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T. Arai^a; R. L. McGreevy^b

^a Department of Mathematics and Physics, National Defense Academy, Yokosuka, Japan ^b Studsvik Neutron Research Laboratory, Nyköping, Sweden

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PERCOLATION ASPECTS OF THE METAL–INSULATOR TRANSITION IN EXPANDED Cs

T. ARAI^a and R. L. MCGREEVY^{b,*}

^a *Department of Mathematics and Physics, National Defense Academy,
Yokosuka 239, Japan;*

^b *Studsvik Neutron Research Laboratory, S-611 82 Nyköping, Sweden*

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An 'atom removal' method has been used to produce models of the structure of expanded Cs along the coexistence curve, to points above the critical point, based on a model of the structure at the triple point. A percolation transition in the metallic bond network is found at $\rho/\rho_c = 0.21$, very close to the experimental value for the metal–non-metal transition, which is approximately coincident with the critical point. A tendency towards formation of dimers close to the critical point is also found.

Keywords: Critical point; percolation; metallic bond

1. INTRODUCTION

There have been many papers in the past few years which have examined, from different points of view, the nature of the metal–insulator transition and/or the critical point in expanded alkali metals, principally Rb and Cs. Recently we have described a new, rather simple, method for modelling the structure of expanded Cs, based on an idea which may be characterised as 'correlated percolation' [1]. Given the simplicity of this method, it can reproduce the behaviour of the experimental structure factor as a function of density remarkably well. The method has also been found to work for expanded liquid

*Corresponding author.

alloys such as KPb [2]. The metal–insulator transition/critical point occur sufficiently close together that they cannot easily be distinguished, and in any case the precise definition of a metal–insulator transition is somewhat arbitrary. In an earlier paper concerning RMC modelling of the structure of expanded Cs we had proposed the idea that the transition may be characterised as some form of percolation transition [3]. In the present paper we use the atom removal method to show that there is indeed strong evidence for such a characterisation, and that some interesting results arise concerning dimerisation at low densities.

2. METHOD

We start from a model for the dense fluid, which would typically be the highest density on the coexistence curve (*i.e.*, the triple point), which is obtained either by molecular dynamics simulation (MD) or reverse Monte Carlo modelling (RMC). This model should be in good agreement with the experimentally determined structure factor. We remove atoms from the model, chosen at random but accepted according to a specified criterion based on their local coordination number, until the required lower density, corresponding to a higher temperature state along the coexistence curve, is reached. Small random displacements, with a Gaussian distribution, are added to the position of each atom to account for the increased temperature. The precise criterion for atom removal is not considered important; it is simply viewed as a means to an end, *i.e.*, reasonably close reproduction of the experimentally measured structure factor at a particular density close to the critical point. It would be possible to achieve better agreement by some form of iterative refinement of the criterion, but we have considered that simplicity is more important in the present context. It would also be possible to improve agreement at different temperatures (densities) by slightly modifying the criterion as a function of density, but again we have considered that this is not crucial, particularly as in the present paper we extend the method to temperatures above the critical point for which experimental structural data are not available. During the process of atom removal we

calculate the structure factor, $S(Q)$, the radial distribution function, $g(r)$, and the coordination number distribution of neighbours, $D(n_c)$.

One of us (Arai) has developed a method, details of which will be published elsewhere, to determine the bond percolation transition in a general network. The algorithm is based on the 'Dijkstra method' [4] of calculating the shortest path in a neural network. Each atom position in the original model, *i.e.*, that at the triple point, is defined as a site in the normal percolation sense. We define bonds, again in the normal percolation sense, between sites whose separation is less than 7.5 Å, that is the position of the first minimum in $g(r)$ for the liquid at the triple point (in fact this position does not change significantly as a function of density). As atoms (*i.e.*, sites) and the corresponding bonds are removed the average site occupation probability, p , is clearly the ratio of the density of the model to that at the triple point. The simulation cell is a cube of side L with normal periodic boundary conditions. A reachability function, $R(p)$, is defined as the probability that there is at least one path along bonds between an occupied site and the opposite side of the cell, *i.e.*, a distance L away in either x , y or z directions. A bond percolation transition occurs at $R(p) = 0.5$. Using this method we estimate $p_c = 0.311$ for a simple cubic lattice (a more accurate value is 0.3117 [5]) and 0.2 for a face centred cubic lattice (0.198 [5]).

3. RESULTS AND DISCUSSION

All results have been averaged over a set of five initial starting configurations obtained by MD simulation of 1000 atoms at a density of 0.00832 \AA^{-3} ($T = 303 \text{ K}$), using a potential which has been reported previously [6] and provides very good agreement with the experimental $S(Q)$ and $g(r)$ [7, 8]. 100 different final configurations have been produced by atom removal from each of the initial configurations. The critical point density for Cs is 0.00172 \AA^{-3} [9], equivalent to a site occupation probability of 0.21. Initially we have tested random removal of atoms, but this does not produce good agreement with the experimental data for higher temperatures/lower densities [7, 8] and predicts a percolation transition at $p = 0.18$. In the results presented here we have used a criterion for atom removal chosen to give good

agreement with the experimental structure factor at a density of 0.00268 \AA^{-3} , *i.e.*, at a temperature just below the critical point. The calculated and experimental structure factors are shown in Figure 1. For convenience we have used the same amplitude of random

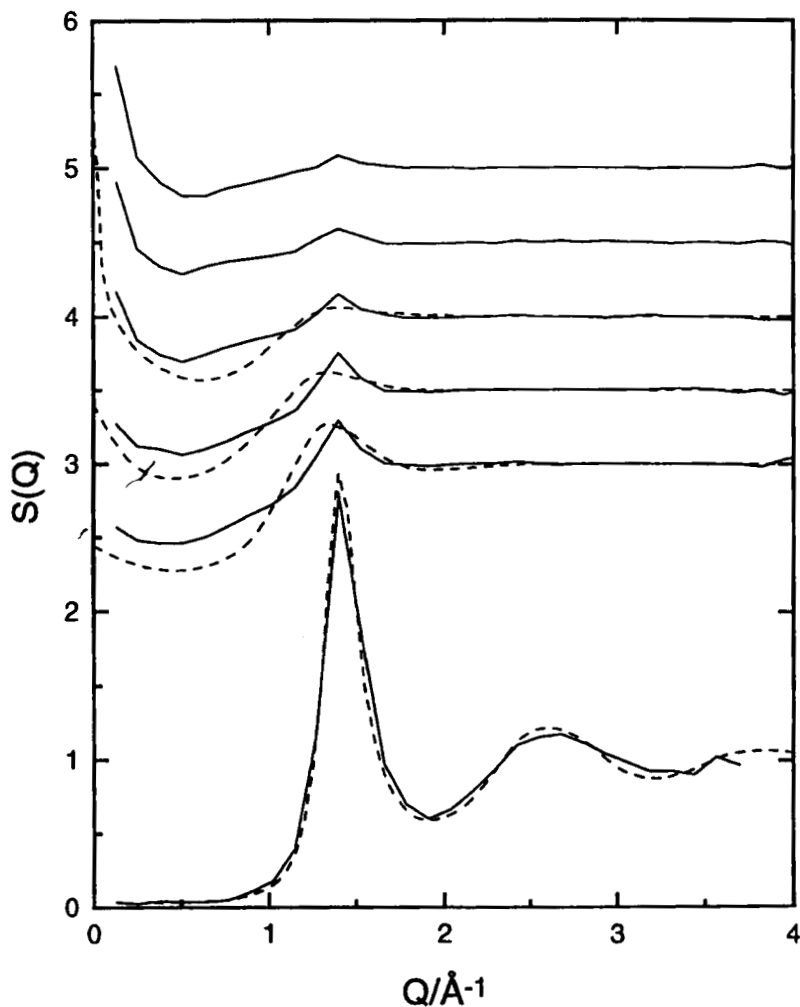


FIGURE 1 Total structure factors, $S(Q)$, for expanded Cs at, in ascending order $\rho = 0.00832, 0.00548, 0.00434, 0.00268, 0.0017$ and 0.0014 \AA^{-3} . Solid curves: experimental data [7]. Broken curves: atom removal method.

Gaussian displacement at all temperatures: this does not make any significant difference to the percolation results. Figure 2 shows $R(p)$; the percolation transition occurs at $p = 0.202$, quite close to the experimental value. Again, we could have deliberately modified the

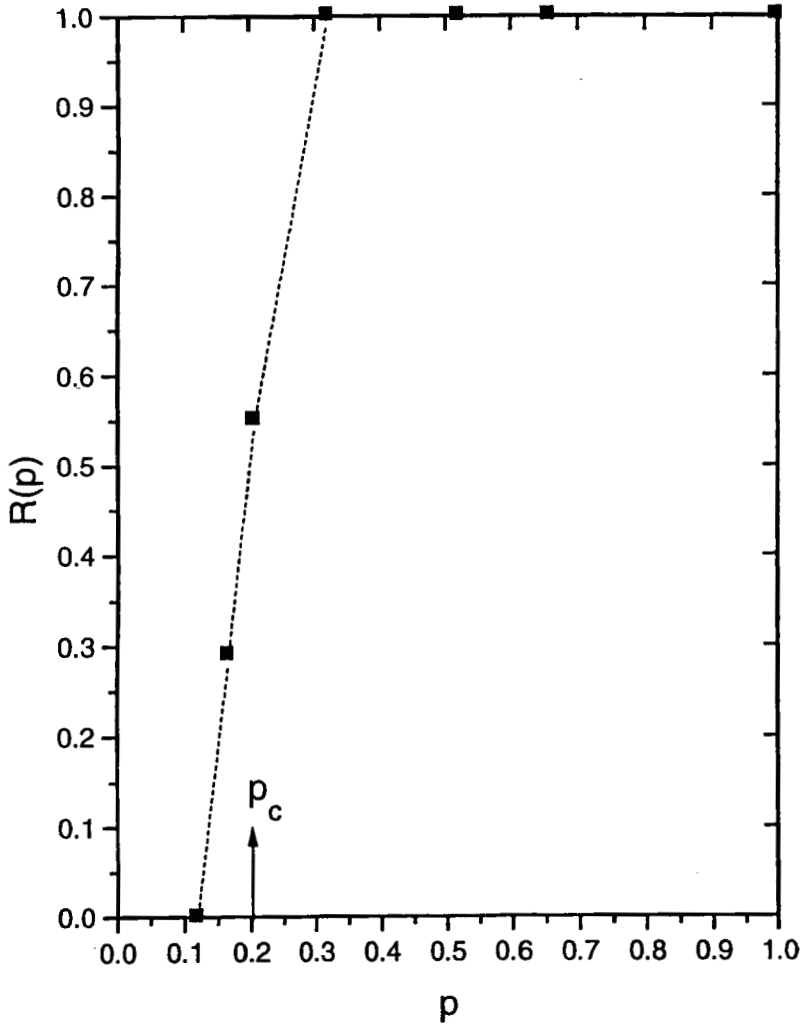


FIGURE 2 Reachability function, $R(p)$, as defined in the text. Circles indicate calculated values. The arrow is drawn at $p_c = 0.21$ (the experimental value for the critical point).

criterion for atom removal to reproduce this quantity exactly, but this would not have been a useful exercise.

The average separation of Cs atoms, defined from the first peak in $g(r)$, stays remarkably constant between the triple point and just below the critical point [7, 8]. If one associates this separation with metallic bonding then clearly the bond percolation transition in the atom removal method is associated with the metal–insulator transition. However it seems unlikely that this is directly associated with the critical point in a general sense. The ratio of the critical point and triple point densities in other simple fluids, *e.g.*, the inert gases, is much higher and hence could not be associated with a bond percolation transition, whatever the local structure (which in any case is not enormously different from that of the alkali metals [10]). This suggests that at the metal–insulator transition in Cs there is a considerable change in the local interatomic potential due to increased electron localisation, and it is this that indirectly determines the critical point.

We have obtained an other interesting result that seems to support this suggestion. In Figure 3 we show the coordination number distribution, $D(n_c)$, as a function of density. At densities close to and above the critical point it is clear that the number of singly coordinated atoms increases significantly; a proportion of these are dimers (see Fig. 4). However there is nothing within the removal criterion used that specifically favours dimers, and the criterion is chosen on the basis of a result at higher density where dimerisation is not apparent. We conclude that this tendency is somehow ‘inherent’ in the criterion necessary to reproduce the data, which takes the place (in a general sense) of the interatomic potential. Dimers are known to exist in the vapour phase, and it has been proposed that dimerisation is significant in driving the metal–insulator transition. A recent theoretical calculation concerning dimerisation in expanded Rb, prompted by inelastic neutron scattering evidence of collective oscillations which could be associated with dimers close to the critical point [11], predicts similar behaviour in terms of the onset of dimer formation as a function of ρ/ρ_c , though the proportion of dimers is somewhat larger. However the agreement would only be expected to be qualitative since ours is a very simple model and theirs a very simple (lattice based) theory.

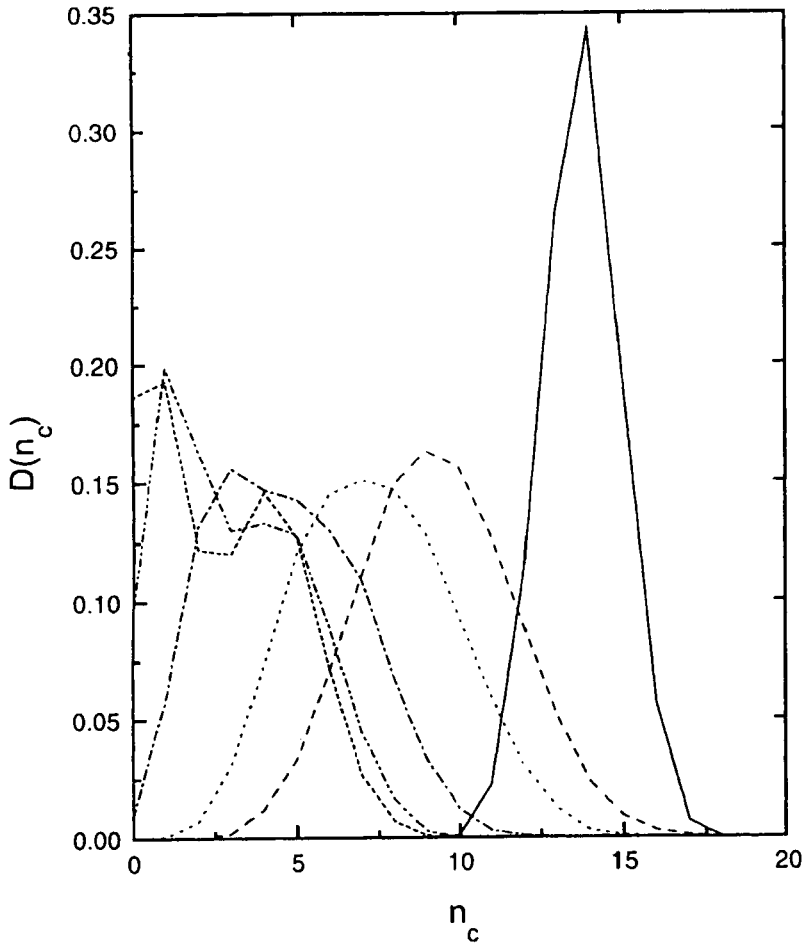


FIGURE 3 Coordination number distribution of near neighbours for $\rho = 0.00832$ (solid), 0.00548 (dash), 0.00434 (dot), 0.00268 (dash-dot), 0.0017 (dash-dot-dot) and 0.0014 \AA^{-3} (short dash).

4. CONCLUSIONS

We have shown that there is strong evidence for associating the metal-non-metal transition in expanded Cs with a percolation transition in the metallic bonding network. There must be a rapid

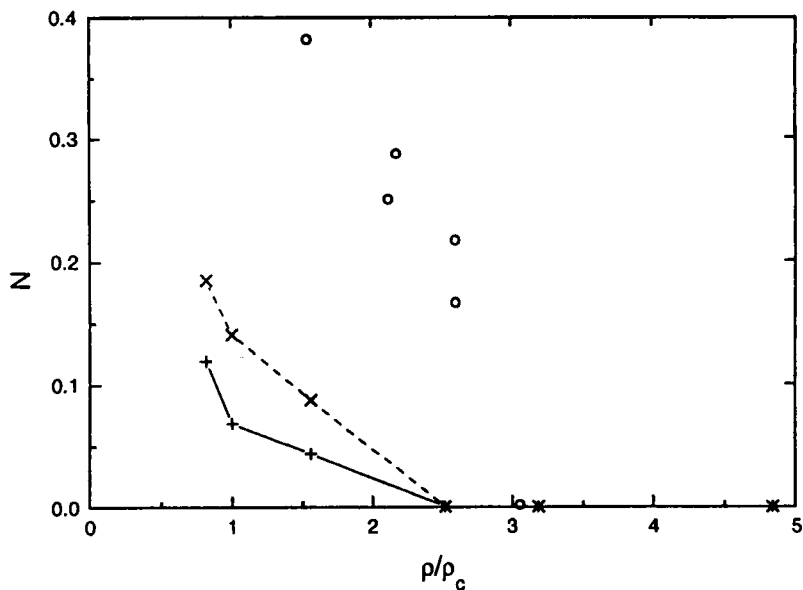


FIGURE 4 The proportion of singly coordinated Cs atoms as a function of density (+) and the proportion of Cs atoms in dimers (x), as obtained using the atom removal method. The proportion of Rb atoms in dimers, from a lattice based model [10], is also shown (o).

change in the interatomic potential at this point, and there is evidence of a trend towards the formation of dimers. These changes are probably responsible for determining the critical point.

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