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Understanding liquid structures

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Abstract. It has often been said that 'the structure factors of all liquids (and glasses) look the same'. Those working in the field know that there is a certain truth to this, as many of the basic features are determined by hard sphere packing. However they also know that there are differences, sometimes subtle, which depend on details of the bonding and local structural arrangement. The initial requirement for understanding these details is an accurate experimental measurement. This is not a trivial task, but even when it has been done the interpretation of the structure factor(s) or radial distribution function(s) often only uses gross features such as peak positions and coordination numbers. This approach makes poor use of the data obtained and it can be misleading. RMC is a method of structural modelling which is based on the experimental data and so makes full use of all the available information. The ability to create a three-dimensional model leads to a greater understanding of the relationship between structure and structure factor, independent of their relationship to the interatomic potential.

1. Introduction

The structure factor $S(Q)$ and radial distribution function $g(r)$ for molten lithium are shown in figure 1. Alkali metals may be regarded as archetypal 'simple liquids'. Apart from a scaling factor their structure factors, in common with those of Ar, Kr, Xe and some transition metals (e.g. Al, Cu), are almost identical; they have the form of a damped oscillatory function of dominantly a single period. The $g(r)$ s are correspondingly similar. Measurement of such a structure factor to a high degree of accuracy (e.g. systematic and statistical errors less than 1%) is difficult even in these days of high intensity x-ray and neutron sources. Given this difficulty it is somewhat surprising that, when such results are obtained, very little use is made of them. A conventional approach may be summarized as follows.

- (a) Transform $S(Q)$ to $g(r)$ (often introducing errors due to truncation).
- (b) Note the position of the first and (sometimes) second peak in $g(r)$.
- (c) Calculate the coordination number, i.e. the area under the first peak (using one of at least four different prescriptions, each of which produces a slightly different result).

Thus the wealth of information inherent in the structure factor is condensed into two or three numbers which represent some 'average' properties. From these averages one then attempts to visualize the local structure, for instance by comparing the values to those for the corresponding crystal structure. In the case of Li the coordination number is ≈ 13 and the first peak in $g(r)$ encompasses both first- and

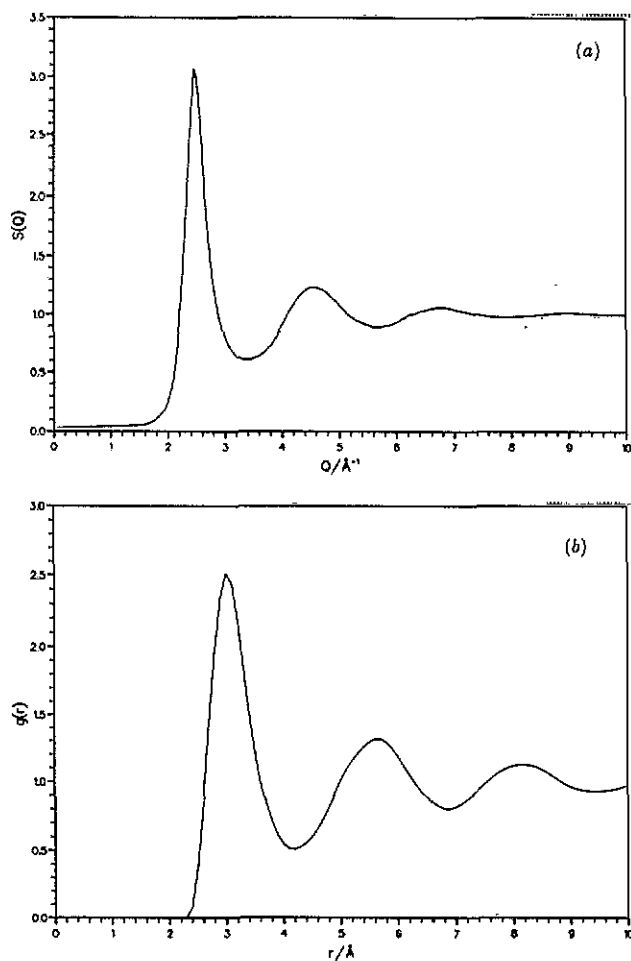


Figure 1. (a) Structure factor $S(Q)$ and (b) radial distribution function $g(r)$ for molten lithium.

second-neighbour distances in the crystal. Given that the crystal structure is BCC, with eight nearest and six second-nearest neighbours, then one immediately considers that the average local environment in the liquid is roughly the same as that in the crystal.

While this *may* be correct the structure, on the basis of the information used, could for instance be icosahedral, hexagonal close-packed, or a mixture of all three. The problem is that liquids do not have a well defined local structure and the coordination number is only an average. $g(r)$ does not decrease to zero after the first peak, so coordination shells are arbitrarily defined. Even if one takes the first minimum in $g(r)$ to define a first coordination shell limit all Li atoms will not have 13 neighbours within this distance; the distribution will probably range from 6 to 20. In addition a liquid can have up to 30% excess free volume in comparison with the crystal, which may be distributed in the form of 'vacancies', so the average coordination number may be *lower* than that expected for a certain crystalline symmetry.

The 'average' analysis also disregards information that may be obvious from consideration of $S(Q)$, but is not readily apparent in $g(r)$. In figure 2 we show $g(r)$

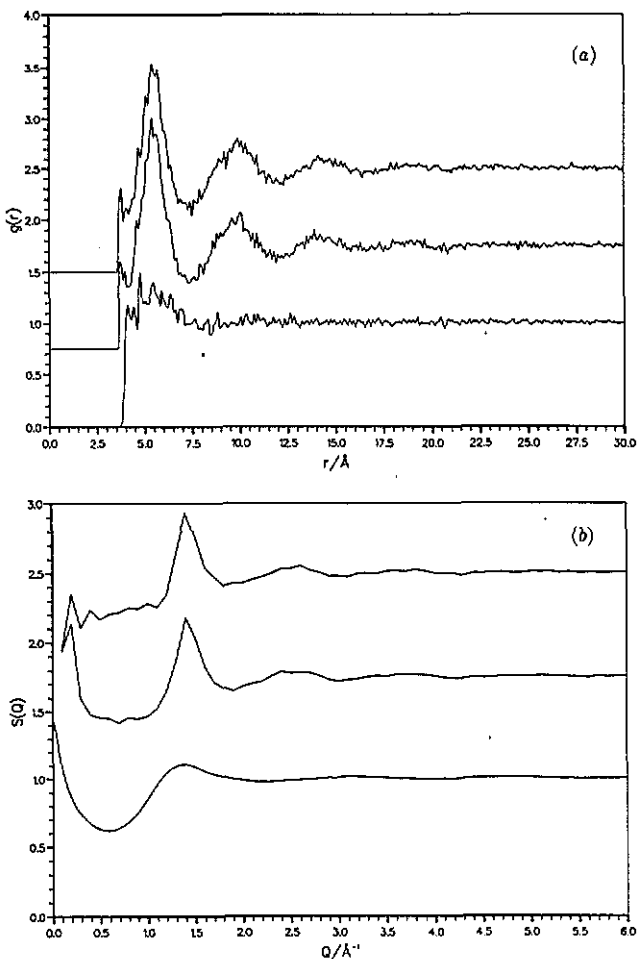


Figure 2. (a) Three radial distribution functions with the same first peak position and average coordination number and (b) the corresponding structure factors. Bottom - $g(r)$ and $S(Q)$ for expanded (low density) Cs. Top - $g(r)$ and $S(Q)$ obtained from a model of high density Cs with atoms removed at random to give the same density as expanded Cs. Centre - as top, but with pairs of neighbouring atoms removed at random.

and $S(Q)$ for expanded (high temperature) Cs (Winter *et al* 1987,1988). The first minimum in $g(r)$ is poorly defined, but in fact occurs at a very similar position to that in low temperature Cs, as does the first peak. The coordination number is ≈ 6.5 . We also show $g(r)$ and $S(Q)$ calculated from two models of low temperature Cs. However, in the first atoms have been removed at random to decrease the average coordination number from ≈ 13 to ≈ 6.5 , and in the second neighbouring pairs of atoms have been removed. We then have three $g(r)$ s all of which have the same 'average' properties, but the structure factors are significantly different. When single atoms have been removed the free volume is uniformly distributed so there is no rise at small Q , but when pairs of atoms are removed the correspondingly larger local density deficit gives some low Q rise. In the real system the $Q \rightarrow 0$ value is very high, indicating large variations in the local density and hence the local structure.

In cases where the first minimum in $g(r)$ is small or zero (though care must

be taken to ensure that this is not due to truncation errors in the transform from $S(Q)$, that is molecular or 'quasi-molecular' liquids, the analysis discussed above is simply transferred to the second and third peaks. For highly structured, non-spherical molecules the inter-molecular part of $g(r)$ or $S(Q)$ is often treated as if it were a simple liquid, even though it is understood that orientational correlations between molecules are probably significant. An extreme case of this is the treatment of network glasses as an arrangement of randomly packed units; e.g. SiO_4 units in vitreous SiO_2 , where each Si is fourfold coordinated to O. However, all oxygens are 'shared' between two units and the packing is far from random; it is the *connectivity* of the network produced that is of greatest importance.

While the analysis described above is perhaps exaggerated the general approach is not uncommon. However, it may be misleading, as has been indicated. In order to understand the liquid structure we must consider the information on the average short range order in the context of *other* information, for instance the macroscopic density and intermediate range density fluctuations (that is the low Q behaviour of $S(Q)$). The only realistic way to do this is through some form of large scale modelling.

2. Simulation

Many liquid structures are modelled using Monte Carlo (MC) or molecular dynamics (MD) simulations. In these cases the results are, of course, totally dependent upon the interatomic potential chosen as input. The 'correctness' of this potential is often assessed by comparison of the predicted $g(r)$ with that determined by experiment. Where agreement is good then one may have confidence in the simulated structure and it can be analysed and examined in detail. Alternatively if the comparison is poor it may be assumed that the potential is inadequate. This is not always justifiable either from the point of view of the experiment or of the simulation, for two main reasons.

(a) Experimental data are measured in Q space. Separation of total structure factors to give partial structure factors for a multicomponent system and/or transformation to r space leads to a redistribution, and sometimes a significant magnification, of errors. Since experimental errors are almost never quoted in r space, being largely unknown, a *quantitative* comparison with simulation cannot really be made. If possible comparison should be made with total structure factors in Q space, where the size and distribution of errors are more likely to be known. If the simulation size is small then the problem of truncation in the transform from r to Q space can be overcome (see Appendix 1).

(b) r space comparison emphasizes the short range structure. Excellent agreement is possible for $g(r)$ at small r while distinct features at low Q in $S(Q)$, indicating particular intermediate range ordering, can be grossly wrong or even missing. Any detailed analysis of intermediate range ordering based on comparison of $g(r)$ only is therefore unjustified. In some cases even models with significantly wrong macroscopic densities can agree well at $g(r)$ level.

If comparison of simulation and experiment is made at $S(Q)$ level and the comparison is good then the simulated structure can be examined in detail. If the comparison is only qualitative, or not even that, then it is difficult to know how to alter the input potential to improve the level of agreement. Such an iterative approach has been used occasionally but is computationally very expensive (e.g. Dzугutov 1989).

3. RMC modelling

The RMC technique has been described in detail by McGreevy *et al* (1990). The algorithm is similar to that for Metropolis Monte Carlo simulation, except that instead of minimizing the potential energy of the system, based on an input interatomic potential, one minimizes the difference between the structure factor(s) calculated from the model and those measured experimentally. It has been shown by Howe and McGreevy (1991b) that, in the case of a system described by pairwise additive potentials, this method produces correct three-body correlations even though the 'input' information (that is the structure factor) is only an orientational average. Where the potential contains significant many-body terms the imposition of suitable constraints can enable the assessment of different structural possibilities.

RMC has many advantages for structural modelling.

(a) All the available data are used in a quantitative and self-consistent manner.

(b) No interatomic potential is required. This is an obvious advantage for the majority of liquids where the available potentials do not quantitatively reproduce the diffraction data.

(c) Large models can be used so structure factors can be modelled directly.

(d) Data sets from different experimental techniques can be readily combined (Keen and McGreevy 1990, Gurman and McGreevy 1990) and constraints determined by other methods or 'chemical knowledge' can be easily applied.

(e) Information on partial structure factors or partial radial distribution functions can be obtained from fewer total structure factors than are required for a conventional solution (see e.g. Howe and McGreevy 1991). While such partials are obviously not unique it has been shown (Pusztai and McGreevy, private communication) that in some cases modelling of a single accurate structure factor for e.g. a two-component system can produce more accurate partials than conventional solution from three less accurate structure factors obtained using isotopic substitution.

4. Analysis of a three-dimensional disordered structure

Once a three-dimensional model of a liquid structure has been obtained it is not clear how that structure should be characterized. Even the three-body correlation function $g^{(3)}(r_{12}, r_{13}, \cos \theta_{123})$ is too complex to visualize, and for all but the largest models would in any case be statistically inaccurate. Such information must be represented in a more compact form.

4.1. Neighbour distribution

While the dangers of interpreting the *average* coordination number have been stressed above it is nevertheless useful to define a local coordination shell, using some arbitrary limit such as the first minimum in $g(r)$, and to examine the *distribution* of coordination numbers for individual ions, $C(n)$. The precise definition of coordination shell then becomes less important and of course the distribution can be examined as a function of the size of the coordination shell.

4.2. Bond angle distributions

Using some definition of coordination shell, the vectors joining any two atoms can be called 'bonds' on the understanding that this does not imply any chemical bonding. The distribution of angle cosines between pairs of bonds with a common central atom, $B(\cos \theta)$, is illustrative of the dominant local 'symmetry' (see Wicks and McGreevy 1991).

4.3. Invariants of spherical harmonics

A useful technique based on spherical harmonic invariants, Q_i (Steinhardt *et al* 1983) has been developed (see e.g. Baranyai *et al* 1987, McGreevy and Pusztai 1990). These contain essentially the same information as the bond angle distributions but in a more compact form. Comparison of the Q_i distribution with those calculated for clusters of known structural symmetry, but with varying degrees of disorder, is a simple method of assessing possible local ordering.

4.4. Bond centre distribution

One aspect of liquid structure that has received considerable attention in the last few years has been intermediate range order. The existence of such order is usually characterized by a peak in the structure factor below the 'main' peak, typically at $Q \approx 1 \text{ \AA}^{-1}$. RMC modelling has shown clearly that these peaks are often due to density fluctuations of a particular component of the liquid and this can be seen quite clearly by direct observation of the three-dimensional structure. These density fluctuations may be due to a tendency of the atoms to cluster. One way of displaying this tendency is to look at the distributions of bonds (as defined above), since where atoms cluster the bonds cluster more strongly. By calculating the structure factor or radial distribution function corresponding to the points at the bond centres the low Q peak can be magnified and the clustering tendency demonstrated clearly (see figure 3 and section 5.1). A bond centre is here defined as the point midway between an atom and one of its neighbours in the first coordination shell, this being defined by the first minimum in $g(r)$.

5. Examples

The structures of many different types of liquids have been studied by RMC modelling, including monatomic liquids (Howe *et al* 1991, McGreevy and Pusztai 1988), liquid metal alloys, molten salts and liquid semiconductors (Howe and McGreevy 1991a, McGreevy and Pusztai 1990, Howe 1989), molecular liquids (Howe 1990a) and ionic solutions (Howe 1990b). Here we will only give a few examples to illustrate how modelling has led to a greater understanding of liquid structure, which could not be obtained from average properties of radial distribution functions.

5.1. Alkali-transition metal alloys

Van der Marel *et al* (1982) proposed that the resistivity of certain alkali-Sn and alkali-Pb alloys which, as a function of composition, show distinct maxima at the equiatomic composition, could be understood in terms of the formation of 'Zintl' ions. The basic idea is that certain complex ions may be stable in alloys when they

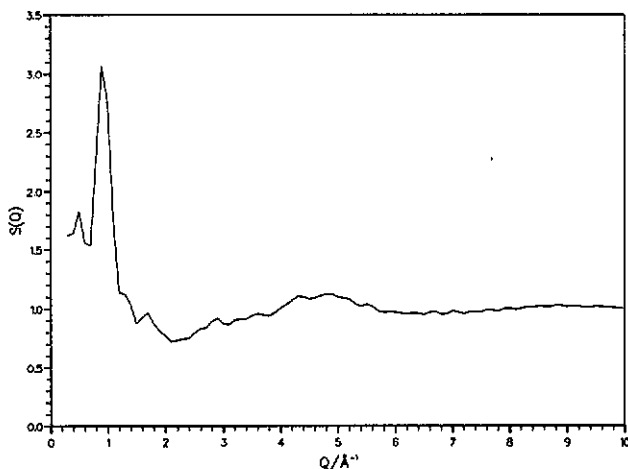


Figure 3. Bond centre structure factor for Pb–Pb bonds in molten KPb. Bond centres are defined as the points midway between an atom and its neighbours in the first coordination shell.

are isoelectronic with known stable molecular or covalently bonded elements. For instance in K–Pb the stable species would be tetrahedral Pb_4^{4-} , which is isoelectronic with the stable P_4 molecule. The four electrons required to form this complex ion are donated at the equiatomic composition by four K atoms.

It has been proposed that the form of the structure factor of molten $\text{K}_{0.5}\text{Pb}_{0.5}$ (see Reijers *et al* 1989 and references therein), in particular the existence of a large ‘first sharp diffraction peak’ (FSDP) at $Q \approx 1.0 \text{ \AA}^{-1}$ is evidence that this liquid is in fact a molten salt of K^+ cations and well defined Pb_4^{4-} anions. RMC modelling of a single total structure factor (for a two-component system) was able to show remarkably that the FSDP was indeed due to Pb–Pb clustering. This cannot be determined simply by ‘looking’ at the data. In figure 3 we show the structure factor corresponding to Pb–Pb bond centres (see section 4.4). This has a very sharp peak at $Q \approx 1 \text{ \AA}^{-1}$, significantly stronger than that in the normal atom–atom structure factor, showing quite clearly that this feature is due to a tendency of Pb atoms to cluster. The experimental structure factor was shown to be consistent with Zintl ion ‘contents’ of between 25% and 100%, but the lower contents showed a strong correlation of the degree of clustering with resistivity as a function of composition. The properties of these materials can therefore be explained in terms of a ‘tendency’ to form Zintl ions, rather than actual formation of a large proportion of well defined complexes. In other words the many-body terms in the potential that would stabilize the ions are not particularly strong.

More recent work on NaTl (McGreevy, private communication) has shown, again for a single total structure factor, that the small FSDP is in this case due to Tl–Tl correlations. Here the Zintl ion would be the infinite diamond lattice, Tl^- being isoelectronic with Si, and indeed the Tl^- ions are found to form clusters with the appropriate bond angles. It would seem, therefore, that the Zintl ion picture, while not being correct in an absolute sense, does contain the right ‘ingredients’.

5.2. Molten salts

Conventional analysis of isotopic substitution neutron diffraction data on molten CuCl (Eisenberg *et al* 1982) suggested that the Cu–Cu distribution was extremely disordered. Numerous simulations failed to reproduce such behaviour. RMC modelling (McGreevy and Pusztai 1990) showed that the experimental data were in fact consistent with a more ordered cation distribution, similar to that found in molten LiCl. However, while in LiCl cations are dominantly octahedrally coordinated, as they are in the LiCl crystal structure (rocksalt), in CuCl cations are tetrahedrally coordinated, as they are in CuCl crystal structure (zinc blende). Both liquids therefore have structures which are disordered forms of their corresponding crystal structures.

Molten $ZnCl_2$, $MgCl_2$ and nickel halides have average cation–anion coordinations close to four and cation–cation partial structure factors with a well defined FSDP. This has been interpreted as indicating well defined tetrahedral coordination for all these melts (Biggin and Enderby 1981, Biggin *et al* 1984, Newport *et al* 1985, Wood and Howe 1988, Wood *et al* 1988), despite the fact that the physical properties of $ZnCl_2$ are considerably different from the others. RMC modelling has shown that $ZnCl_2$ is indeed tetrahedrally coordinated, explaining its high viscosity and glass forming ability, and in agreement with the various crystalline polymorphs. However, the other melts are dominantly octahedrally coordinated (in terms of angular correlations), as they are in their corresponding crystal structure ($CdCl_2$ type). Again the RMC structural models are found to be consistent with other physical information on which they are not based.

5.3. Molten germanium

Ge is a liquid whose structure is extremely difficult to interpret by conventional means because the radial distribution function (see figure 4) has a single sharp first peak, with subsequently no well defined minimum or indeed any other well defined feature (Salmon 1988). The definition of a coordination shell is therefore rather arbitrary but would give a value for the average coordination of 4–8. RMC modelling (Howe *et al* 1991) shows immediately that the dominant local coordination is tetrahedral, as in crystalline or amorphous Ge, but with considerable penetration of ‘second’ neighbours into the first coordination shell. If a first shell is defined by symmetrizing the first peak in $g(r)$ then it is possible to produce a structure, that is in agreement with the diffraction data, with 96% fourfold coordination. Metallic conductivity in molten Ge cannot therefore be attributed to octahedral coordination.

5.4. Expanded caesium

Nield *et al* (1991) have shown that the changes in the structure factor and radial distribution function of Cs along the liquid–vapour coexistence curve (Winter *et al* 1987, 1988), despite a linear decrease in the average coordination number with density, are in fact due to an increase in the range of coordination numbers as the critical point is approached, i.e. stronger fluctuations. The structures obtained suggest that the metal–non-metal transition, which is approximately coincident with the critical point, is due to a percolation transition in the network of ‘metallic’ bonds. By a simple model, based on the bond network, they have reproduced the experimentally determined resistivity as a function of density remarkably well.

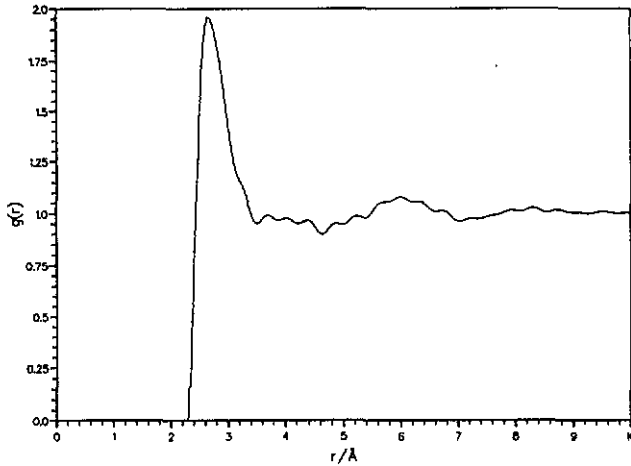


Figure 4. Radial distribution function for molten germanium.

6. Conclusions

It is not the aim of this paper to suggest that RMC modelling is the *only* way of understanding liquid structure. However, it is the intention to suggest that such complex structures cannot be understood without *some form* of modelling or simulation, and that such models should be in *good agreement* with the measured data (i.e. structure factors). No model will, of course, ever be completely unique, but the natural self-consistency of modelling methods does overcome many of the possibly misleading aspects of conventional interpretations in terms of 'average' quantities. *The production of a three-dimensional model leads to a greater understanding of the liquid structure and hence of many other properties which depend on that structure.*

Acknowledgments

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Appendix 1. Comparison of simulated and experimental structure factors

If the simulation size is small then the radial distribution function $g_S(r)$ will still have significant oscillations at $r = L/2$, where L is the length of the simulation cell (here assumed to be cubic). There will then be truncation errors in the transform to $S_S(Q)$. Since the experimental data $S_E(Q)$ are measured in Q space they do not contain such errors, so they cannot be compared to the simulated $S_S(Q)$. This could be calculated directly without truncation errors at Q values determined by the symmetry of the simulation cell, i.e. $Q = (2\pi/L)(n_1, n_2, n_3)$, but the net of points is sparse at low Q .

The truncation problem can be overcome in the following manner. The simulated radial distribution function $g_S^L(r)$ is a section of the complete radial distribution function $g_S(r)$, multiplied by a step function

$$f(r) = 1 \quad r < L/2$$

$$f(r) = 0 \quad r > L/2$$

$S_S^L(Q)$ is therefore the convolution of the 'true' structure factor $S_S(Q)$ and the transform of $f(r)$

$$f(Q) = \frac{\sin(QL/2)}{Q}$$

$$S_S^L(Q_j) = \frac{1}{\pi} \int S_S(Q_i) \left(\frac{\sin(|Q_i - Q_j|L/2)}{|Q_i - Q_j|} - \frac{\sin(|Q_i + Q_j|L/2)}{|Q_i + Q_j|} \right) dQ_i$$

If the experimental structure factor $S_E(Q)$ is similarly convoluted with $f(Q)$

$$S_E^L(Q_j) = \frac{1}{\pi} \int S_E(Q_i) \left(\frac{\sin(|Q_i - Q_j|L/2)}{|Q_i - Q_j|} - \frac{\sin(|Q_i + Q_j|L/2)}{|Q_i + Q_j|} \right) dQ_i$$

then it can be compared directly to $S_S^L(Q)$. While the *shape* of the structure factor has been modified by the convolution all the *intensity* information is maintained so a quantitative comparison of experiment and simulation can be made. If $g_E(r)$ is flat already at $r = L/2$ then the convolution will not alter $S_E(Q)$.

This method is particularly useful for crystals where there is long range order and hence no simulation can be large enough that $g_S(r \rightarrow L/2) \rightarrow 1$. An example of an unconvoluted structure factor and the corresponding convoluted structure factor and RMC fit is shown in figure 5.

Appendix 2. Assessment of the quality of experimental data

If one takes a structure factor or radial distribution function from the literature then, if no realistic assessment of errors is given, it is necessary to assume that the data are 'correct'. If a simulation or model is compared to the data and there is some disagreement then this implies that the potential used in the simulation is wrong. One may then go to a great deal of effort to improve the potential or model to obtain better agreement with the data. If the data contain significant errors then obviously this effort is wasted, so some method of assessing the data *a priori* is required.

Experimental diffraction data contain statistical and systematic errors. The Q spacing of data points should be small compared to any feature in $S(Q)$, so high frequency statistical noise is effectively removed by transforming to $g(r)$. Systematic errors can arise from sources such as incorrect subtraction of sample container or background and incorrect treatment of absorption or inelastic scattering. These errors are (normally) of low frequency in Q compared to oscillations in the structure factor and so contribute significantly at low r in $g(r)$. Since $g(r)$ should be zero below some distance r_0 determined by the closest approach of two atoms, the deviation

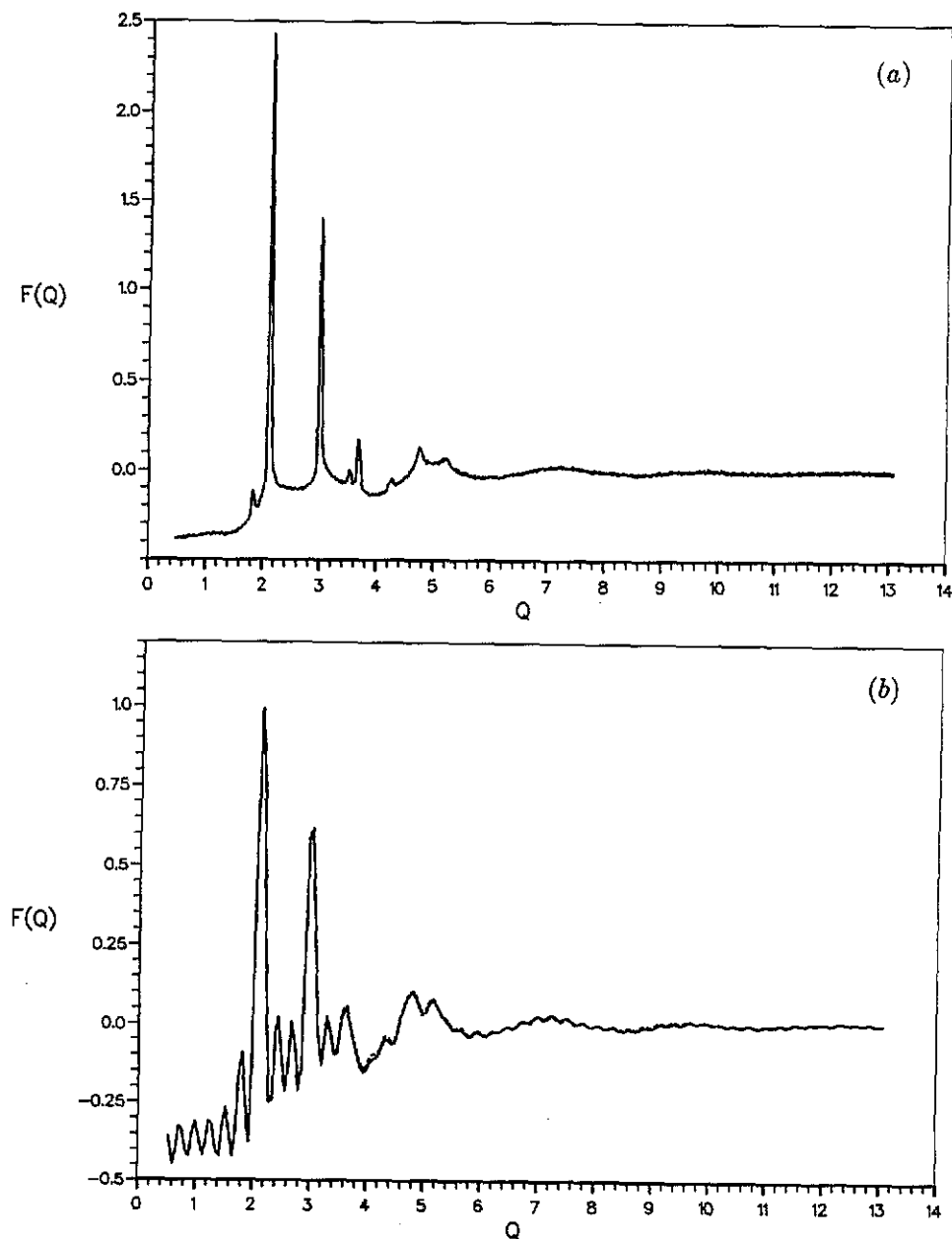


Figure 5. (a) Experimental structure factor $S_E(Q)$ for AgBr at 684K. (b) $S_E(Q)$ convoluted with $f(Q)$ (see Appendix 1) in comparison with the RMC fit.

from zero can be used to assess the level of systematic errors. However, truncation errors caused by a limited Q range can also contribute to $g(r < r_0)$ so they must be distinguished.

The method of assessment is therefore as follows.

(1) Transform $S_E(Q)$ directly to $g_E(r)$. Note that it is not uncommon for the published $S_E(Q)$ and $g_E(r)$ not to be related by a direct transform since smoothing

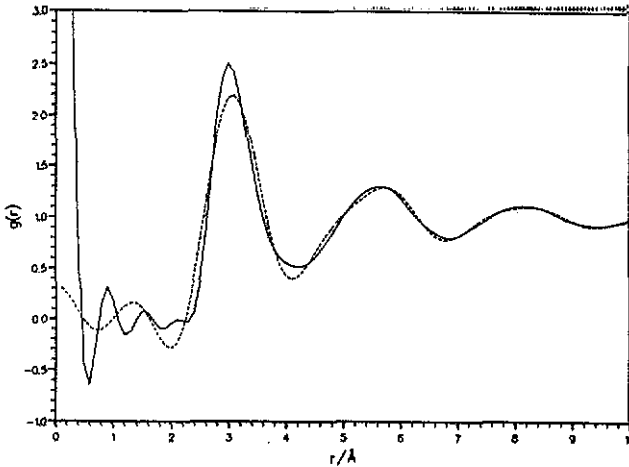


Figure 6. Radial distribution functions containing truncation errors obtained for a structure factor which has been offset from its correct high Q level (solid curve) or truncated while still oscillatory (broken curve). The periods of the truncation oscillations are $2\pi/Q_{\max}$.

and iterative transform techniques are often used.

(2) If there are significant oscillations about zero at $r < r_0$ they may be due to truncation. This can be checked since the period in r should be approximately $2\pi/Q_{\max}$. As experiment and simulation should be compared in Q space (see Appendix 1) truncation errors are not a problem. Two examples of truncation error are shown in figure 6.

(3) Significant systematic errors usually lead to $g(r < r_0)$ being either dominantly positive or negative and increasing (or decreasing) significantly as $r \rightarrow 0$. Note that there may be superimposed truncation oscillations. The error level can be estimated by setting $g(r)$ to zero for $r < r_0$ and then back-transforming to Q space. The back-transformed structure factor is then compared with the original. Since any model will automatically have $g(r < r_0) = 0$ this comparison will give a first estimate of the best level of agreement that can be obtained with the experimental data. However back transformation is *not* a method of removing errors from data. Systematic errors in $S(Q)$ produce errors at all r in $g(r)$; they can just be 'seen' most easily for $r < r_0$. An example of a structure factor with significant systematic error and the corresponding $g(r)$ are shown in figure 7.

(4) If the direct transform of the experimental $S(Q)$ leads to a $g(r)$ that is very flat below r_0 then either the data are extremely good, or the structure factor is actually the back-transform of a modified $g(r)$. There is no way of knowing which.

(5) Many neutron diffraction measurements are performed with containers made of materials such as vanadium, or TiZr 'zero' alloy, which have small coherent scattering and hence an almost flat diffraction pattern. Small errors in container subtraction are therefore relatively unimportant. However, there are also many experiments which use silica containers. Since silica is a glass its structure factor is often qualitatively comparable with that of the material it contains. Errors in container subtraction can therefore lead to modulations of the sample structure factor which are significant but 'invisible'. However, the Si-O bond length in silica is well defined, giving a sharp peak at 1.8 \AA in $g_{\text{SiO}}(r)$. If the container subtraction is modified slightly this peak

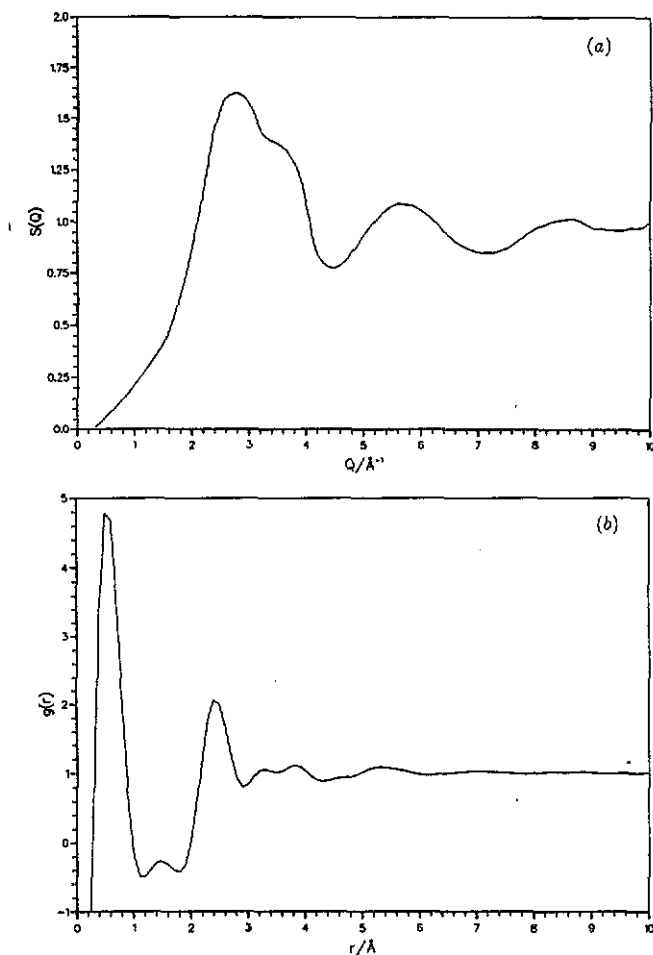


Figure 7. (a) Example of a structure factor containing significant systematic errors (these are not obviously visible) and (b) the corresponding radial distribution function. The large peak in $g(r)$ at $\approx 0.6 \text{ \AA}^{-1}$ is unphysical and due to the errors.

is usually apparent in the sample $g(r)$, and the amount of subtraction can then be modified to minimize the silica contribution. $g(r)$ s obtained by direct transformation of structure factors taken from the literature should be examined for such a feature if the experiment used a silica container.

References

- Baranyai A, Geiger A, Gartrell-Mills P R, Heinzinger K, McGreevy R L, Palinkas G and Ruff I 1987 *J. Chem. Soc. Faraday Trans. II* **83** 1875
- Biggin S and Enderby J E 1981 *J. Phys. C: Solid State Phys.* **14** 3129
- Biggin S, Gay M and Enderby J E 1984 *J. Phys. C: Solid State Phys.* **17** 978
- Dzugutov M 1989 *Phys. Rev. A* **40** 5434
- Eisenberg S, Jal F-J, Dupuy J and Chieux P 1982 *Phil. Mag. A* **46** 195
- Gurman S J and McGreevy R L 1990 *J. Phys.: Condens. Matter* **2** 9463
- Howe M A 1989 *Physica B* **160** 170

- 1990a *Mol. Phys.* **69** 161
— 1990b *J. Phys.: Condens. Matter* **2** 741
Howe M A and McGreevy R L 1991a *J. Phys.: Condens. Matter* **3** 577
— 1991b *Phys. Chem. Liq.* at press
Howe M A, McGreevy R L, Pusztai L and Borzsak I 1991 *Phys. Chem. Liq.* at press
Keen D A and McGreevy R L 1990 *Nature* **344** 423
McGreevy R L and Pusztai L 1988 *Mol. Simul.* **1** 8359
McGreevy R L, Howe M A, Keen D A and Clausen K N 1990 *Neutron Scattering Data Analysis (IOP Conf. Ser. 107)* p 165
McGreevy R L and Pusztai L 1990 *Proc. R. Soc. A* **430** 241
Newport R J, Howe R A and Wood N D 1985 *J. Phys. C: Solid State Phys.* **18** 5249
Nield V M, Howe M A and McGreevy R L 1991a *J. Phys.: Condens. Matter* **3** 7519-25
Nield V M, Keen D A, McGreevy R L and Hayes W 1991b in preparation
Reijers H T J, van der Lugt W, van Dijk C and Saboungi M-L 1989 *J. Phys.: Condens. Matter* **1** 5229
Salmon P S 1988 *J. Phys. F: Met. Phys.* **18** 2345
Steinhardt P J, Nelson D R and Ronchetti M 1983 *Phys. Rev. B* **28** 274
van der Marel C, van Oosten A B, Geertsma W and van der Lugt W 1982 *J. Phys. F: Met. Phys.* **12** 2349
Wicks J D and McGreevy R L 1991 *Physics of Fluids (IOP Conf. Ser.)* at press
Winter R, Bodensteiner T, Glaser W and Hensel F 1987 *Ber. Bunsenges. Phys. Chem.* **91** 1327
Winter R, Noll F, Bodensteiner T, Glaser W, Chieux P and Hensel F 1988 *Z. Phys. Chem.* **156** 145
Wood N D and Howe R A 1988 *J. Phys. C: Solid State Phys.* **21** 3177
Wood N D, Howe R A, Newport R J and Faber J Jr 1988 *J. Phys. C: Solid State Phys.* **21** 669