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REVIEW

Determination of Three Body Correlations in Simple Liquids by RMC Modelling of Diffraction Data. I. Theoretical Tests

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In theory all the information regarding the three dimensional structure of a liquid is contained in the pair distribution function $g(r)$ or, equivalently, the structure factor $A(Q)$, for a system with purely pairwise additive potentials. RMC is a method for modelling the structures of disordered systems based on the experimentally measured structure factor(s). We have performed some theoretical tests of the method, using input data calculated from simulations for various systems, which show that RMC does indeed work successfully if the potentials are pairwise additive. In cases where they are not then the imposition of constraints, e.g. modelling molecular systems with molecules rather than atoms, can enable the three dimensional structure to be determined. When the potentials are very complex, which usually makes the problem unsuitable for MC or MD simulations, RMC with constraints is still a valuable way of distinguishing between various structural possibilities.

KEY WORDS: Reverse Monte Carlo method, pairwise additive potentials.

1 INTRODUCTION

One of the main aims in the study of the liquid state is to determine the structures of liquids and to understand how they depend on the interatomic forces. By this we do not mean that we wish to know the instantaneous position of every atom but rather, since liquids do not generally have long range order, to parameterise the short range order in terms of various correlation functions. However a liquid is macroscopically isotropic, so diffraction data only give information on the pair correlation function, $g(r)$. There are various theoretical methods for using $g(r)$ to obtain information on three body correlations but these involve approximations which are often inadequate. Monte Carlo (MC) or molecular dynamics (MD) computer simulation methods may be used to investigate all aspects of structure and dynamics but it is rare that the structure produced agrees with the diffraction data within its errors, and it is difficult to know how to alter interatomic potentials to improve the level of agreement. Since a hard sphere model is often a good first approximation to the structure of a liquid it is important that structural models are in *good* agreement with the data if deviations from hard sphere behaviour are to be understood in any detail.

The recently developed Reverse Monte Carlo¹ (RMC) method of structural modelling overcomes many of these problems. RMC does not necessarily produce

the 'correct' answer, but then neither does any other technique; indeed one of the major contributions of the method has been to stress this point. However the information that may be obtained from a model that agrees quantitatively with diffraction data, even though for instance it may contain features that would be energetically unfavourable, may be more useful in understanding the *type* of structure than a model which is energy minimised, e.g. one produced by an MC or MD simulation, but agrees only qualitatively with the data. This is even more true when investigating small differences between structures.

In this paper we describe the RMC method and report some theoretical tests of its validity. In a later paper we will review the information that may be obtained on three body correlations, with particular emphasis on elemental liquids.

2 RMC METHOD

The aim of RMC is to produce three dimensional structural models of a system that are consistent with the available diffraction data, within the errors of that data. To do this we use a modification of the standard Metropolis Monte Carlo (MMC) method² where, instead of minimising the system energy we minimise the difference between the calculated and experimental spectra. Here we will only describe the basic method as a fuller description is available elsewhere³.

The algorithm for RMC is as follows.

1) Start with an initial configuration, i.e. a set of coordinates in a box representing atomic positions, with periodic boundary conditions. Calculate (C) the radial distribution function

$$g_0^C(r) = \frac{n_0^C(r)}{4\pi r^2 dr \rho}$$

where ρ is the atom number density and $n^C(r)$ is the number of atoms at a distance between r and $r + dr$ from a central atom, averaged over all atoms as centres. Transform to the structure factor

$$A_0^C(Q) - 1 = \rho \int_0^x 4\pi r^2 (g_0^C(r) - 1) \frac{\sin Qr}{Qr} dr$$

Calculate

$$\chi_0^2 = \sum_{i=1}^m [A_0^C(Q_i) - A^E(Q_i)]^2 / \sigma^2(Q_i)$$

where $A^E(Q_i)$ is the experimentally measured structure factor and σ is a measure of the experimental error.

2) Move one atom at random. Calculate the new $g_n^C(r)$ and $A_n^C(Q)$ and

$$\chi_n^2 = \sum_{i=1}^m [A_n^C(Q_i) - A^E(Q_i)]^2 / \sigma^2(Q_i)$$

3) If $\chi_n^2 < \chi_0^2$ the move is accepted. If $\chi_n^2 > \chi_0^2$ the move is accepted with probability $\exp(-(\chi_n^2 - \chi_0^2)/2)$. Otherwise it is rejected.

4) Repeat from step 2.

It can immediately be seen that χ^2 in RMC is equivalent to U/kT in MMC. χ^2 will initially decrease until it reaches an equilibrium value about which it will oscillate. The resulting configuration should be a three dimensional structure that is consistent with the experimental structure factor within the experimental error. Further independent configurations may then be collected by continuing to run the simulation under the same conditions as for MMC.

RMC is easily adapted so that different functions are used. The basic method outlined above is for modelling the structure factor of a one component system. Instead of modelling $A^E(Q_i)$ we could alternatively model $g^E(r_j)$ (the two are *not* identical), and χ^2 becomes

$$\chi^2 = \sum_{i=1}^{m_r} [g^C(r_j) - g^E(r_j)]^2 / \sigma^2(r_j)$$

This is obviously computationally faster since a transform is not required during each iteration. For a multicomponent system where different total structure factors (indicated by index k)

$$F_k^E(Q_i) = \sum_{\alpha, \beta} c_\alpha c_\beta \bar{b}_\alpha \bar{b}_\beta (A_{\alpha\beta}(Q_i) - 1)$$

have been measured, for instance using neutron diffraction with isotopic substitution, we then have

$$\chi^2 = \sum_k \sum_{i=1}^m [F_k^C(Q_i) - F_k^E(Q_i)]^2 / \sigma_k^2(Q_i)$$

c_α is the concentration and \bar{b}_α the coherent scattering length of component α ; $A_{\alpha\beta}(Q)$ are the partial structure factors. In the same way results from neutron and X-ray diffraction measurements may be combined⁴. In fact any data set may be used if a spectrum S^C can be calculated from the structure and compared to the experimental S^E . This has been done for EXAFS⁵ and may be possible in some cases for NMR.

The above algorithm is normally used in conjunction with a set of constraints. The purpose of these constraints can be to compensate for some errors in the experimental data; the imposition of a minimum 'hard sphere' radius for atoms is useful in this respect. Constraints can also be used to 'forbid' or 'discourage' certain

structural features that would be consistent with the data but are known to be unlikely from other information, e.g. chemical bonding ideas, or to deliberately investigate the range of possible structures that are consistent with the data.

3 UNIQUENESS

The three dimensional structure produced by RMC is *not* unique, it is simply a model that is consistent with the data and any additional constraints. Other methods that produce structures which are equally consistent with the data are equally valid and there is no way of determining which is 'correct' *in the absence of any additional information*. One possible disadvantage of RMC is that it tends to produce the most disordered structure that is consistent with the data and constraints, i.e. the configurational entropy is maximised. However this is sometimes counteracted by the ability to include additional constraints.

In the special case of a system for which the interatomic potential is *purely* pairwise additive there is a theoretical justification⁶ for the determination of the three dimensional structure from a one dimensional $g(r)$ or $A(Q)$. Given that the potential uniquely determines the structure

$$\phi(r) \rightarrow g^{(2)}(r_1, r_2), g^{(3)}(r_1, r_2, r_3) g^{(4)}(\dots)$$

where $g^{(2)}(r_1, r_2) = g(r)$ and $g^{(n)}(\dots)$ are the n -body correlation functions, then for a pairwise additive potential there is a *functional* relationship between $\phi(r)$ and $g(r)$ such that

$$g^{(2)}(r_1, r_2) \rightarrow \phi(r)$$

i.e. $g^{(2)}$ uniquely determines ϕ . This is not to say that we can write down the relationship, but merely that one exists. If $g(r)$ determines $\phi(r)$ and $\phi(r)$ determines the structure, then $g(r)$ determines the structure i.e.

$$g(r) \rightarrow g^{(3)}(r_1, r_2, r_3), g^{(4)}(\dots)$$

While the potentials in real systems are never purely pairwise additive (though such potentials are used in the majority of MMC and MD simulations), and an experimentally determined $A(Q)$ is neither complete or absolutely accurate, the above result does indicate that a precisely measured $g(r)$ or $A(Q)$ does contain a *great deal* of information about the three dimensional structure. RMC is a possible way of attempting to extract this information.

4 TESTS OF RMC

It is difficult to obtain three-particle correlation functions directly from experimental results and thus difficult to know whether those obtained by RMC are correct.

However this is not true of computer simulation results; any correlation functions obtainable by RMC can also be calculated for MD or MMC simulations. This means some general tests of RMC can be performed by using as input data the structure factors, or radial distribution functions obtained from a simulation. When a satisfactory fit to this input data has been obtained various correlation functions can be calculated from the RMC configurations and compared with those obtained from the original simulation.

4.1 Hard sphere liquid

The first test was on a hard sphere liquid. Starting from a configuration of 4096 atoms placed at random positions in a cubic box of 68.52 Å a hard sphere MMC simulation was performed using a hard sphere diameter of 3.5 Å (packing fraction 0.29). After equilibration the simulation was continued, saving one configuration after every 4096 accepted moves, until a total of 20 configurations had been saved. For each of these the radial distribution function $g(r)$, the structure factor $A(Q)$, the 'bond-angle' distribution $b(\theta)$, and the coordination number distribution $P(N)$ were calculated and then averaged. $P(N)$ is defined as the probability of an atom having exactly N neighbours within a certain distance, and $b(\theta)$ is the probability that two such neighbours form with the central atom an angle of θ . The results are shown in Figure 1.

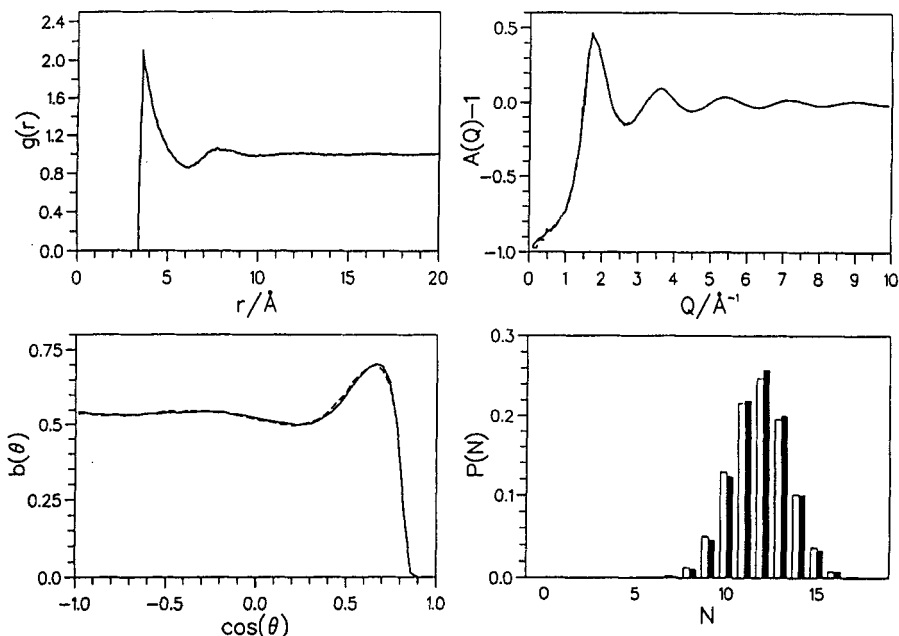


Figure 1 The radial distribution function (top left), structure factor (top right), 'bond angle' distribution (bottom left) and coordination number distribution (bottom right) for the MMC hard sphere simulation (solid line and filled bars) and for the RMC calculation fitting to the MMC $S(Q)$ (broken line and open bars).

Two separate RMC calculations were then performed, both starting from a random configuration of 4096 atoms as in the MMC simulation, one fitting to the MMC $g(r)$ and one to the MMC $A(Q)$. In the former case, as $g(r)$ is clearly zero at $r \leq 3.5 \text{ \AA}$ (the hard-sphere diameter of the simulation) this distance was used as the closest distance of approach; in the latter a smaller distance was chosen indicating that the hard sphere constraint is unnecessary if good (in this case ideal) data are available. Using a small value of σ (0.01) so as to get an excellent fit with the simulation data, both RMC calculations were run until convergence and thereafter, saving one configuration in 4096, until 20 configurations had been saved from each.

The functions $g(r)$, $A(Q)$, $b(\theta)$, and $P(N)$ were calculated. In Figure 1 they are compared with those from the original simulation. The differences in three-body correlations are very small and in fact are much smaller than the variation of these correlations between the original 20 MMC configurations.

In the absence of experimental data RMC is much like a hard sphere simulation so it might be argued that this result is to be expected especially as we have used the hard sphere diameter, in the form of the cut-off, as a constraint in our calculation. However it is the requirement of fitting to the data that is the real constraint: to get a good fit to the data the $g(r)$ must be zero, or very close to zero, in this region. The cut-off simply makes sure that it is exactly zero and that there are no particles unreasonably close to one another (a handful of such distances might still produce a fit within the known errors).

4.2 Lennard-Jones liquid

The second test was on a Lennard-Jones liquid. An MMC simulation was performed, starting from a random configuration of 4000 atoms, using a density of 0.0176 \AA^{-3} and a Lennard-Jones potential with parameters $\sigma = 3.36 \text{ \AA}$, $\epsilon/k_B = 123.2 \text{ K}$ -values that have been used for simulations of liquid argon⁷. 20 configurations were saved and the average calculated structure factor was used as input to RMC. The results obtained are shown in Figure 2 and can be seen to be in good agreement with one another as was the case for the hard sphere liquid.

4.3 Liquid of Hard Dumbbells

On the basis of the theoretical justification for RMC already discussed these results would have been expected because both the hard sphere and Lennard-Jones systems involve only two-body interactions. We now turn our attention to a system that contains, in terms of atoms, many-body interactions. The example chosen is that of a liquid of diatomic molecules.

For the MMC simulation the molecule has been represented as a hard dumbbell, i.e. two intersecting hard spheres. The hard sphere diameter was 2.8 \AA , the bond length 1.1 \AA , and the atomic number density 0.037 \AA^{-3} (values roughly appropriate to liquid nitrogen). Starting with a configuration of 2000 molecules placed at random positions with random orientations an MMC simulation was performed, saving 20 configurations after reaching equilibrium. From these the structure factor was

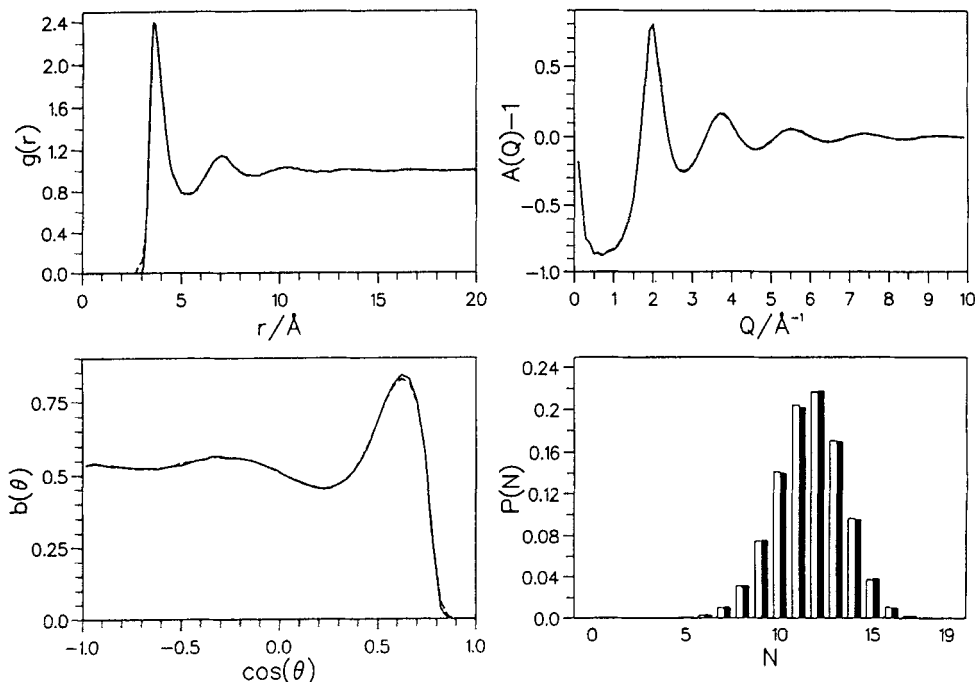


Figure 2. The radial distribution function (top left), structure factor (top right), 'bond angle' distribution (bottom left) and coordination number distribution (bottom right) for the MMC Lennard-Jones simulation (solid line and filled bars) and for the RMC calculation fitting to the MMC $S(Q)$ (broken line and open bars).

calculated and used as the experimental input in an RMC calculation with a configuration of 4000 atoms. The result at convergence, from just one configuration this time, is shown in Figure 3. Despite excellent agreement with $g(r)$ and $S(Q)$, $P(N)$ not correct: only 44% of the atoms have the one fold coordination of diatomic molecules even though the average coordination number is 0.98, very close to 1.0.

It can be seen, then, that when many body interactions are present RMC may fail to reproduce the structure correctly. However the structure produced is consistent with the experimental data so we must conclude that when many-body interactions are present the structure factor, even for an elemental system, does not contain sufficient information to enable the determination of all features of the structure. To produce a more accurate structure using RMC further constraints must be introduced based on other experimental data or on theoretical considerations. In cases such as this example, where we know the system is molecular, that is relatively easy. One way is to use molecular units, rather than atoms, as the particles that can be moved, and now also rotated, in the RMC calculation. This method has been described in detail elsewhere⁸.

Such an RMC calculation has been performed using a configuration of 2000 diatomic molecules, assuming that the bond length of the molecule is known. After

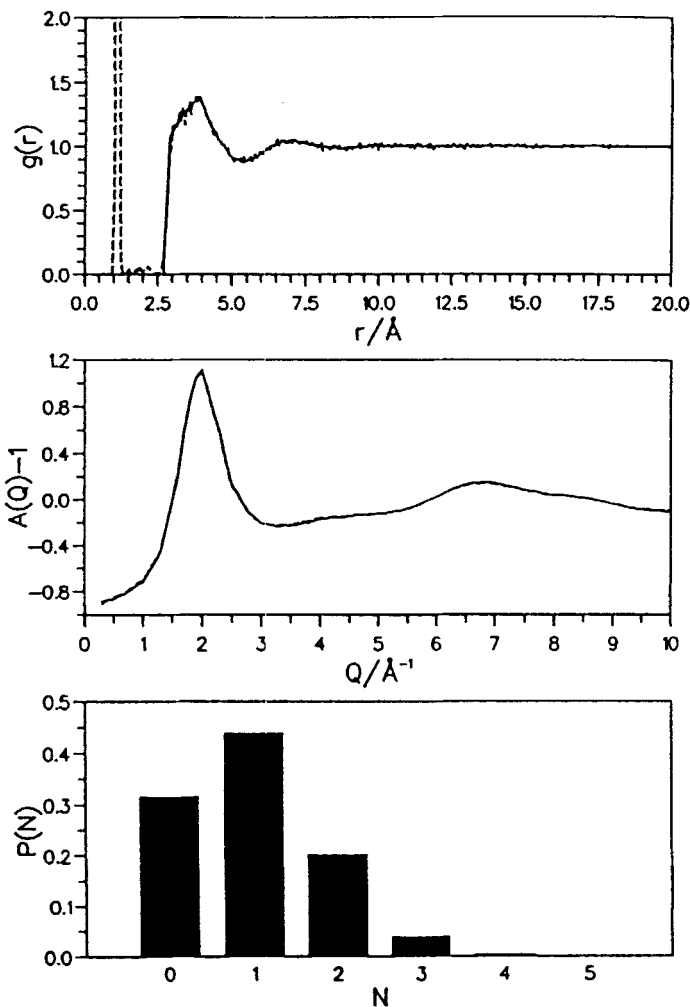


Figure 3. The radial distribution function (top), the intermolecular part of the structure factor (centre), for the MMC hard dumbbell simulation (solid line) and for the RMC calculation (broken line) and (bottom) the coordination number distribution for the RMC calculation.

convergence the radial distribution function and structure factor for the molecular centres have been calculated and are shown in Figure 3 in comparison with those obtained from MMC. For diatomic molecules the equivalent to $g(r)$ for atoms is $g(r, \theta, \phi)$ where θ and ϕ describe the relative orientation of the molecules. This function can be expanded as a series of spherical harmonic functions and their coefficients. The first coefficient is the molecular centres $g(r)$ (Figure 4); some of the higher ones are shown in Figure 5. Although the statistics of these are relatively poor they are in good agreement with those obtained from MMC.

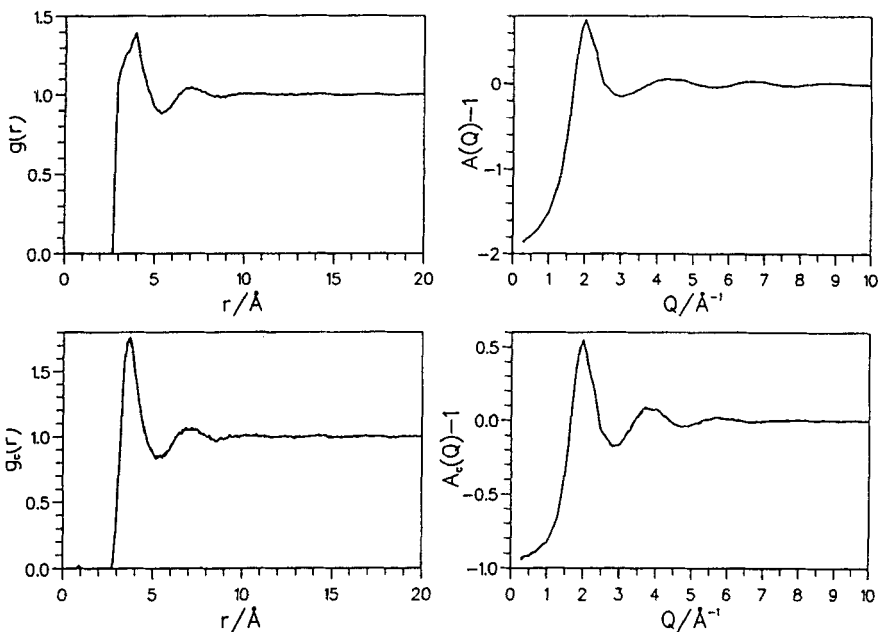


Figure 4. Comparison of RMC results (broken line), using a molecular unit in the calculation, with those for the MC simulation (solid line) of a liquid hard dumbbell molecules. Shown are the radial distribution functions (right) and structure factors (left) for the atoms (top) and the molecular centres (bottom).

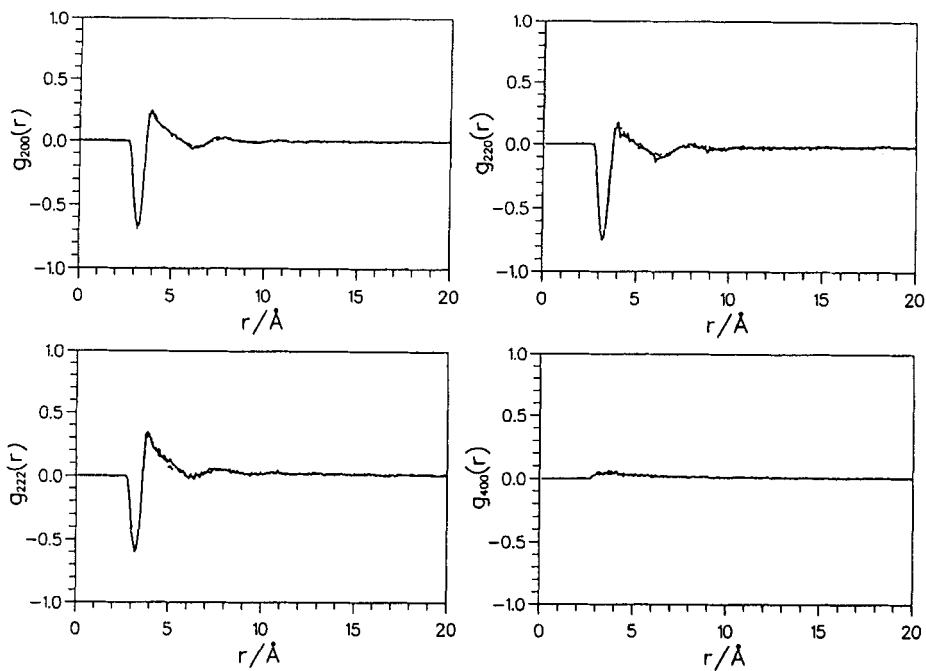


Figure 5. Comparison of spherical harmonic coefficients of $g(r, \theta, \phi)$ for RMC (broken line), using a molecular unit in the calculation, and MMC (solid line) for a liquid of hard dumbbell molecules.

4.4 Diatomic Liquid with Non-central Forces

Our final test used the results of Rodger *et al.*⁹. They performed a molecular dynamics simulation of liquid chlorine using an anisotropic atom-atom effective pair potential which includes dipolar and quadrupolar terms. We fitted to their calculated $g(r)$. Because of the small size of their configuration (128 molecules in a truncated octahedral simulation box) their $g(r)$ is truncated before the oscillations die out. We used a larger number of molecules: 500 in a cubic box. The molecular centres correlation function and three of the higher order spherical harmonic coefficients are shown in Figure 6. The agreement, although not perfect, is again seen to be fairly good. The differences may be due to the small size of the original MD simulation.

5 DISCUSSION

The above results have shown that RMC is a suitable method for obtaining three body correlations for a monatomic liquid which can be described by a pairwise additive potential. For two component liquids¹⁰ it has been shown that three body correlations can be correctly determined from three total structure factors; three

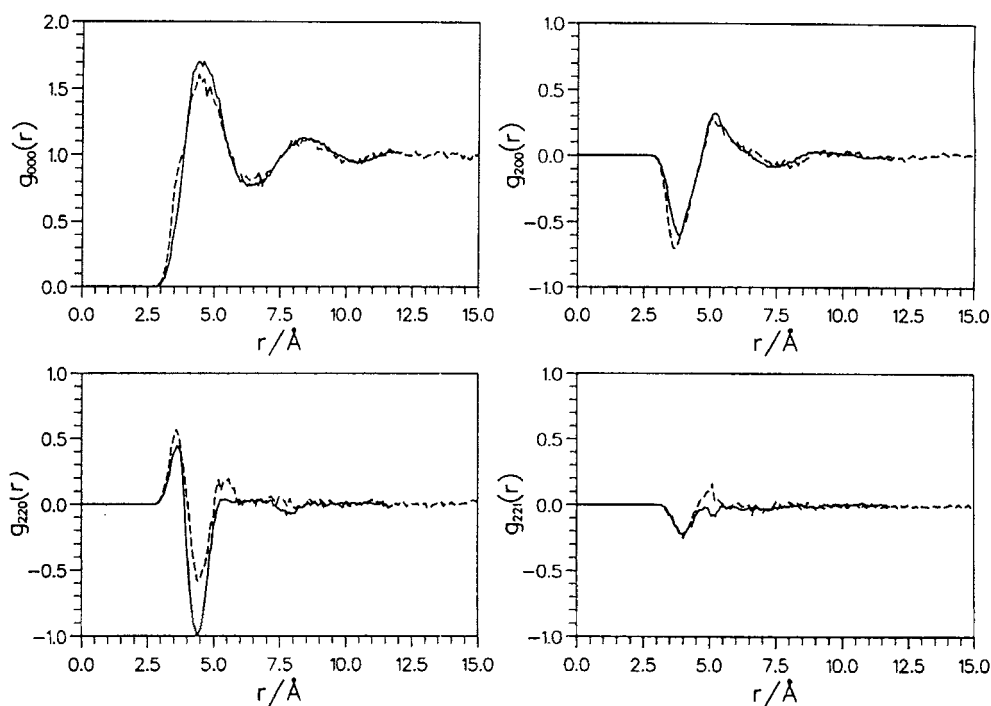


Figure 6. Comparison of spherical harmonic coefficients of $g(r, \theta, \phi)$ from RMC (broken line) and MMC (solid line) for liquid chlorine.

are of course required to determine the three partial radial distribution functions. In some cases a good approximation to the correct partial structure factors can in fact be obtained from only one total structure factor.

Where purely pairwise additive potentials are not applicable then RMC may produce the correct result, but will not necessarily do so. If many body terms are small and an effective pairwise potential could be used then RMC will work, since it does not 'know' that potential is only effective, but when many body terms are significant RMC will produce a structure which is generally less ordered than the 'real' one. However the application of constraints on the coordination of atoms is particularly powerful in this context, since these may be thought of as the very simplest form of many body potential. For instance diatomic molecules can be created from atoms by requiring each atom to be singly coordinated within a pair of specified distances; flexible S_8 ring molecules can be created from atoms by starting with a structure that contains rigid rings but only requiring that each atom retains its original two-fold coordination.

Where suitable constraints may not be known it is possible to use them to investigate the *range* of structures that are consistent with the data available; these structures may then be assessed in the light of other information that is not readily quantifiable in the form of constraints¹¹. It should however be noted that the application of constraints in cases where they are not appropriate, e.g. a Lennard Jones liquid, can lead to a structure that still fits the 'experimental' structure factor extremely well but has incorrect three body correlations. This is an interesting point since it suggests that the normal RMC algorithm, without constraints, achieves a suitable sampling of the parameter space (parameters being the atomic coordinates) to enable a 'correct' inversion from $g(r)$ to the three dimensional structure. The application of constraints restricts the parameter space that can be sampled, so the 'correct' answer will only be obtained if it is within the sampled region. Constraints should therefore be used either when they are known to be correct, or in the sense of empirical parameters.

The above discussion has assumed that the available data are 'perfect'. However real data will have a finite range, a finite resolution and will contain both statistical and systematic errors. Obviously the higher the quality of the data then the better will be the RMC results. The accuracy achievable in present day diffraction experiments is such that the errors in three body correlations determined by RMC modelling may be significantly smaller than the natural fluctuations in the liquid, i.e. they are not significant. However if information on longer range correlations is required then the data may be insufficient. For example in Figure 7 we show two structure factors for liquid rubidium close to the melting point, obtained by fitting to experimental data¹². They are almost identical, but one corresponds to a liquid structure while the other corresponds to a highly disordered crystal structure. The short range order in the two is identical, but the latter has long range order. However this is sufficiently weak that Bragg peaks would only be visible at much higher resolution. This example illustrates that the information that may be obtained using RMC is, in the end, dependent upon the quality of the original data, just as the results of MMC or MD simulations depend on the potential.

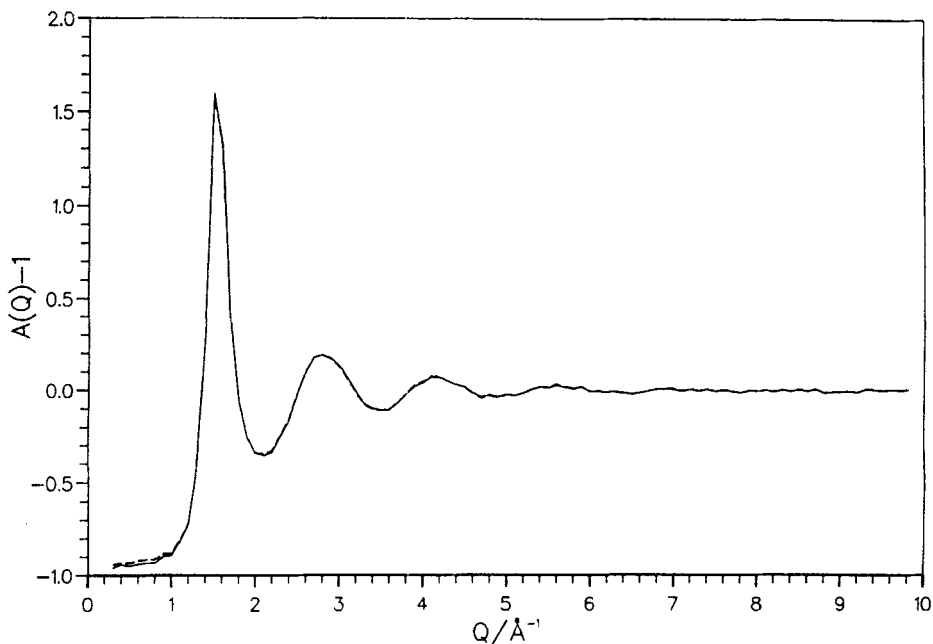


Figure 7. Two structure factors obtained from RMC for molten rubidium. The solid line corresponds to a truly liquid like structure but it can be shown that the broken line corresponds to a highly disordered crystalline structure.

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