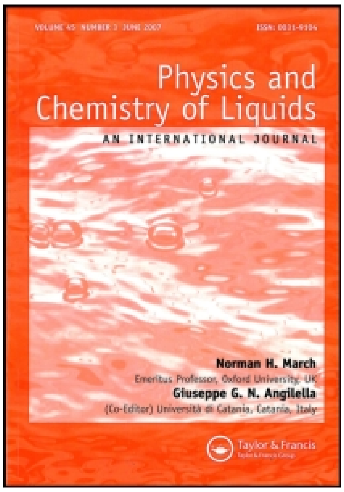

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The Structure of Liquid ^{4}He across the λ-point

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THE STRUCTURE OF LIQUID ^{4}He ACROSS THE λ-POINT

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Reverse Monte Carlo (RMC) modelling has been used to create three dimensional particle configurations of condensed ^{4}He that are consistent with diffraction data at ten different temperatures across the superfluid transition. Here it is shown that all observable changes in the data are within the experimental uncertainties, so no conclusions can be drawn concerning possible structural differences between normal fluid and superfluid. The local structure is found to be dominantly icosahedral.

KEY WORDS: Reverse Monte Carlo modelling, superfluid transition.

1 INTRODUCTION

^{4}He undergoes a phase transition at the λ-point, $T_\lambda = 2.17$ K. Above this temperature it behaves as a normal fluid, while below it may be considered to be a mixture of normal fluid and superfluid. The superfluid concentration increases as T decreases, being 1 at $T = 0$ K. It has generally been believed that the occurrance of the superfluid phase can be detected by a change in atomic structure. This idea was supported by two series of diffraction experiments on liquid ^{4}He; that of Svensson *et al.*[1] used neutron diffraction while that of Wirth and Hallock[2] was an X-ray diffraction measurement. It was emphasized in both studies that the height of the principle peak of the structure factor, $A(Q)$, reached its maximum at or near T_λ, indicating maximum structural order.

The aim of the present work was to investigate more detailed features of the local atomic structure, such as bond angle distributions, in order to understand the microscopic nature of the transition. To calculate such three body correlations it was necessary to produce three dimensional particle configurations which were consistent with the experimental structure factors. This was achieved by using the Reverse Monte Carlo (RMC) method[3]. Detailed description of this technique can be found elsewhere[4], therefore only a brief summary is given here. The algorithm is similar to that for Metropolis Monte Carlo simulation[5], except that instead of minimising the potential energy of the system, based on an input interatomic potential, one minimises the difference between the structure factor calculated from the model and that measured experimentally. It has been shown that, in the case of a system described by pairwise additive potentials, this method produces correct three body correlations[6,7].

The two experimental sets of structure factors, $A(Q)$, and radial distribution functions, $g(r)$, for liquid ^{4}He referred to above differ slightly (see Figure 1). While these differences may seem small they are in fact larger than the differences observed at the λ-point. The X-ray data may contain residual systematic errors due to e.g. Compton scattering while for neutron diffraction from a light atom such as ^{4}He inelastic scattering is likely to be the major problem. The low r part of $g(r)$, obtained by direct transform of the experimental $A(Q)$, should be zero for r values below the closest approach distance of two atoms, but will in practice not be due to errors in the data. If it is set to zero and the resulting $g'(r)$ transformed back to Q space, the difference between the original and back-transformed $A(Q)$ gives a first order estimate of the level of systematic error. From this it was estimated that errors in the neutron diffraction data were larger, so the X-ray data were used for modelling. A comparison of original and back-transformed X-ray data is shown in Figure 2. The differences in peak height are comparable to those found to occur at the λ-point, so even for

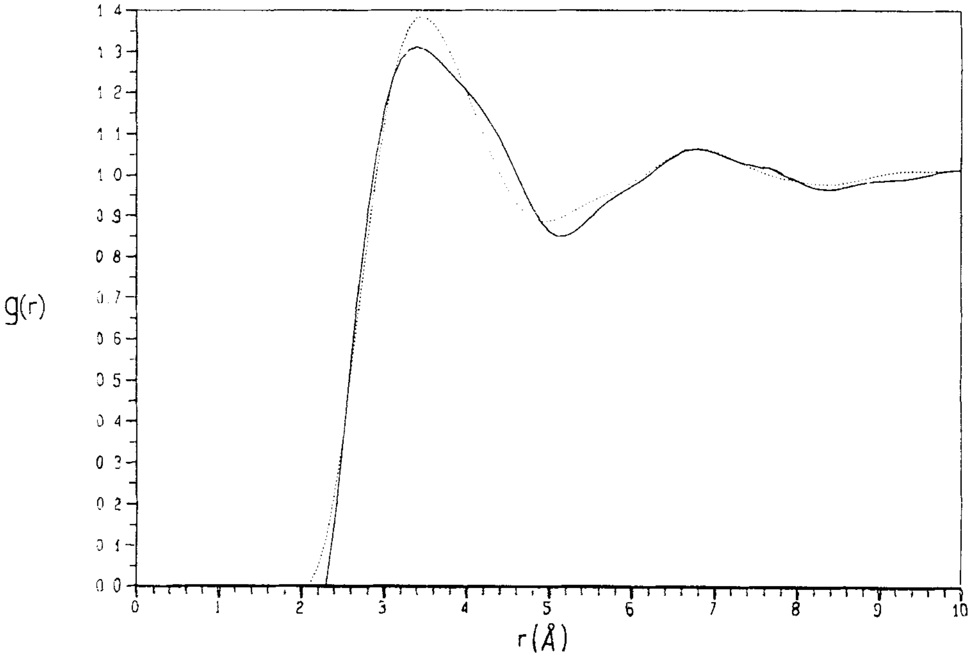

Figure 1 Comparison of radial distribution functions from neutron diffraction[1] (solid curve) and X-ray diffraction[2] (broken curve).

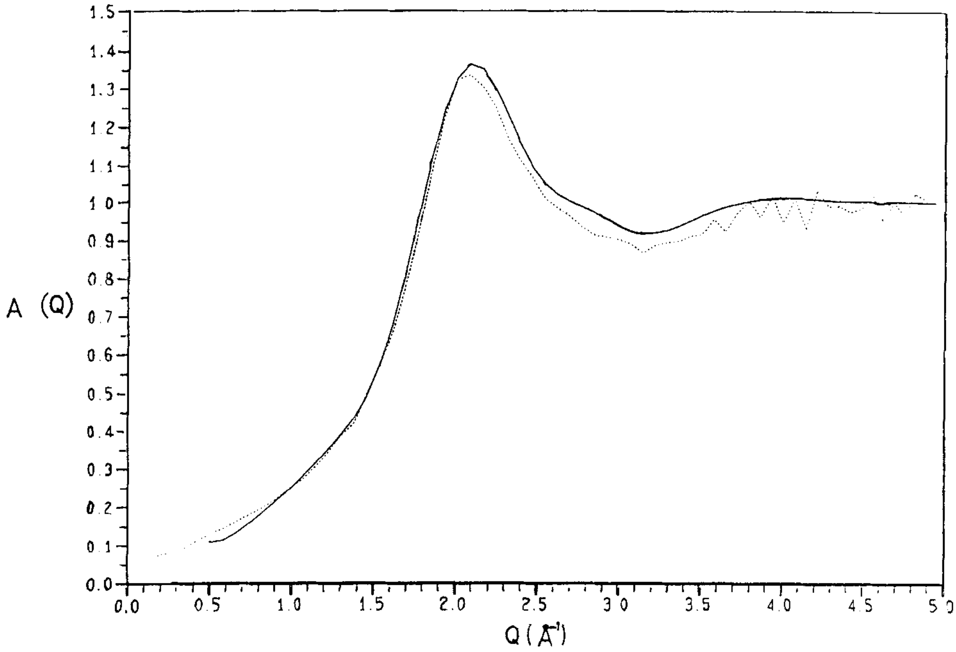

Figure 2 Experimental structure factor $A(Q)$ (broken curve) and the inverse transform of $g'(r)$ (solid curve) at 1.16 K.

the X-ray data any changes proposed are likely to be within the experimental error.

2 SIMULATION DETAILS AND RESULTS

Of the three sets of X-ray structure factors published, that with a density of 150.3 kg m^{-3}, corresponding to a number density of $\rho = 0.0226$ Å^{-3}, was chosen. Configurations of 3264 particles were contained in a cubic box of side 52.47 Å, with periodic boundary conditions. Structure factors at temperatures of $T = 1.16$, 1.30, 1.40, 1.60, 1.75, 2.10, 2.35, 2.50, 2.80 and 3.50 K were modelled independently. Both random particle distributions and an fcc lattice were used as initial configurations, with no differences detected in the final particle configurations. Due to the lack of high Q data from X-ray diffraction, and the poor statistics at the highest Q measured, it was necessary to use a constraint on the allowed distance of closest approach of two particles. Values from 2.0 to 2.5 Å were tested, the final value used being 2.2 Å.

Both $g(r)$ and $A(Q)$ were modelled; the two are not equivalent because the distribution of errors is different. The structure factor and RMC fit at 1.3 K are shown in Figure 3, with $g(r)$ calculated from the RMC model in Figure 4. The small peak on the left hand side of the first peak in $g(r)$ reflects the existence of small systematic errors in the data being modelled.

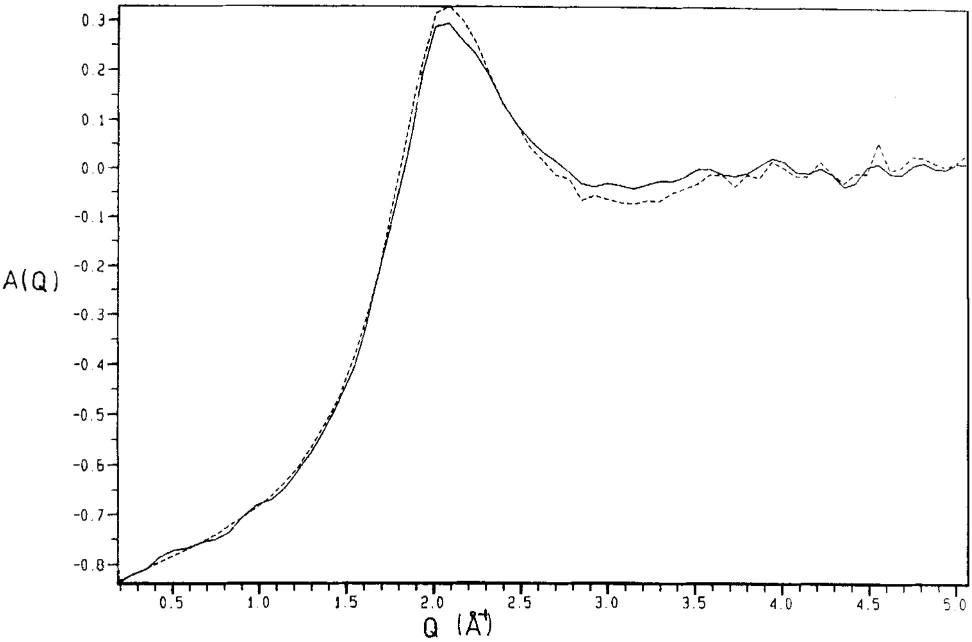

Figure 3 Experimental $A(Q)$ (broken curve) and RMC fit (solid curve) at 1.3 K.

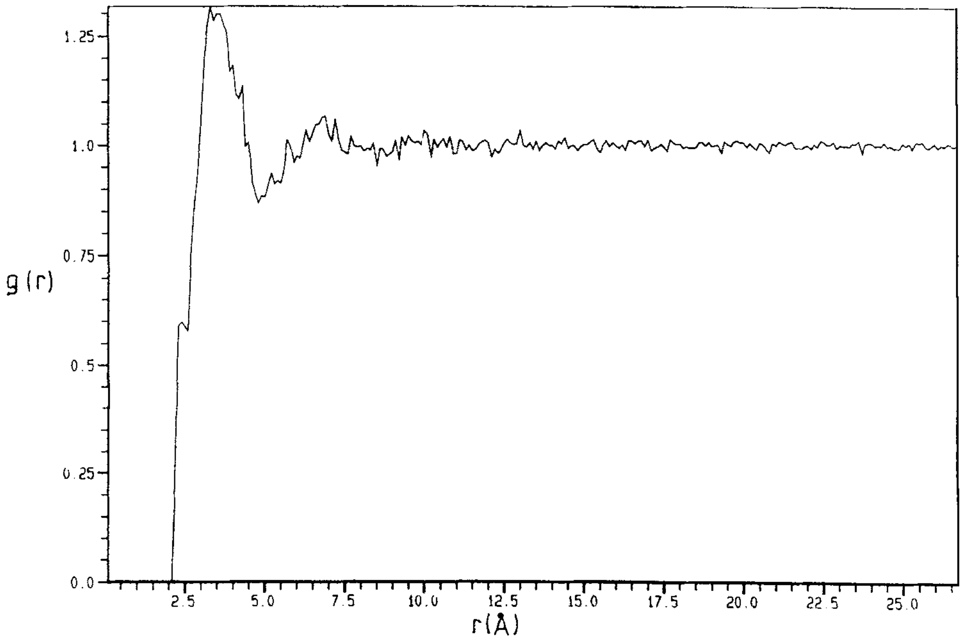

Figure 4 $g(r)$ from RMC model fitted to $A(Q)$ at 1.3 K.

It is possible to call the vectors joining pairs of atoms 'bonds' on the understanding that no particular chemical bonding is implied. Here we define any two atoms to be connected if their separation is less than the distance of the first minimum in $g(r)$, 5.0 Å. The distribution of angle cosines between bonds with a common central atom, $B(\cos\theta)$, is then calculated. This is shown in Figure 5 for all ten temperatures. It can be seen that the distributions are identical within statistics.

A more sensitive means of characterising local orientational ordering is the use of rotational invariants of spherical harmonics[8], Q_l. These can be computed from the polar angles Θ and Φ of bonds with respect to a fixed coordinate system. The Q_l distribution (where $l = 0, 1 \ldots, 10$) is characteristic of local symmetries of 'clusters' formed by centres and their neighbours in the first coordination shell. Although they cannot be interpreted directly, it is convenient to compare them with a reference set which has been calculated for a series of perfect and distorted clusters of known symmetries[9–11]. Q_l distributions for six temperatures are shown in Figure 6. Again there are no differences within statistical errors.

The structure factor shown in Figure 2 is characteristically different from that of other 'simple' liquids. The structure factors of Ar, the alkali metals and some transition metals are almost identical, apart from a scaling factor[12]. The first peak height is ≈ 2.7, in comparison with ≈ 1.4 for ^{4}He; in addition ^{4}He has a much broader low Q tail. $g(r)$ for ^{4}He has a correspondingly lower and broader first peak. The average coordination number, calculated to the first minimum in $g(r)$, is 11–12, with

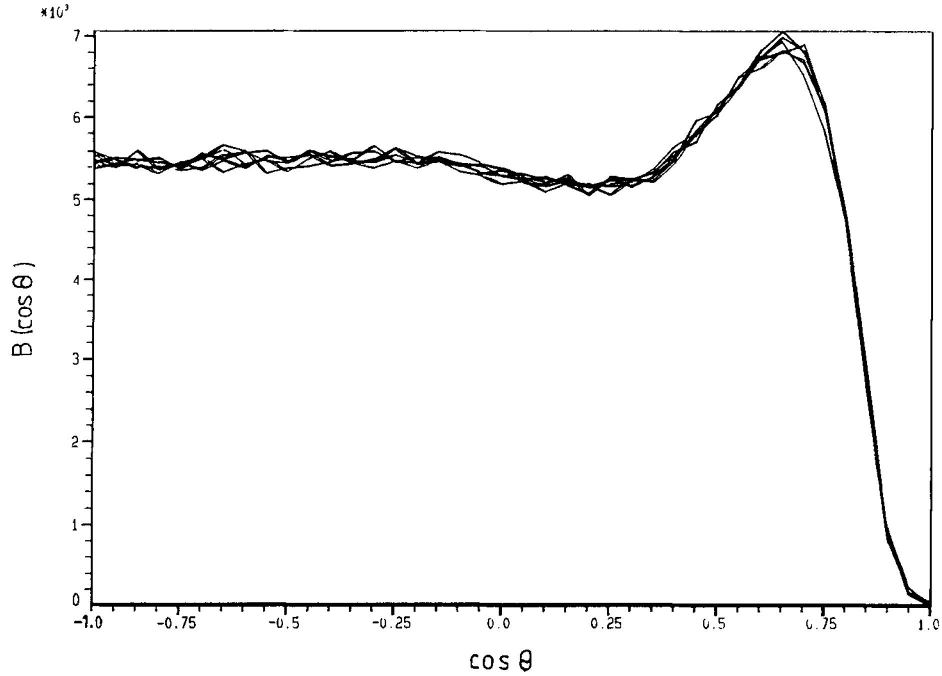

Figure 5 Bond angle cosine distributions at ten temperatures.

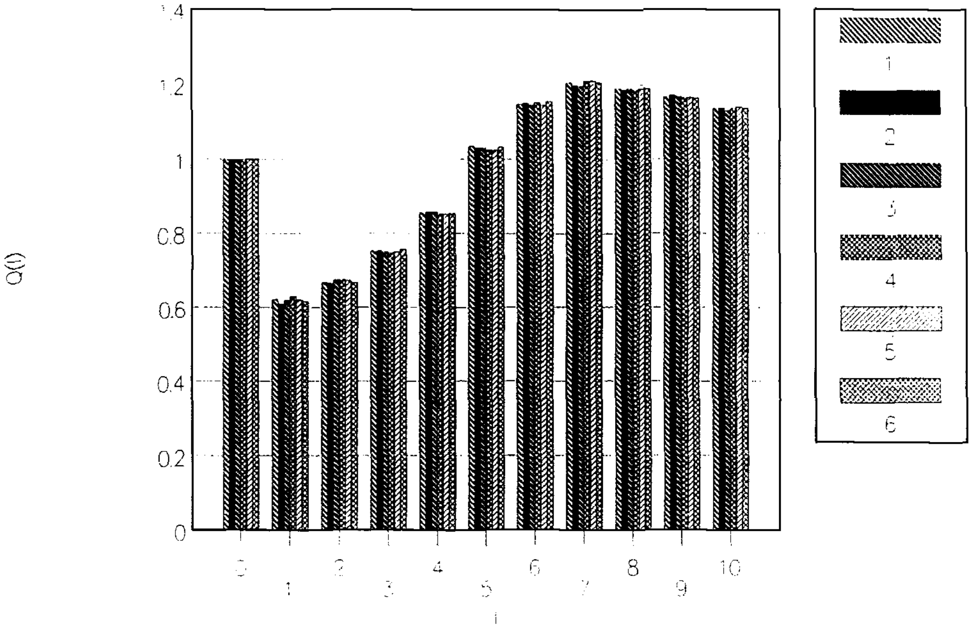

Figure 6 Spherical harmonic invariants. 1: 1.16 K; 2: 1.40 K; 3: 1.75 K; 4: 2.10 K; 5: 2.35 K; 6: 2.80 K.

the number of neighbours of individual atoms within this distance varying from 5 to 17; for 'simple' liquids the average coordination is slightly higher, 13–14, and the distribution is narrower. These differences are also reflected in the bond angle distributions. For 'simple' liquids $B(\cos\theta)$ has peaks at $\cos\theta \approx 0.6$, -0.35 and -1.0 and analysis of the Q_l distribution suggests that the structure is basically hexagonal close packed. However $B(\cos\theta)$ for ^{4}He (Figure 5) peaks at $\cos\theta \approx 0.7$ and shows no distinct peaks at other angles and Q_l analysis suggests that the local structure is dominantly icosahedral. While the broader $S(Q)$ and $g(r)$ can be simply understood because of the low mass of ^{4}He and the large zero-point motion, the icosahedral order has no simple explanation.

3 DISCUSSION

The differences between structure factors for liquid ^{4}He measured across the λ-point have been shown to be within experimental error. Modelling of the data has found no measurable changes in local orientational order. It can therefore be concluded that, on the basis of the X-ray measurement of Wirth and Hallock^2, there are no changes in the local structure of ^{4}He across the superfluid transition. It is important to stress that—considering the current level of agreement between simulated and measured $A(Q)$s, as well as the level of self-consistency of the experiments available—further investigations are necessary. These should probably include new inelastic neutron scattering measurements in order to obtain accurate dynamic structure factors, $S(Q, \omega)$, which would help to evaluate neutron diffraction experiments correctly.

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