complication in the process of moving the atoms under a changing constraint system. The method adopted was one in which the molecules were initially given a directional translation from their assigned random positions to produce closer packing. The first step was to introduce approximately 70% of the molecules and then to use a random number generator to displace molecules away from one corner of the box, allowing rotation in the movement.

This process creates space for additional molecules to be placed and the routine is followed until the required number density is achieved. If necessary, the process can be made easier by a small reduction in the σ-value as discussed above. Another way of ensuring that all the molecules can be placed in the box would be to use the crystal structure for the initial arrangement but this is regarded as undesirable because it imposes an ordered configuration on the assembly and may lead to residual effects in the final structure. This effect has already been noted [13] in the modelling of amorphous networks using the bond-switching approach developed by Wooton, Winer and Weaire. [14]

c) *Data for liquid phosphorus*

Neutron diffraction results for liquid phosphorus have been reported by Granada *et al.* [10] for a range of temperatures but the features of the $d_L(r)$ curve do not change significantly in the 10–50°C range; the results are shown in Figures 2 and 3. The analysis presented in the paper was based on the separation of intra- and inter-contributions by fitting the high Q-value data to a molecular form-factor, $f_1(Q)$, and transforming the $D_M(Q)$ function to give $d_L(r)$. In the case of phosphorus there is only one bondlength and the form-factor simplifies to

$$f_1(Q) = \frac{1}{4}[1 + 3j_o(Qr)\exp(-\gamma_{pp}Q^2)].$$

The intra-molecular correlations have a single feature at 2.210 ± 0.004 Å that is responsible for the regular oscillatory structure in the high Q-value region of the $S_M(Q)$ data. The detailed fit also includes a Debye-Waller term to represent the vibrational characteristics of the molecule. In this case the root mean-square

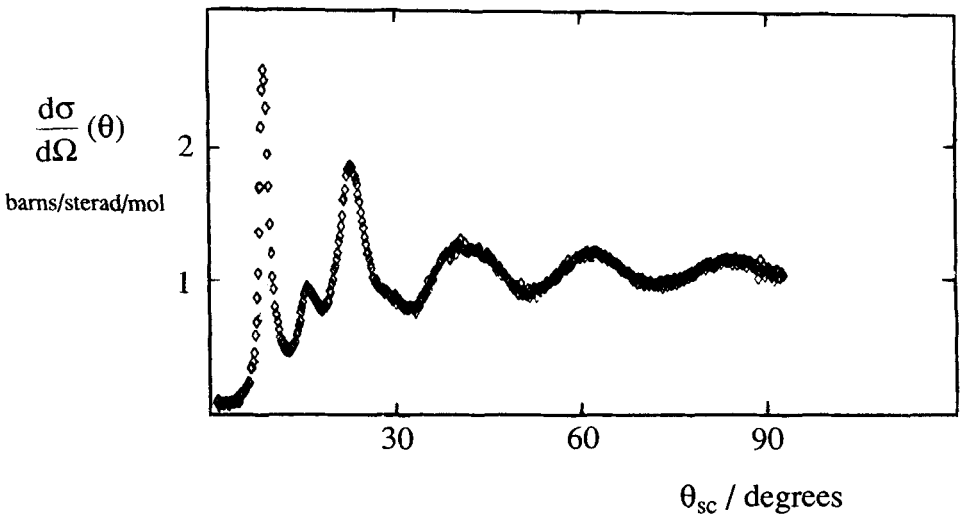


Figure 2 The measured neutron diffraction pattern for liquid phosphorus (P_4) at 20°C.

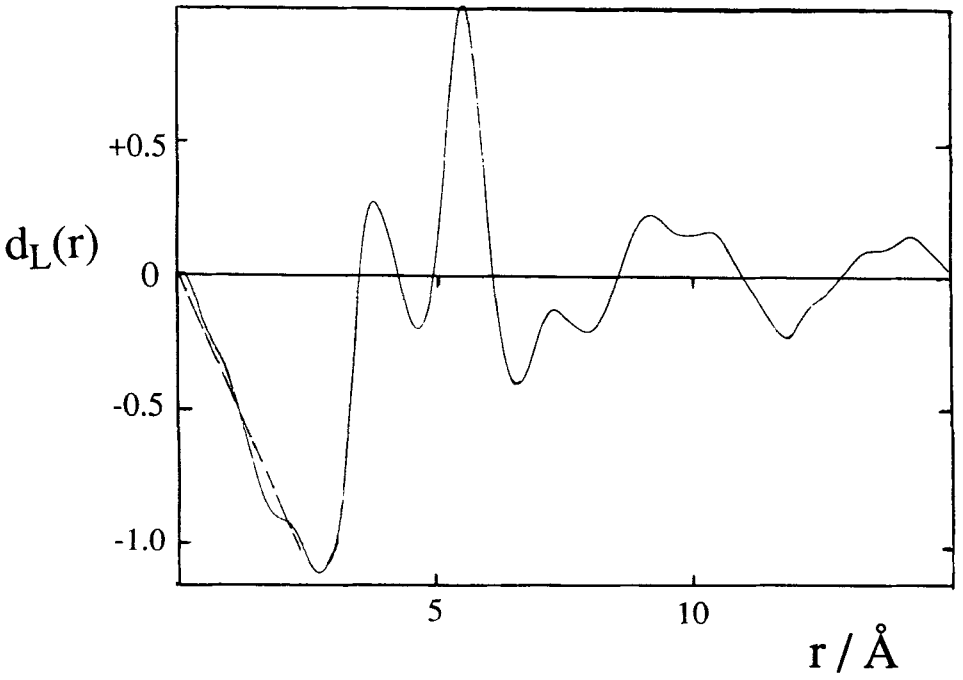


Figure 3 The intra-molecular pair correlation function, $d_L(r)$ derived from data presented in Figure 2.4.

amplitude of vibration is 0.05 Å which is sufficiently small to be neglected in the treatment of inter-molecular correlations. However, it would be significant if the RMC routine is used to fit the $S_M(Q)$ data rather than the extracted $D_M(Q)$ function. It is apparent that the philosophy of using RMC on the 'least-processed' data can lead to difficulties (see Sec. 5). The double peak in the inter-molecular function $d_L(r)$ is typical of liquids composed of tetrahedral molecules [7] and differs considerably from that shown by atomic or ionic liquids.

In the present case it was chosen to fit the inter-molecular $g_L(r)$ function derived from the experimental data using the standard RMC routines with the modification for molecules previously described. The box size was taken to be 40 Å with an assembly of 560 molecules and an arbitrary cut-off value of 3 Å was initially taken for σ. The RMC routine generated a curve with appropriate general features but underestimated the size and sharpness of the first inter-molecular peak. Extending the run time did not improve this discrepancy, suggesting that the imposed conditions did not allow the routine to develop sufficient close-contact interactions. The implied reason is that the orientational correlations in the real liquid are more marked than the model allows. A trial run was made with the cut-off value reduced to 2.21 Å, equivalent to the bondlength and this change did enable the fit in the peak region to be better defined but it also led to a separate sharp feature at lower values of the $g(r)$ function which is clearly unphysical and also to some loss of agreement over the rest of the $g(r)$ curve.

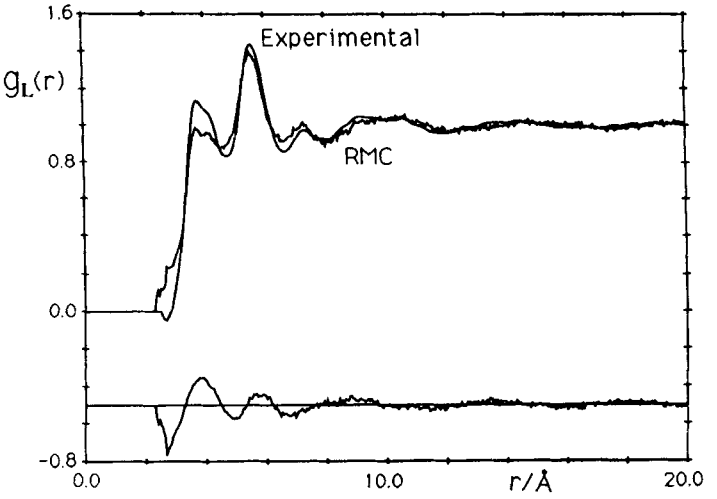


Figure 4 The experimental data and optimal RMC fit to the $g(r)$ function of liquid phosphorus at 20°C; the residual function is shown below the main curves.

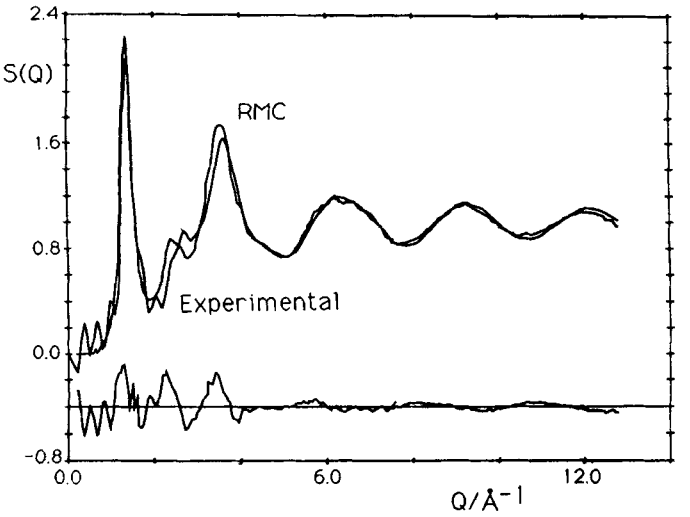


Figure 5 The $S_M(Q)$ functions are residual corresponding to the data given in Figure 4.

In view of the problems described above, a separate set of calculations in Q-space were made using the $S_M(Q)$ data and retaining a low cut-off value of 2.21 Å. A fit based on the Q-value data obviously emphasises different characteristics of the structure and appears to work well suggesting that the problems of interpretation in the $g(r)$ data arise from subtle effects involving close contact between adjacent molecules. However, the transformed function still showed similar discrepancies in r-space so that the two routines were effectively giving similar results. The preferred

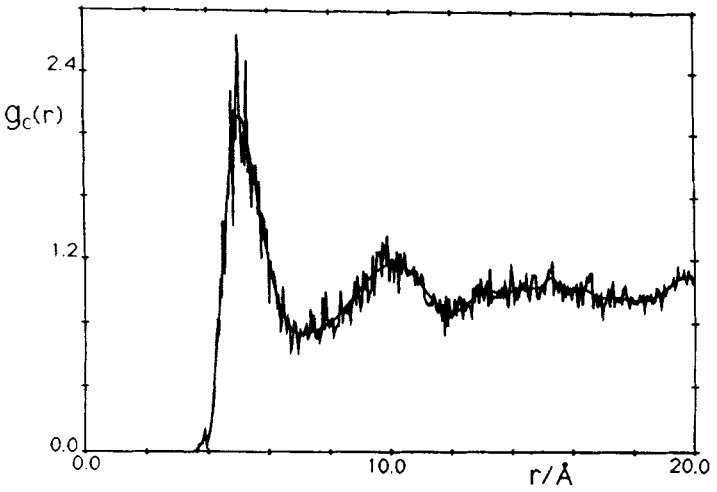
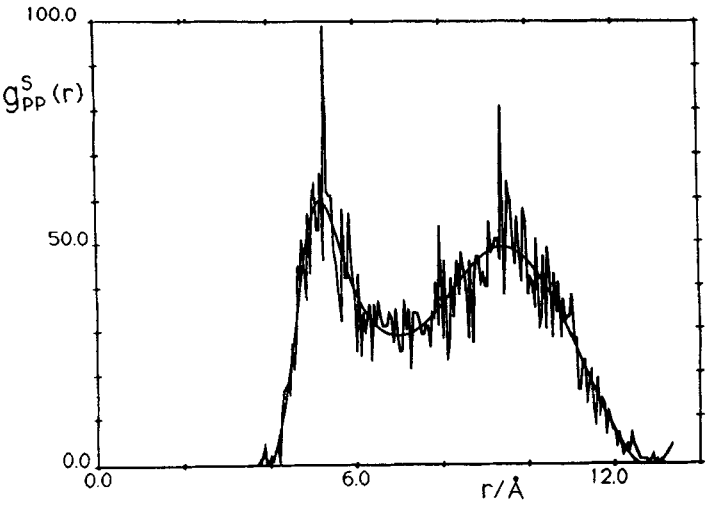


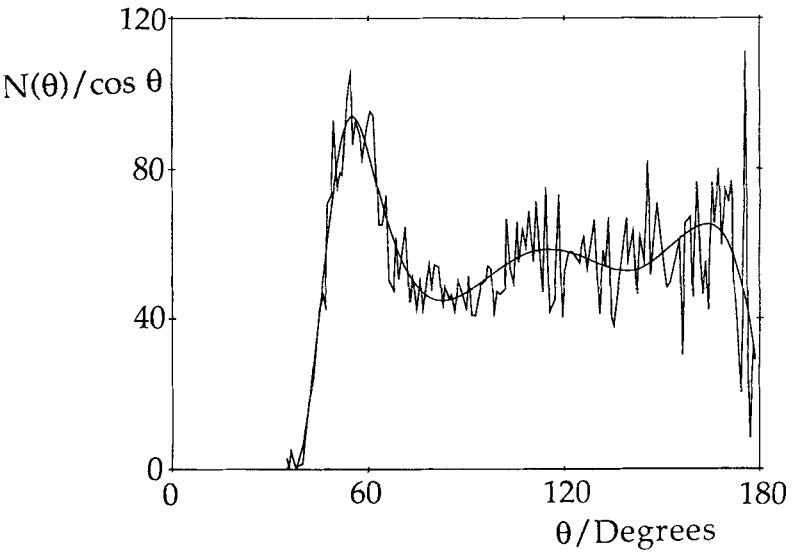
Figure 6 The centre-centre correlation function $g_c(r)$ for the RMC fit; the croses are from the array and the line is a smoothed curve through the points.

route was therefore to use the $g_L(r)$ data in the hope that the fit to the close-contact region (3–5 Å) would be improved. The final result using this procedure is shown in Figure 4; the corresponding curve for the structure factor is given in Figure 5 with the experimental data. The agreement in peak heights for $S_M(Q)$ is impressive and the small deviations in the oscillatory part ($> 6 Å^{-1}$) may be attributed to the use of a rigid molecule. The residual function is shown in the lower part of the figure and by transforming this curve over the 2–4 $Å^{-1}$ range it can be demonstrated that the main difficulties occur in the close contact position around 3 Å.

The P_4 molecule is an interesting structure in which the P-P bonds are constrained to be at 60° whereas other phosphorus compounds, such as amorphous red phosphorus [15] have well-defined bond angles in the region of 100°. The shape of the phosphorus molecule in which the P $\hat{P}$P angle is only 60° is therefore dependent on a complex electronic distribution in which distortions from spherical symmetry around each atom can be expected. The effect of these changes is thought to give enhanced electron density along the ridge of the tetrahedron edge. The choice of σ as a defining parameter is therefore crucial and should be chosen to be equivalent to the close contact of two isolated atoms defining the shortest distance between the atomic centres. However, the geometrical constraints imposed by the rest of the molecule may mean that only a few atoms in the assembly can occupy these positions. This appears to happen for phosphorus. If σ is taken to be too small, the possibility of inter-locked molecules with multiple contact points is possible within the model but may be forbidden in the real system due to the repulsive effects arising from the ridge of electrons. It is therefore apparent that the orientational correlations of adjacent molecules will be sensitive to the choice of σ and some compromise must be made to allow convergence to be achieved without moving into a physically unacceptable solution. Under these circumstances it is possible that the



(a)



(b)

Figure 7 Centre-centre correlations within the first neighbour shell a) spatial correlations b) angular correlations.

specification of a single value for σ is inappropriate and the interaction cannot be modelled on the simple basis of superimposing a spherical site-site hard core contour for each atom. More work will be required to investigate the possibility but the RMC technique cannot itself be used to probe matters further using the available data. Measurements of the X-ray structure factor using new synchrotron radiation methods [16] to give a detailed measurement of the electron distribution would be a major step forward and some preliminary measurements have already been made [17].

d) *Convergence criteria*

The previous discussion has revealed some unexpected features in the use of the RMC programme with molecular systems. The present analysis has been undertaken within the basic philosophy of introducing minimal constraints into the search routine on the assumption that the χ^2 minimisation will eventually find a satisfactory optimum solution within the error criteria of the original experimental data. It is now clear that a random search routine may be very inefficient in arriving at a highly specialised solution because many of the moves are rejected and the convergence becomes very slow. The fundamental unit defining the structure is the single molecule which requires six co-ordinates ($\mathbf{r}$, θ, ϕ, ω) rather than the three used for an atomic (ionic) assembly. The available phase space in which the search is conducted is therefore more extensive and the ideal solutions will probably require a close coupling of the angular and spatial features. It is, in fact, this property which makes these liquids of particular interest in the first place. The present analysis therefore provides only a preliminary investigation of the circumstances in which the RMC procedure can be used. It indicates that much more attention should be devoted to the choice of moves which can in some sense relate to the molecular symmetry and the local environment. It should therefore be possible to devise a more sophisticated algorithm to check the efficiency of the convergence route in the hope of improving the optimisation process. A possible gain in computing time will obviously be offset by additional complexity in the choice of an efficient search procedure. The situation is somewhat analogous to experience of Monte Carlo codes using energy criteria in which an apparent solution with a converged energy minimum can suddenly switch to a new mode with a lower value. This feature is often associated with the creation of a particular configuration which allows space for an unusual transition as for instance in conformational equilibrium of butane in the liquid phase. There is a rich field for extended studies of the liquid phosphorus data using a more sophisticated method of approach which would allow for rotational re-ordering of neighbouring molecules when a move was being assessed. These considerations have not been incorporated into the present study but will form a basis for future work.

4 GEOMETRICAL FEATURES IN THE MODEL REPRESENTATION

a) *Centre-centre correlations*

Although the model predictions are not in full agreement with the experimental data, it is still useful to consider the additional information which can be extracted

from the optimised configuration. The centre-centre correlation function $g_c(r)$ is shown in Figure 6; the crosses are the data extracted from the fit and the line is a spline function representation. It is remarkable that the complex pattern given by the $d_L(r)$ data results in such a simple curve resembling the behaviour of an atomic liquid. The co-ordination number for the first peak $\rho_L^c(r)$ is estimated to be 11.5 ± 0.5 molecules for integration over the range 4.0 to 7.0 Å in the centre-centre-correlation function. This value is very close to the value of 12 given by a close-packed arrangement of spheres (fcc or hcp) so it is interesting to examine the correlations between the molecules within this first neighbour shell by evaluating the centre-centre distances between pairs of molecules. This process is carried out for all molecules in the box to give the distribution shown in Figure 7a. The double-peaked distribution has peaks at distances of 5.22 and 8.94 Å with a ratio that is $\sqrt{3}$ within experimental error. It therefore seems that the molecules occupy a disordered close-packed arrangement which contains more structural organisation than would be achieved in a random close-packed assembly of spheres. The actual values are also interesting in relation to the molecular geometry. If the bond length is 2.21 Å and the hard core diameter of a phosphorus atom is 3.0 Å, the circumscribing sphere has a radius of 2.85 Å. If the molecules are free to rotate independently then the centres separation must be greater than 5.7 Å. On the basis of this figure more than 70% of the nearest-neighbour group of molecules are in an interlocked position. Furthermore, the closest distance that the molecules can approach is 3.4 Å corresponding to the limiting low-r point on the curve. An alternative interlocked

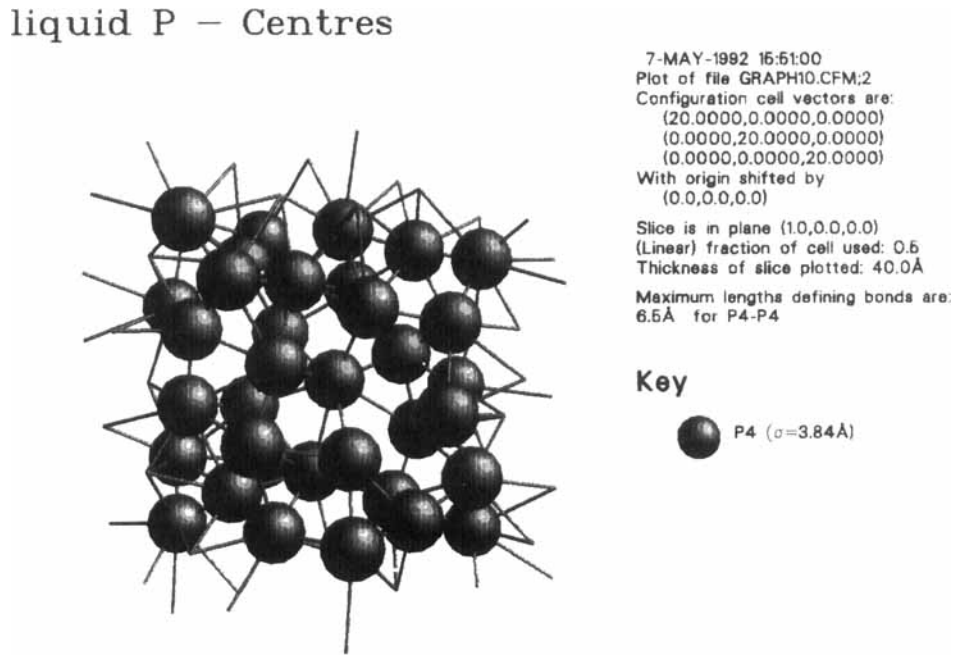


Figure 8 A computer graphics representation of molecular centres taken from a mid-slice of the computed array. (see colour plate).

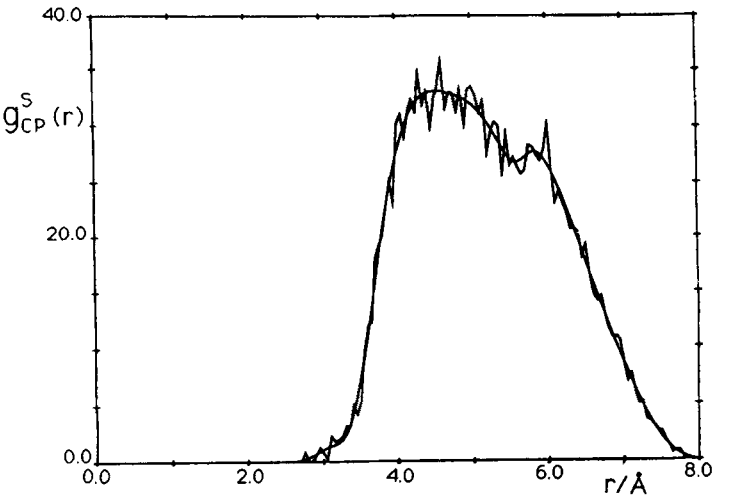
situation with anti-symmetric molecules which have three atoms of each molecule in contact leads to a slightly longer distance of 3.8 Å but this is a very specific configuration in which any rotational movement leads to a rapid increase in the centres separation and is not expected to contribute strongly to the general distribution.

If the co-ordination number of the nearest neighbour group in the shell is assumed to be four in analogy with the close-packed ordered arrangement it becomes apparent that the distribution around the peak is markedly asymmetric. This feature implies that the molecules within the shell are not on average uniformly distributed around the reference molecule. The variation is presumably a result of kinetic effects in which molecules have shorter times in contact due to collision or alternatively arise from the restricted space available from correlated orientations of adjacent molecules. This feature can also be investigated for the computer configuration by determining the angle subtended by all pairs of molecules within the shell at the central point of the defining sphere. A close-packed arrangement of touching spheres would give four at 60°, six at 120° and one at 180°. The evaluated distribution, averaged over all molecules in the box gives the distribution shown in Figure 7b. The smoothed function has a peak at 57° with a width (FWHH) of about $20(^{-1}_{+10})°$ followed by a broad distribution which peaks at 110° so these results support the overall conclusion. A computer graphics representation for a region in the centre of the box is given in Figure 8 which provides a visualisation of the arrangement; the lines are drawn to represent molecules with separation of ≤ 6.5 Å. The basic structure of the liquid, as represented by correlation of centres, appears to be remarkably simple in spite of the apparent complexity of the original data shown in Figure 3.

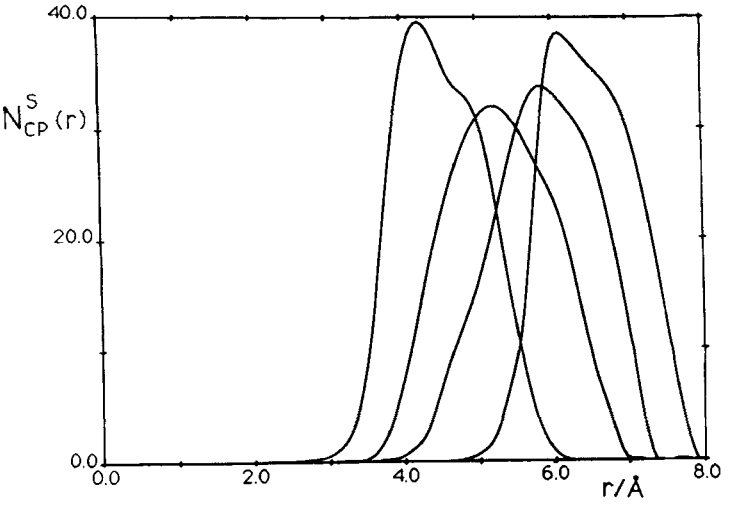
b) *Orientational Correlations*

The geometrical considerations affecting orientational correlations are thought to originate from the preferential positioning of an atom from an adjacent molecule in the 'hollow' created between the contours of three tetrahedrally co-ordinated atoms. This suggestion was first made by Powles [1] who evaluated the effects on the diffraction pattern for an alignment of molecule axes in the so-called 'Apollo-model'. It was later suggested [8] that the molecular axes need not remain parallel and it was more likely that rotation occurred due to interaction with other molecules until further contact points were established. The sequence is discussed in ref. 8, leading to a complex arrangement of fully interlocked atoms. This type of approach has been further developed in the work of Misawa [18] where specific orientated correlations are represented by an extended parameter set that can be fitted to the observed data. The key point in these methods is that the geometrical contours of the molecule are expected to result in particular configurations which dominate the structural arrangement and this may not actually occur in the real liquid. The configuration generated by the RMC routine enables these conjectures to be examined.

The first consideration is whether the closest inter-molecular distance does arise from the location of neighbouring atoms in the hollow. This is most conveniently studied by evaluating the distribution function from the centre of the reference molecule to the closest atom of all surrounding molecules. Since there are approximately twelve neighbours and only four hollows, there will be competition for this preferred location and it is possible that there is an effective blocking of this position due to inter-neighbour interactions. The total centre-atom pair correlation function



(a)



(b)

Figure 9 Centre-atom correlations within the first molecular shell a) composite data and smoothed fit b) resolved co-ordination numbers for 1st, 2nd, 3rd and 4th neighbour distances.

$g_{CP}(r)$ is shown in Figure 9a corresponding to distances from the centre of the reference molecule to all four atoms of the surrounding molecules in the first shell. This distribution may be broken down into components for the 1st, 2nd, 3rd and 4th nearest atoms and the smoothed curves corresponding to the co-ordination numbers are given in Figure 9b. There is no clear-cut evidence for location of an atom at a specified position within the hollow although the distribution of nearest atoms does have an asymmetric shape. In the case of phosphorus, the hollow is less well formed than in other tetrahedral molecules so the actual criterion 'in the hollow' is not precisely defined. It would be possible to look at the displacement of these atoms from a line representing the symmetry axis of the reference molecules but this detailed approach does not seem justified in the present case. The experimental data for the atom-atom correlation function show some discrepancies with the computer configuration (Section 4a) in this region, which may indicate that the local correlations in the real liquid are more ordered than given by the computer representation.

Several other features concerning the orientational characteristics of the first shell have also been evaluated without obtaining any indication of a dominant configuration. A computer graphics representation is given in Figure 10. This overall visualisation is very instructive because it reveals that there is less close-contact between molecular contours than might at first be expected. The constructed molecules in the picture have a hard core, σ, of 3 Å but as already noted in Figure 10, this

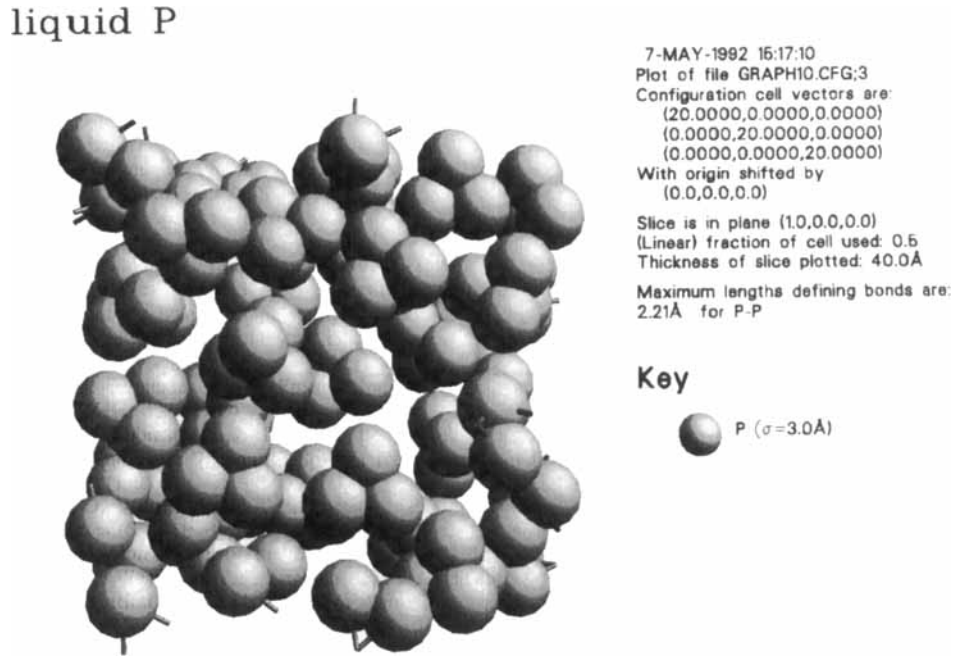


Figure 10 A computer graphics representation of the distribution of P_4 molecules in the computer array. (see colour plate).

is simply a limiting distance and most atoms are much further apart. As a result, the translational disorder appears to reduce the probability of a single dominant local configuration. However, this does not mean that orientational correlations are not present, but simply that they are more subtle than simple geometric considerations would suggest. The full analysis of orientational alignment for tetrahedral molecules is much more complicated than for the diatomic case due to the equivalence of different molecular axes arising from the four-fold symmetry. In the present circumstances of this preliminary study it is inappropriate to pursue this line of investigation until an improved fit is obtained for the critical region of 3–5 Å.

It is interesting to compare the results of the RMC method with those of a specified orientational approach. The fits given by Misawa [18] to the liquid phosphorus data show a different kind of discrepancy to those exhibited in Figure 2. It is notable that the main peaks are substantially under-estimated in this model and the residual function extends over a wider Q-range (4–8 $Å^{-1}$) where the present fit is satisfactory. Although no attempt has been made to make a quantitative comparison of χ^2 values it seems likely that the RMS model gives a better representation of the data. This is possibly not surprising if the assumption of an 'interlocked' geometry is subsequently found to be unjustified. There is obviously a need to investigate liquids composed of tetrahedral molecules with a larger anisotropy (ξ) value but the indications are that the data for phosphorus do not support the generalised 'Apollo configuration'.

5 SUMMARY

The present study has extended the use of the RMC routine to the investigation of molecular liquids. Several new aspects of setting the initial configuration and optimising the convergence procedures have been examined. The de-coupling of intra- and inter-molecular contributions is seen to overcome some problems but there remain further questions about the treatment of translational/rotational moves to achieve unbiased convergence in a situation where the phase space being accessed has more implicit parameters than in the conventional RMC calculations.

A satisfactory representation of the experimental data for liquid phosphorus has been obtained using an assembly of rigid P_4 molecular units. The configuration has been examined by the evaluation of various functions depending on the positions of molecular centres as well as the atom co-ordinates. It is found that the centre-centre correlation function has a much simpler structure than expected and is similar to that of an atomic liquid. The molecule co-ordination number is found to be nearly twelve and the structure corresponds to a disordered close-packed distribution.

The investigation of orientational features is less revealing although there is clear evidence that some form of orientational correlation exists. The disordered distribution of angles within the first neighbour shell and the relatively broad distributions of centre-atom correlations suggest that various models for local orientation of adjacent molecules based on the geometrical contours are probably too simplistic. However, it must be recognised that phosphorus does not have a high anisotropy and also that the fitted results are not sufficiently precise in this crucial region ($1 \leq r \leq 4$ Å). There is some evidence to suggest that the experimental data may

require enhanced correlations to improve the fit but it is not clear whether this could be achieved by running the program for a longer period. The current model does not appear to support the specific orientational correlations involving interlocking of neighbouring molecules.

The computational resources used in the present study enabled the data to be obtained within reasonable time and a typical run from initial configuration to optimised fit required 72 hrs of CPU time on a VAX 3100 system. The box size was found to be adequate for the present requirements as judged by the sharpness of the main diffraction peak (Figure 5). Increasing the size of the box would lead to a narrowing of the computed fit arising from lower truncation effects but the increase in computing time for relatively small improvements would be prohibitive in this case and would not be expected to yield any significant improvement in the final results. It seems much more likely that further improvements will require a more sophisticated constraint system based on the unusual shape of the electron distribution in the P_4 molecule but this additional complexity is not justified at the present stage of the data treatment.

6 CONCLUSION

This preliminary investigation has demonstrated that the RMC routine can be used to aid interpretation of data for molecular liquids provided the molecular conformation is incorporated into the search routine as a basic piece of information. The present work has been for a homonuclear system but there is no reason to doubt that a similar procedure could not be used for other molecules of similar size and symmetry. The possible use of larger molecules where there is a greater overlap of inter- and intra-molecular terms will require separate investigation and likewise for molecules which have a lower symmetry. It seems possible that more sophisticated algorithms may be necessary to improve the acceptance rate of each trial 'move' to overcome the rather slow convergence properties resulting from the increased dimensions of the phase-space search. The present work has opened up several possible lines of exploration and it is hoped to be able to expand the current experience in future publications.

Acknowledgements

We wish to thank Dr. Rob McGreevy for making the basic RMC programm available to us in the first instance and for several discussions on the specific application to the case of phosphorus. The computational facilities used in the project were provided by the University of Kent and by the SERC as part of the SERC PUNNET network for general studies undertaken by the Scattering Group at UKC into the properties of disordered condensed matter. ANN wishes to acknowledge the financial support of the SERC in the form of an SERC Advanced Fellowship. The work was undertaken as an undergraduate project within an Erasmus exchange programme set up with the University of Marburg and we wish to acknowledge financial support from the EC through the Erasmus scheme which has enabled one of us (MS) to undertake studies at UKC.

References

[1] P.A. Egelstaff, D.I. Page and J.G. Powles, "Orientational correlations in molecular liquids by neutron scattering: CCl_4 and $GeBr_4$. The structure of molecular liquids by neutron scattering", *Mol. Phys.*, **20**, 881 (1971). J.G. Powles, *Advances in Physics*, **22**, 1 (1973).

[2] J.C. Dore, "Diffraction studies of spatial correlations in disordered molecular assemblies", p. 45 in 'Molecular Liquids: New perspectives in Physics and Chemistry', NATO ASI, J. Teixeira-Dias (ed), Kluwer (pub) 1002.

[3] C. Andreani, J.C. Dore and F.P. Ricci, "Structural characterisation of diatomic fluids by diffraction studies", Rep. on Progress in Physics, **54**, 731 (1991).

[4] R.L. McGreevy and L. Pusztai, "Reverse Monte Carlo Simulation: a new technique for the determination of disordered structures", *Mol. Sim.*, **1**, 359 (1988).

[5] M.A. Howe, "Orientational correlations in the liquid halogens", *Mol. Phys.*, **69**, 161, (1982).

[6] V.F. Sears,"Thermal neutron scattering lengths and cross-sections for condensed matter research" Chalk River Report AECL-8490.

[7] J.H. Clarke *et al.*, "Neutron diffraction studies of tetrachloride liquids", p. 277 in Faraday Discussion No. 66 on "Structure and Motion in Molecular Liquids", *Chem. Soc.*, (pub), 1979.

[8] J.C. Dore, "Neutron diffraction studies of simple molecular liquids", p. 543 in Highlights of Simple Liquids, F. Barocchi *et al.* (eds) Nuo Cim. **12D**, (1990).

[9] J.H. Clarke *et al.*, "Neutron diffraction studies of Phosphorous 1. Reactor and pulsed neutron measurement at 50-degrees-C", *Mol. Phys.*, **42**, 861 (1981).

[10] J.R. Granada and J.C. Dore, "Neutron diffraction studies of Phosphorous 2. The super-cooled liquid and plastic crystal phases", *Mol. Phys.*, **46**, 757 (1982).

[11] The RMC Single programm was provided by Dr. Robert McGreevy.

[13] L. O'Mard private communication; results obtained during a simulation of amorphous ice.

[14] F. Wooton, K. Winer and D. Weaire, "Computer generation of structural models of amorphous Si and Ge", *Phys. Rev. Lett.*, **54**, 1392 (1985).

[15] S.R. Elliott, J.C. Dore and E. Marseglia, "The structure of Amorphous Phosphorous", *J. Phys. Colloq.*, C8, **46**, 349 (1985). H. Farman, J.C. Dore and S.R. Elliott, in preparation.

[16] G. Bushnell-Wye *et al.*, "The use of Synchrotron X-rays to exploit the Warren-Mavel fluorescence detection technique in studies of disordered-systems", *Rev. Sci. Inst.*, **63**, 1154 (192).

[17] J.C. Dore, K. Hofer and G. Bushnell-Wye, unpublished data.

[18] K. Misawa, "Structure factor of X4 Tetrahedral molecular liquids - competition between intra-molecular and intermolecular atomic spacings", *J. Chem. Phys.*, **93**, 6774 (1990).

[19] M.A. Howe and R.L. McGreevy, "RMC: Does it work and if so, when?", p. F305 in 'Recent Developments in the Physics of Fluids', W.S. Howells & A.K. Soper (eds), Adam Hilger (pub. 1992).