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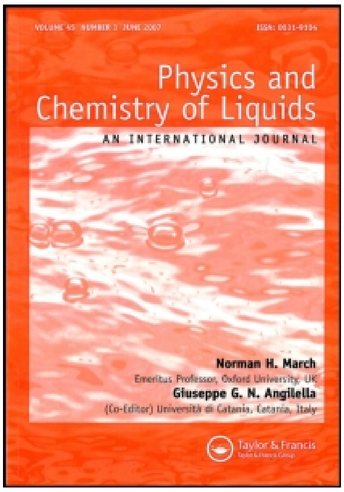

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A New Technique for Modelling the Structure of Expanded Liquid Metals Along the Liquid-Vapour Coexistence Curve

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A NEW TECHNIQUE FOR MODELLING THE STRUCTURE OF EXPANDED LIQUID METALS ALONG THE LIQUID-VAPOUR COEXISTENCE CURVE

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We have developed a simple technique for modelling the structure of expanded liquid metals along the liquid vapour coexistence curve which may be characterised as a 'correlated percolation' method. Starting from a model for the liquid at high density, e.g. near the triple point, obtained either by molecular dynamics simulation or reverse Monte Carlo modelling, we keep the size of the model and the atomic positions fixed and remove atoms, according to criteria which depend on the coordination number distribution, until the required lower density, corresponding to a higher temperature, is reached. Small random Gaussian displacements are then added to the position of each atom to account for the increased temperature. The structure factor of the resulting model is quite close to that measured experimentally. Changes in the structure factor as the liquid expands can thus be separated into the effects of density fluctuations and temperature (or entropy).

Keywords: Expanded liquid; caesium; correlated percolation; structure factor; coordination number

1. INTRODUCTION

The publication of high quality neutron diffraction data for expanded liquid caesium along the liquid-vapour coexistence curve [1] has prompted a considerable number of computer simulation, modelling and theoretical studies [e.g. 2–7], aimed at describing and explaining

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the changes in the structure factor, $S(Q)$, and radial distribution function, $g(r)$, that were observed. Some of these studies also investigated the possible link between the metal-insulator transition and the critical point, which occur very close together (depending on the precise definition of the metal-insulator transition). The structural features may be summarised as:

a) $S(Q)$ rises rapidly at low Q as T increases and ρ decreases (Q is the momentum transfer, T the temperature and ρ the number density).

b) Oscillations in both $S(Q)$ and $g(r)$ become heavily damped at high T.

c) The positions of the first peak and first minimum in $S(Q)$ and $g(r)$ do not change significantly.

d) The average coordination number, $\bar{n}_c$, obtained by integrating the area under the first peak in $g(r)$, decreases linearly with ρ.

Such features suggest that the liquid does not simply expand uniformly as ρ decreases, but rather that atoms 'prefer' to retain similar local arrangements even though the average separation between atoms increases considerably (the density changes by a factor of 5 between the triple point and the critical point). The 'non-uniformity' gives rise to significant density fluctuations on a mesoscopic scale, causing the rise in $S(Q)$ at low Q.

These features can be investigated by molecular dynamics simulation, but it is necessary to use a state-dependent potential to obtain reasonable agreement with experiment [3] and hence one cannot easily obtain a simple picture of how the structure and potential are related. We have previously carried out a reverse Monte Carlo (RMC) modelling study of expanded Cs [2]. The models obtained could be used to qualitatively explain the increase in electrical resistivity as T increases, and suggested that both the critical point and the metal-insulator transition could be considered as a form of percolation transition.

The behaviour of $S(Q)$ and $g(r)$, and the results of the RMC study, suggest that there may be a method of constructing a model of the low density (expanded) liquid, starting from a model for the high density liquid. This paper describes the development of such a method which, because of its simplicity, leads to a clearer understanding of the structural changes that occur.

2. METHOD

In Figure 1 we show the experimentally determined $S(Q)$ and $g(r)$ for liquid Cs at $T = 303$ K, $\rho = 0.00832$ Å^{-3} (near the triple point) and $T = 1673$ K, $\rho = 0.00434$ Å^{-3}; the critical point occurs at $T = 1924$, $\rho = 0.00172$ Å^{-3} [8]. We also show $S(Q)$ and $g(r)$ from a molecular dynamics (MD) simulation of 1000 atoms, corresponding to the former thermodynamic state. This is in very good agreement with the experimental results [9]; details of the potential have already been published [3]. Here, in order to be consistent, we will define atoms to be neighbours if their separation is less than 7.5 Å, approximately the position of the first minimum in $g(r)$ at all temperatures (see Figure 1). Previously we have shown [10] that removal of atoms at random

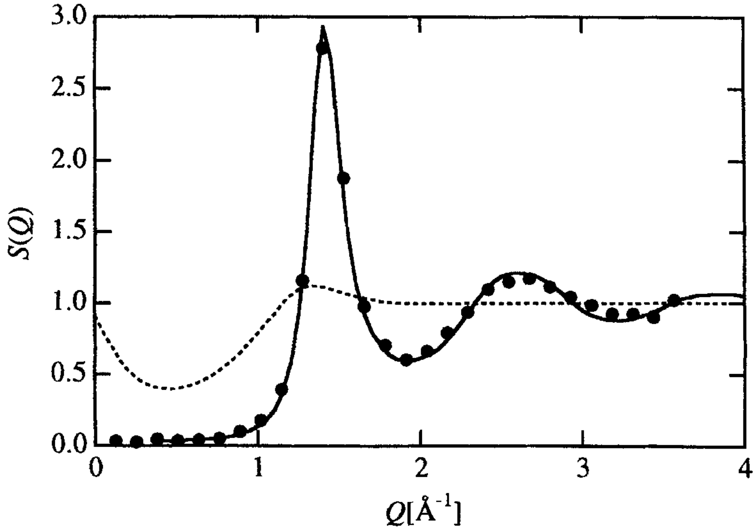


FIGURE 1 (a) $S(Q)$ and (b) $g(r)$ for liquid Cs. Solid curve: Experimental results at $T = 303\,K$, $\rho = 0.00832$ Å^{-3}. Filled circle: MD results at $T = 303\,K$, $\rho = 0.00832$ Å^{-3} Broken curve: experimental results at $T = 1673\,K$, $\rho = 0.00434$ Å^{-3}.

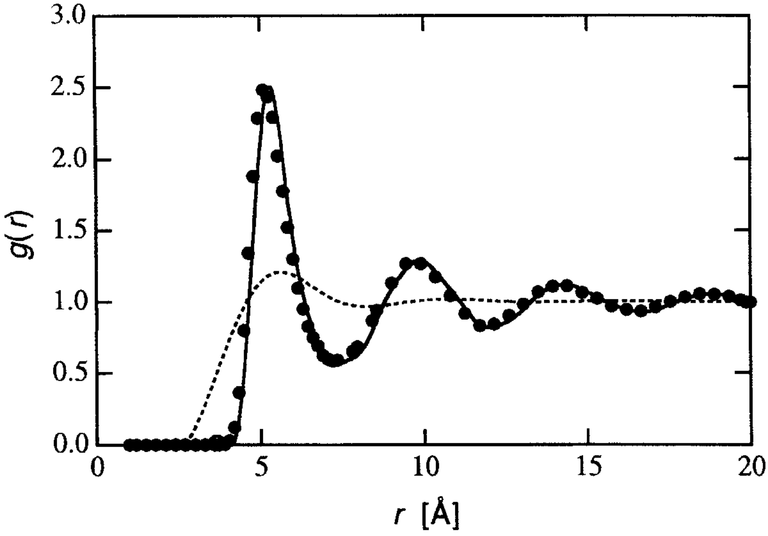
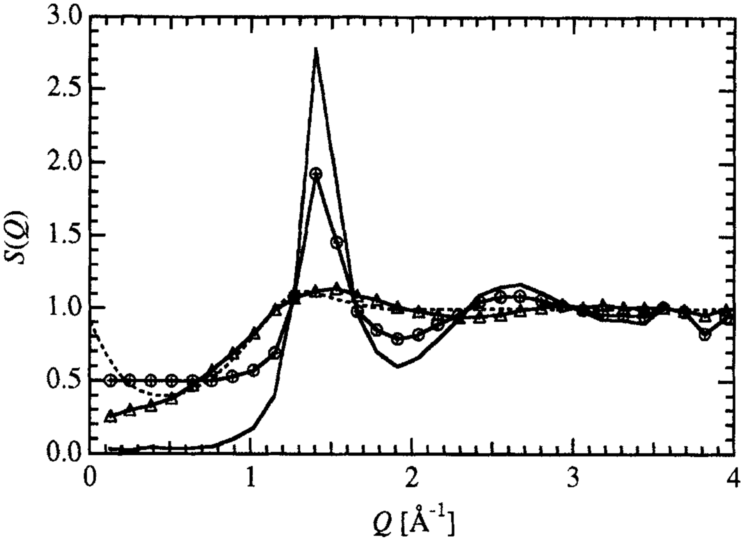


FIGURE 1 (*continued*)

from a structural model for a simple liquid, or of neighbouring pairs of atoms at random, leads to $g(r)$'s with very similar average properties, but only in the latter case does the structure factor rise at low Q. This suggests that $S(Q)$ at low Q is sensitive to the coordination number distribution of neighbouring atoms, $D(n_c)$, as opposed to the average coordination number, $\bar{n}_c$, and forms the basis for our method. We start from the MD model for the high density (low temperature) liquid and remove atoms, according to specified criteria involving $D(n_c)$, until the required lower density (higher temperature) is reached. The model size and atomic positions are fixed.

In Figure 2 we compare $S(Q)$, $g(r)$ and $D(n_c)$ for Cs at $T = 303\,K$, $\rho = 0.00832$ Å^{-3}, from MD and at $T = 1673\,K$, $\rho = 0.00434$ Å^{-3}, from experiment (which may be regarded as the 'target'), hard sphere Monte Carlo (HSMC) simulation and for removal of atoms at random. It can be seen that random removal hardly changes $g(r)$ and hence $S(Q)$ simply decreases in amplitude by a factor of 2 corresponding to the density change, since

$$S(Q) = \rho \int 4\pi \frac{\sin Qr}{Qr} (g(r) - 1)\, dr \tag{1}$$



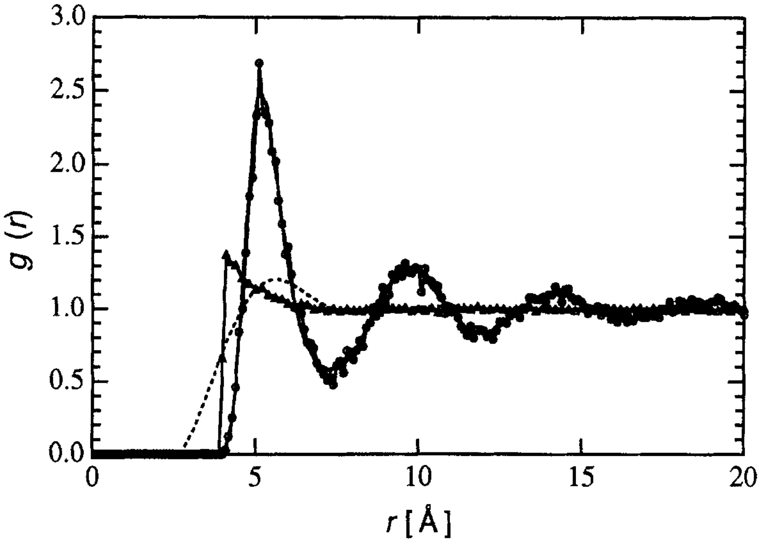


FIGURE 2 (a) $S(Q)$, (b) $g(r)$ and (c) $D(n_c)$ for liquid Cs. Filled circle: MD results at $T = 303\ K$, $\rho = 0.00832$ Å^{-3}. Broken curve: experimental results at $T = 1673\ K$, $\rho = 0.00434$ Å^{-3} Open triangle: HSMC results at $\rho = 0.00434$ Å^{-3}, hard sphere diameter $\sigma = 4$ Å. Open circle: results for $\rho = 0.00434$ Å^{-3} obtained by random removal.

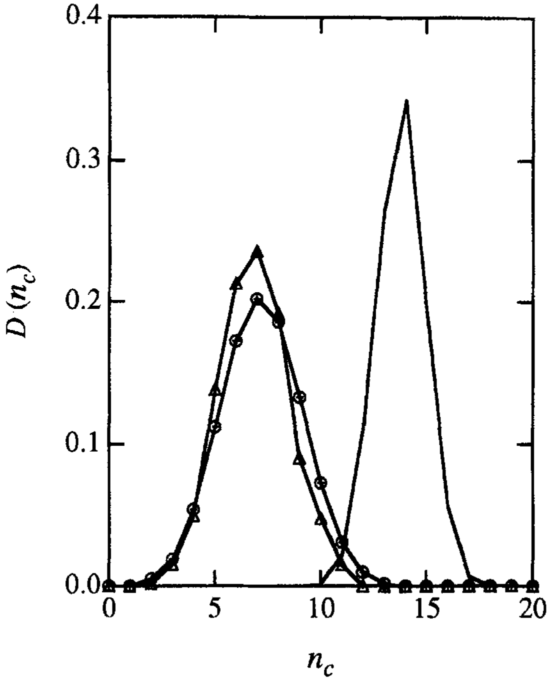


FIGURE 2 (*continued*)

$S(Q)$ from HSMC is in good agreement with experiment for $Q > 0.7\,\text{Å}^{-1}$ but does not rise at lower Q. It is then clear that, as expected, random removal of atoms is not a suitable method.

In Figure 3 we make similar comparisons for two different criteria of atom removal, one in which atoms with lower and higher coordination numbers are preferentially removed and the other in which only those with lower coordination numbers are preferentially removed. This may be described as a 'correlated percolation' method [11]; the percolation aspects will be discussed in more detail in a later paper. It should be stressed that the precise criteria for atom removal are not important; they are only the means by which the low density structure is created and it is possible that different criteria can produce the same final result. The results shown here may be considered to represent the typical behaviour found using many different criteria. In one case $D(n_c)$ has a rather symmetric shape and $S(Q)$ is low at low Q, while in

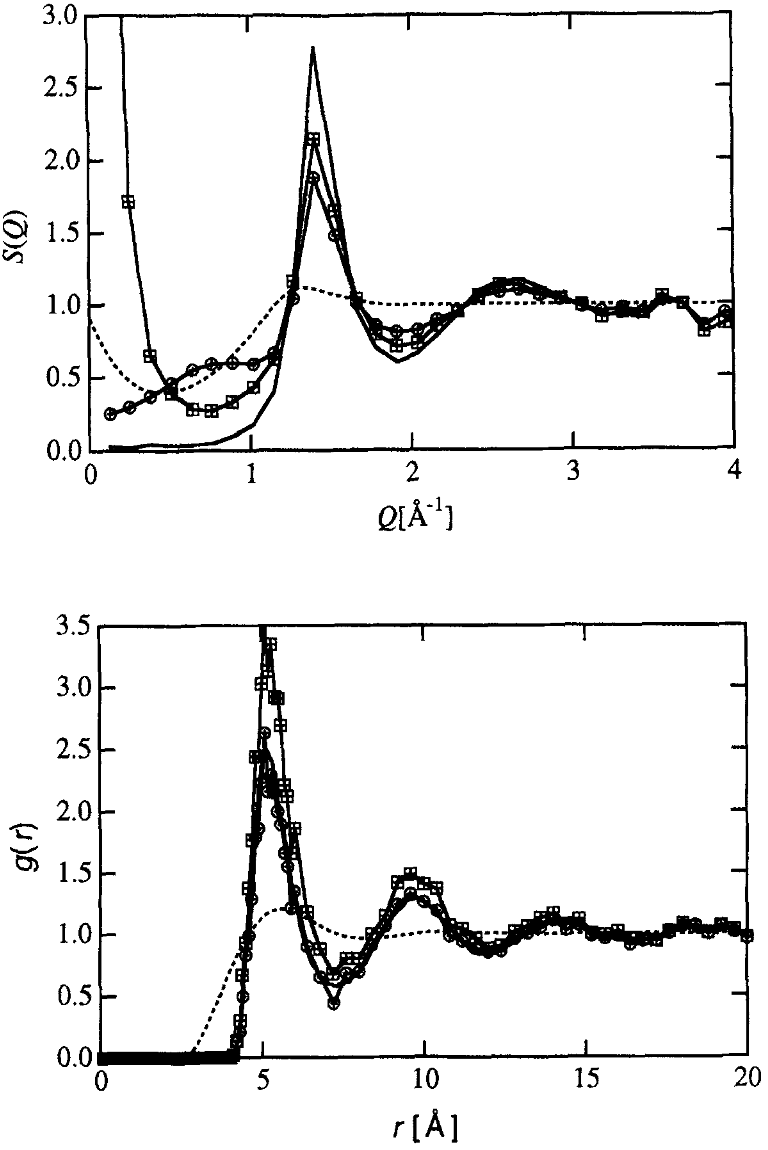


FIGURE 3 (a) $S(Q)$, (b) $g(r)$ and (c) $D(n_c)$ for liquid Cs. Filled circle: MD results at $T = 303\,K$, $\rho = 0.00832$ Å^{-3}. Broken curve: experimental results at $T = 1673$ K, $\rho = 0.00434$ Å^{-3}. Open circle: results for $\rho = 0.00434$ Å^{-3} obtained by removing preferentially both higher and lower coordination numbers. Open square: results for $\rho = 0.00434$ Å^{-3} obtained by removing preferentially only lower coordination numbers..

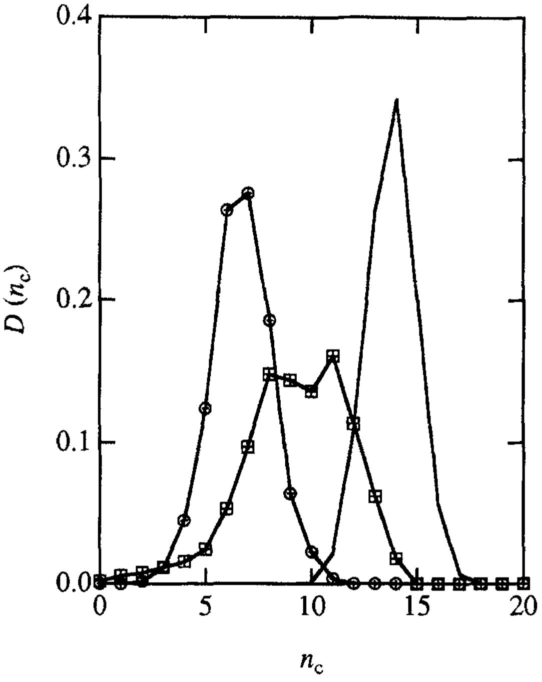


FIGURE 3 (*continued*)

the other case $D(n_c)$ has a broader, more asymmetric shape and $S(Q)$ rises very steeply at low Q. However in both cases the first peak and subsequent oscillations in $S(Q)$ and $g(r)$ are too sharp in comparison with the experimental 'target'; in fact they are relatively independent of the removal criterion. By modifying the width and symmetry of $D(n_c)$ we can therefore alter the behaviour of $S(Q)$ below 1 $Å^{-1}$ to obtain the required result, but not above 1 $Å^{-1}$. It can be seen that the first peak in the 'target' $g(r)$ is considerably broader than those from atom removal. Clearly if we do not change the atomic positions, but only remove atoms from the original structure, we cannot reproduce such a broad peak. Some additional step is therefore necessary to account for this broadening.

Following atom removal we have then added random displacements, with a Gaussian distribution, to the position of each remaining atom. Results are shown in Figure 4 for the same removal criterion and three different standard deviations for the displacement distribution. It can be seen that this procedure causes no change to $S(Q)$ at low Q, but the first peak and subsequent oscillations in $S(Q)$ and $g(r)$ become more heavily damped as the standard deviation increases, giving much better agreement with the 'target'. Again these are general results found for all the atom removal criteria tried.

Figure 5 shows the best results obtained by a combination of atom removal and Gaussian displacement. Agreement with experiment is not perfect, but we have nevertheless obtained a general understanding of how the structure factor changes along the coexistence curve. To a good approximation the effect of increasing T only alters $S(Q)$ above 1 Å^{-1} and this can be reproduced by a simple model of uncorrelated thermal fluctuations. Decreasing ρ only alters $S(Q)$ below 1 Å^{-1} and this can be reproduced by modifying $D(n_c)$, using a suitable criterion for atom removal, so that it is slightly broader and more asymmetric than would be the case for random removal. These two effects are largely independent.

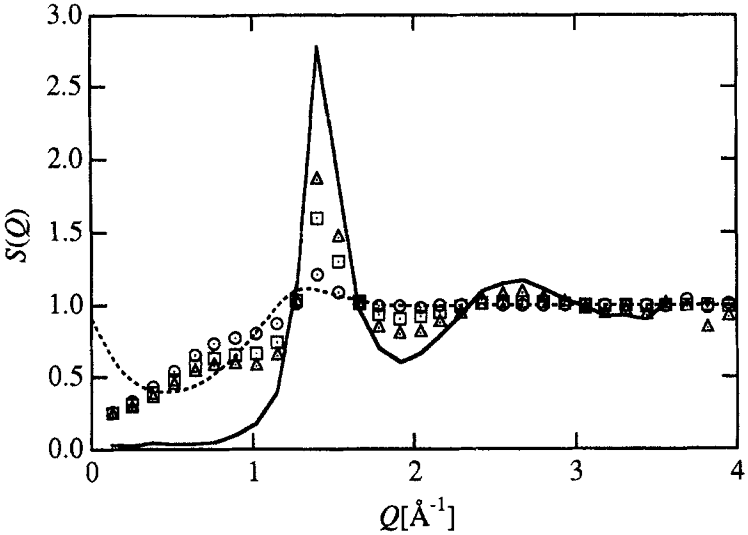
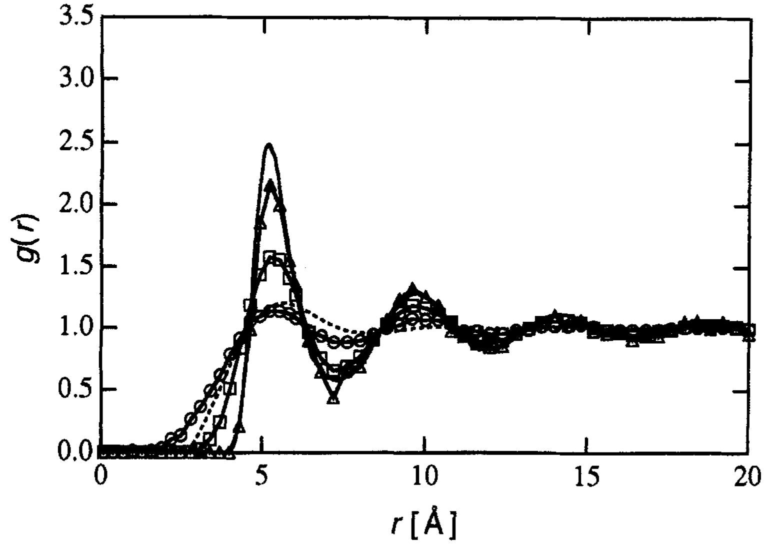


FIGURE 4 (a) $S(Q)$, (b) $g(r)$ and (c) $D(n_c)$ for liquid Cs. Filled circle: MD results at $T = 303\,K$, $\rho = 0.00832$ Å^{-3}. Broken curve: experimental results at $T = 1673\,K$, $\rho = 0.00434$ Å^{-3}. Open triangle, open square, open circle: results for $\rho = 0.00434$ Å^{-3} obtained by removing preferentially atoms with both higher and lower coordination numbers, followed by random Gaussian displacements of the remaining atoms with standard deviations 0.0, 0.8 and 1.5 Å respectively.



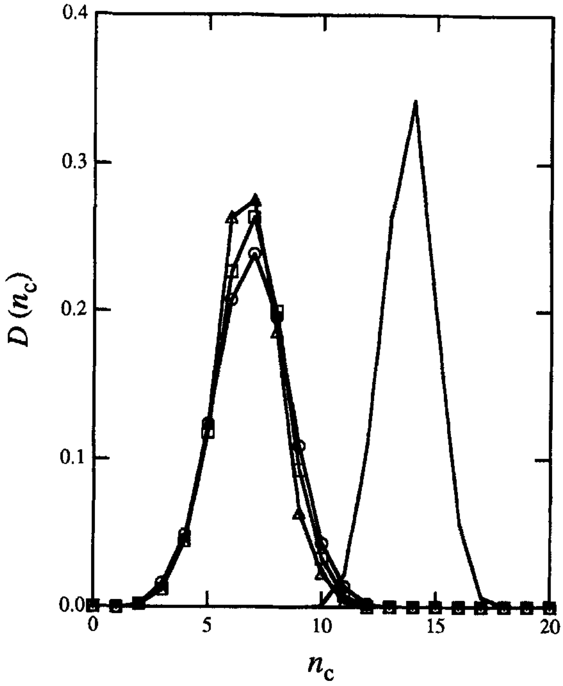


FIGURE 4 (*continued*)

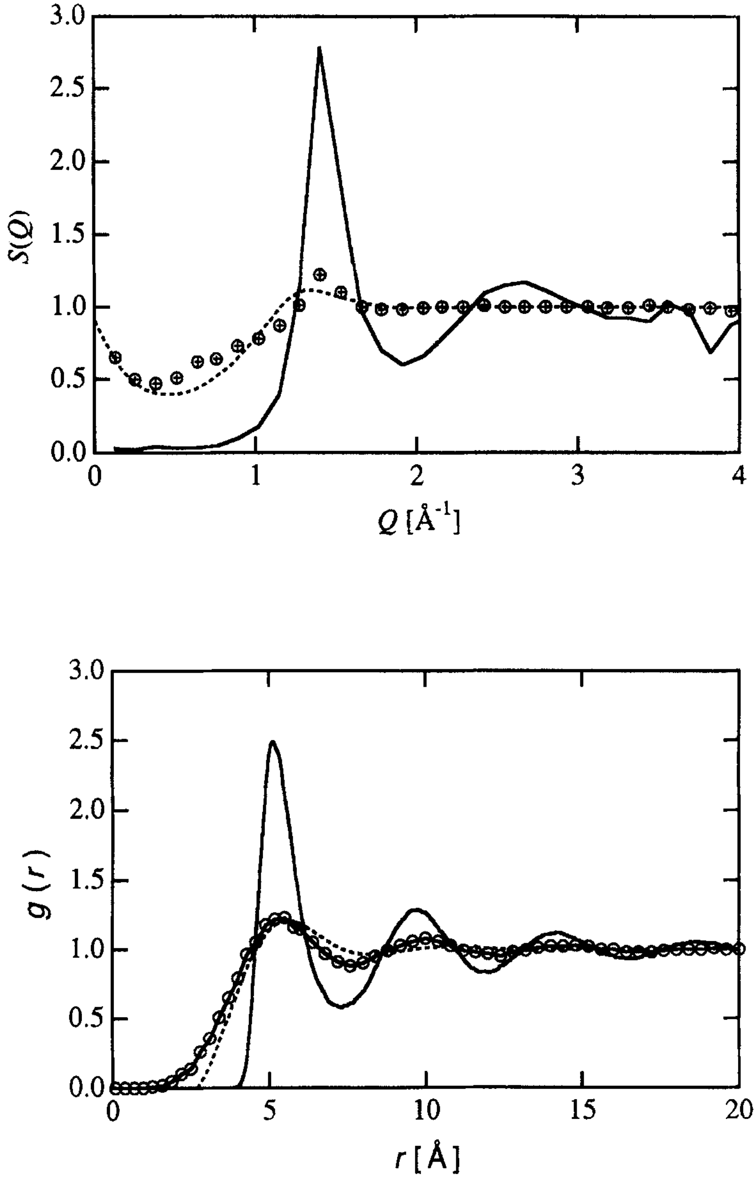


FIGURE 5 (a) $S(Q)$, (b) $g(r)$ and (c) $D(n_c)$ for liquid Cs. Solid curve: MD results at $T = 303\,K$, $\rho = 0.00832$ Å^{-3}. Broken curve: experimental results at $T = 1673\,K$, $\rho = 0.00434$ Å^{-3}. Open circle: best results for $\rho = 0.00434$ Å^{-3} obtained by removing preferentially atoms with coordination numbers 5, 9 and 10, followed by random Gaussian displacements of the remaining atoms with standard deviation 1.5 Å.

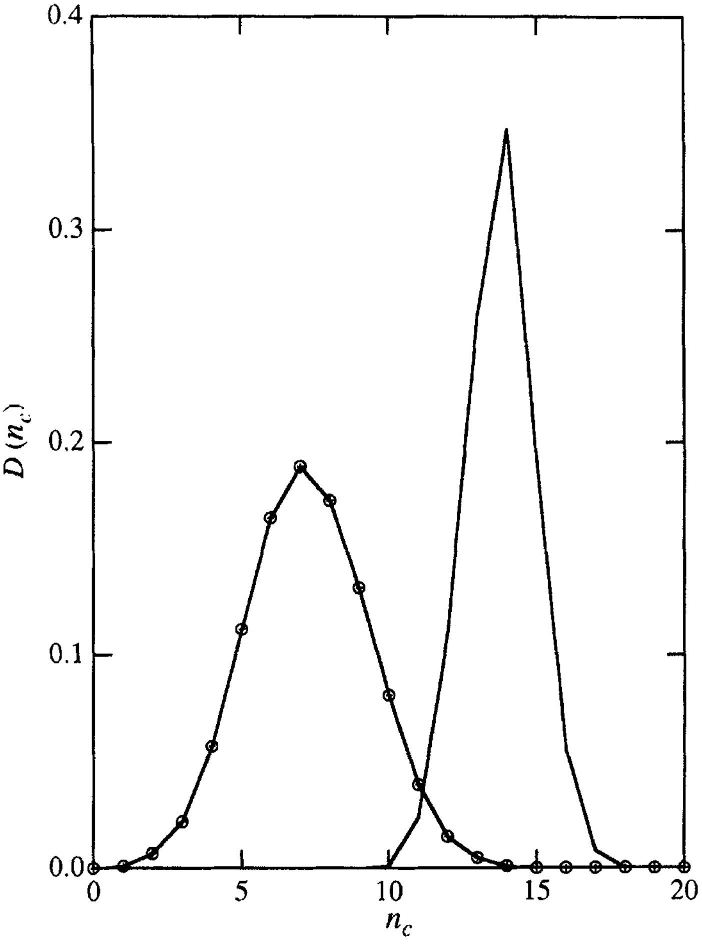


FIGURE 5 (*continued*)

3. DISCUSSION

We have developed a simple method for modelling the structure of expanded Cs along the liquid vapour coexistence curve. Since the characteristic behaviour of other liquid metals (e.g. Rb [12], Hg [13]) is the same as that of Cs it is expected that the method will work equally well in these cases. We will publish results separately showing that it can also be applied to liquid metal alloys. It is clear that any detailed experimental study of the approach to the critical point must concentrate on the low Q part of the structure factor, below 1 Å^{-1}, since changes in the high Q part have been shown to be purely due to temperature fluctuations whose effect is well understood. This places a severe requirement on experiments, since it is usually difficult to measure accurate results in the region 0.1-0.5 Å^{-1}.

It has been found that the low Q part of $S(Q)$ can be reproduced by requiring that the coordination number distribution, $D(n_c)$, becomes slightly asymmetric with respect to the result for random atom removal. It is not our intention to draw any detailed conclusions from this, but rather to simply draw attention to it. However, to a first approximation, it might be considered to be due to an increased importance of many body interactions as ρ decreases. At high densities all atoms have many neighbours and the effect of many body interactions can be well reproduced by an *effective* two body potential. However, as the average coordination number decreases then many body forces on atoms with different coordination numbers become more different (in a simple sense $\Delta n_c/\bar{n}_c$ increases) and cannot be reproduced within an effective two body potential. Our method reproduces the correct behaviour of $S(Q)$ up to close to the critical point. This suggests that there is no need to invoke any special many body effects that produce Cs dimers or trimers, even if it is expected that such species are present in the low density gas phase.

It is possible to produce results that are in even better quantitative agreement with the experimental $S(Q)$ by a modified RMC type procedure. In this case the atom removal procedure is iteratively modified in order to fit $S(Q)$ below 1 Å^{-1}. However this is more time consuming and does not lead to any increased understanding, so it has not been pursued here.

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