The metal-nonmetal transition in expanded caesium

The metal–non-metal transition in expanded caesium

V M Nield, M A Howe and R L McGreevy

Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK

Abstract. The structure factor of expanded caesium along its liquid–vapour coexistence curve has been modelled using the RMC method. It is shown that as the density decreases a considerable amount of clustering takes place, which can be associated with a strong tendency to maintain metallic bonding. Some finite atomic clusters are present close to the critical point as well as 'weak links' within infinite clusters, suggesting that the metal–non-metal transition can be thought of as a bond percolation transition. The resistivity of the bond network is calculated from the structure in two ways—by applying Kirchoff's laws (delocalized electrons) and by using a random-walk (hopping conduction) approach—with remarkable success.

1. Introduction

The relationship between the liquid–gas (LG) and metal–non-metal (MNM) transition has been extensively studied, particularly in the region of the critical point. Away from this region the density difference between the coexisting liquid and gas phases is large, and the MNM transition occurs at the same time as the LG one. However, its position close to the critical point is difficult to study because of the high temperatures and pressures involved; for caesium $T_c = 1924$ K, $P_c = 9.25$ MPa and $d_c = 0.38$ g cm^{-3} (Jüngst et al 1985). For mercury it has been ascertained that the transition to non-metallic behaviour is continuous and occurs significantly below the critical point (Hensel 1990). However for the alkali metals the MNM transition is discontinuous, occurring at, or very close to, the LG critical point (Winter et al 1988). In the last few years the first structural measurements have been made on expanded alkali metals along their liquid–vapour coexistence curves (Winter et al 1987, Franz et al 1980). This has led to renewed effort in the calculation and understanding of the resistivity of these systems (e.g. Hensel and Uchtmann 1989 and references therein).

In the present work the application of reverse Monte Carlo (RMC) modelling to neutron diffraction data for expanded caesium along the coexistence curve (Winter et al 1987, 1989) is reported. The possibility of treating the MNM transition as a bond percolation problem is considered. The effect of structure on the resistivity has been investigated in two ways, the first using Kirchoff's laws and the second a random walk approach.

2. RMC modelling

2.1. Details

The RMC modelling technique (McGreevy and Pustzai 1985) is similar to Metropolis Monte Carlo analysis, except that one seeks to minimize the difference between the experimental and calculated structure factors, rather than the energy. Hence no interatomic potential function is necessary—a definite advantage in the present case where the large range of densities makes the choice of suitable potentials particularly difficult. The experimental structure factors were measured in a limited Q-range ($0.3\ \text{Å}^{-1}$ to $3\ \text{Å}^{-1}$) and so an extrapolation to lower Q-values was performed by the experimentalists. In some cases it was found necessary to add a 'tail' above the high-Q limit, for the purposes of modelling. No 'tail' was added for the 323 K structure, one with damped oscillations was used at 573 K, and the 'tails' used in all other cases were structureless. Reasonably good RMC fits were obtained (figure 1) for all temperatures except the highest one. The poor agreement in this case seems likely to be the result of inaccuracies in the low-Q extrapolation (R Winter, private communication) and the limited simulation size, which becomes relevant as the correlation length diverges at the critical point.

2.2. Results and discussion

It is well known that along the liquid–vapour coexistence curve of caesium the positions of the first maximum and first minimum of the radial distribution function remain approximately constant, with values of about 5.5 Å and 7.5 Å respectively, as illustrated in figure 2. (The first minimum has the slightly higher value of 7.8 Å in the lowest density measurements.) In a simple sense this implies that the 'metallic bond' has a mean length of 5.5 Å and a maximum length of 7.5 Å. In all of the following therefore two caesium atoms are taken to be bonded if their centres are joined by a vector of length less than 7.5 Å. The resulting bond networks (figure 3) give an indication of the paths 'available' for electron transport. At high densities the bond network is dense and evenly distributed over the whole of the configuration box (the structure is approximately hexagonal close packed). Clustering occurs as the density decreases, keeping many atoms highly coordinated. However the average coordination number, Z, drops because of an increase in the number of atoms on the surface of clusters. This explains on an atomic level the steady decrease in Z, at almost constant nearest neighbour distance, as the density decreases (figure 4). It is also apparent that in the lower density cases there are 'weak links' in possible conduction pathways, because of the low coordination of some atoms, an observation which suggests the applicability of percolation theory to the MNM transition.

3. Bond percolation

A bond percolation transition is best pictured by considering a configuration box containing an infinite cluster of bonds (i.e. bonds connecting opposite sides of the box). As individual bonds are slowly removed a point is reached where the last path connecting opposite sides of the box is broken and only finite clusters remain. This point is termed the percolation threshold, and is characterized by the critical average bond number (coordination number), Z_c. It is proposed that the MNM transition
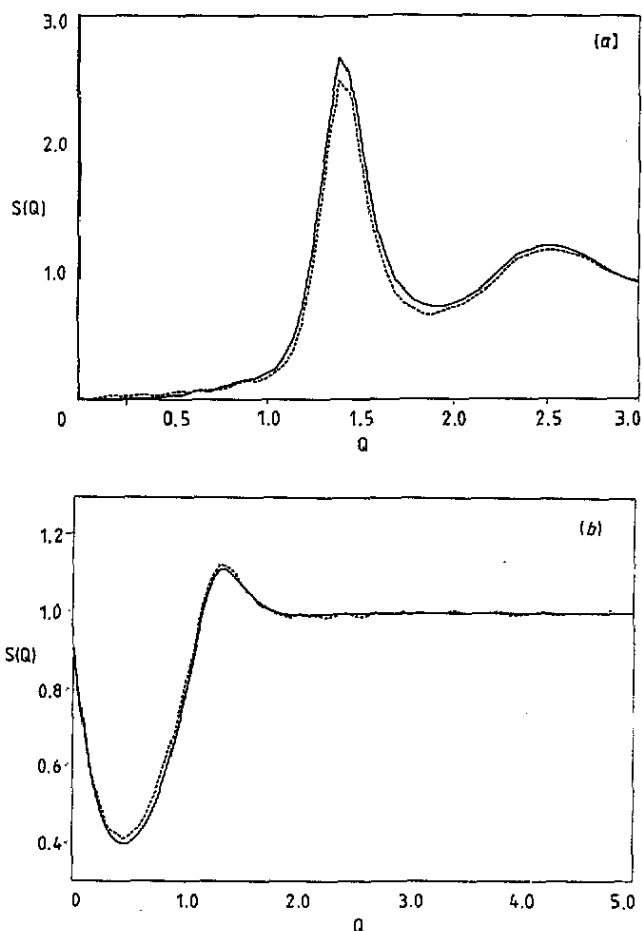
Figure 1. Experimental structure factor (solid line) and RMC fit (dashed line) at (*a*) 323 K and (*b*) 1673 K.

corresponds to this threshold, an idea supported by the observation of finite as well as infinite clusters in the bond network for caesium at the lowest density. Z_c has been computed to be 2.7 for a totally random configuration (Pike and Seager 1974). The method of calculation involves a fixed array of atoms, with only the number of bonds changing. This obviously does not correspond to the present case, where the atom positions are changing and clustering is occurring as the transition is approached, but should give a reasonable lower limit. (Z_c must be higher in the present case because clustering means that many atoms stay highly coordinated.) In figure 4 it can be seen that $Z_c = 2.7$ gives a MNM critical density of 0.31 g cm^{-3}, compared to 0.38 g cm^{-3} for the LG critical point. This is of the correct order and corroborates the percolation model proposed.

4. Resistivity calculations

The calculations which follow are not intended to reproduce the experimental resistivity quantitatively, but rather to stress the crucial role of the atomic structure, in
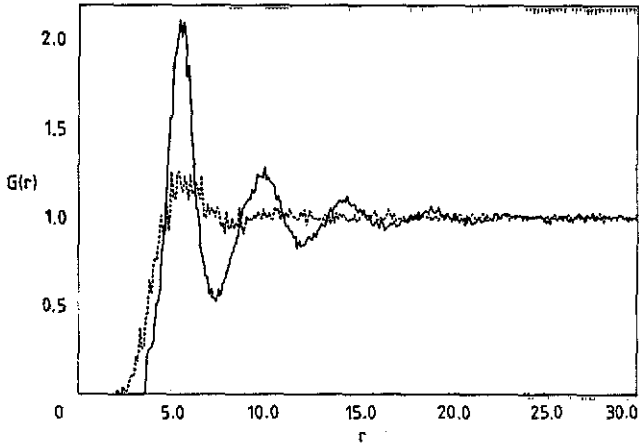
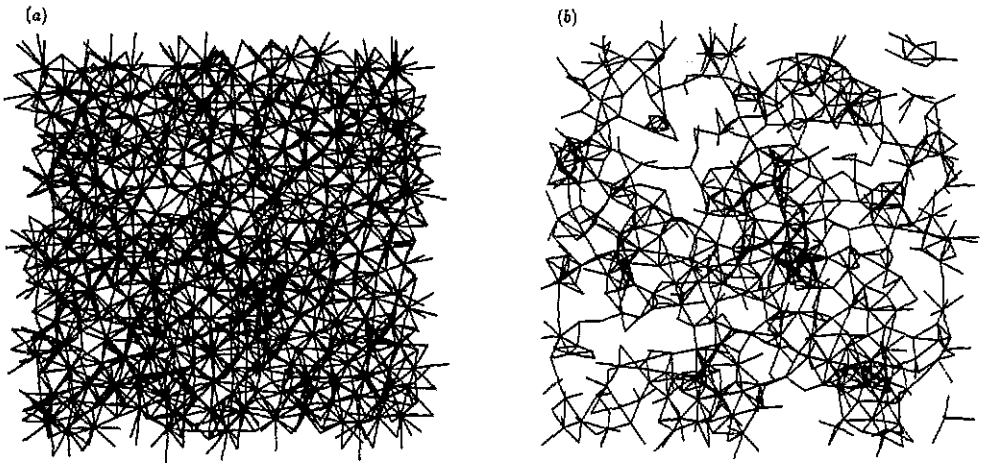**Figure 2.** RMC model radial distribution functions at 323 K (solid line) and 1673 K (dashed line).

Figure 3. Bond networks at (*a*) 323 K and (*b*) 1673 K.

particular the development of clustering, on electron transport. Two calculations have been performed, focusing on different possible conduction processes. In the first, using Kirchoff's laws, the electron wave functions are considered to be completely delocalized. This is clearly applicable at high densities. The second, using a random walk technique, assumes that electron wave functions are essentially localized but with 'hopping' allowed between bonded atoms, and so is better suited to low densities. The lowest density data set has been excluded from the calculations owing to the poor RMC fit and the sensitivity of the results in this case to small structural changes.

To apply Kirchoff's laws to the bond network a potential was set up across the z-direction of the configuration box and all the atoms allotted a value at random. Atoms were then picked arbitrarily, and the potentials of their neighbours modified to satisfy Kirchoff's current law (the sum of the currents at any node is zero). This procedure was repeated until convergence. Ohm's law was used to calculate the network resistance from the current flowing through the z-faces, assuming unit resis-
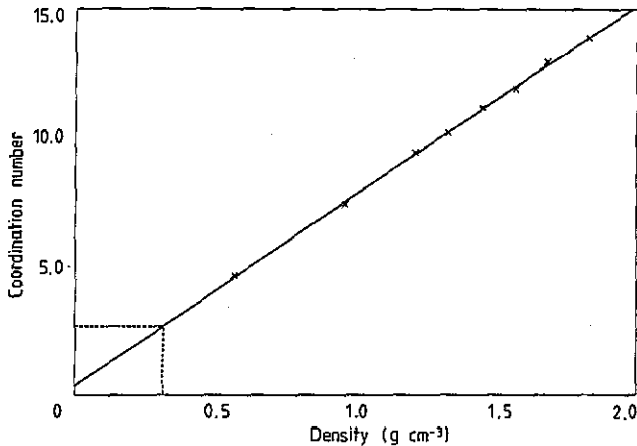
Figure 4. Average coordination number, Z, calculated by integration of $g(r)$ up to 7.5 Å, as a function of density. The data have been extrapolated to predict the density of a bond percolation transition corresponding to $Z = 2.7$.

tance for each bond. To a first approximation the effect of thermal motion can be included by multiplying the calculated network resistivities by the temperature. The results were scaled to the highest density measurement, and surprisingly good agreement was found with the experimental resistivity (Winter 1987) as seen in figure 5. The agreement is closest at high densities, as might be expected from the ideas of delocalization implicit in the model, and the divergence at lower densities is slightly stronger than found experimentally.
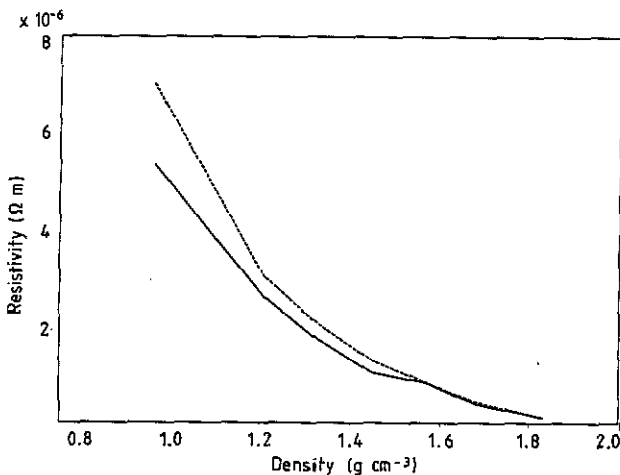

Figure 5. Comparison of the experimental resistivity (solid line) and that calculated using Kirchoff's law (dashed line).

In the random walk approach the basic procedure was to treat a series of totally self-avoiding random walks, performed from an initial atom, as resistors in parallel. Therefore no two walks from the same atom were allowed to pass down the same bond. Only walks which reached a certain vector length (generally taken as the box size) were included, their resistance being equal to the number of bonds involved.

The results were almost independent of the exact walk distance provided it was comparable with the length scale of the model. Twenty walks were permitted from each starting atom (this is greater than the largest Z of any of the atoms). The maximum number of steps (bonds) to complete a walk was decided by investigating the effect on the resistivity of this parameter. Above a certain point a change in the number of steps only scales the results, and so a value in this region was used. After multiplying by the temperature, as before, the behaviour of the resistivity with density is again well reproduced (figure 6). The agreement is seen to be good over the whole density range, which is a little surprising considering that the wave functions are being treated as localized. The results differ from those of the Kirchoff's law method in that the low-density divergence tends to be slightly too small.
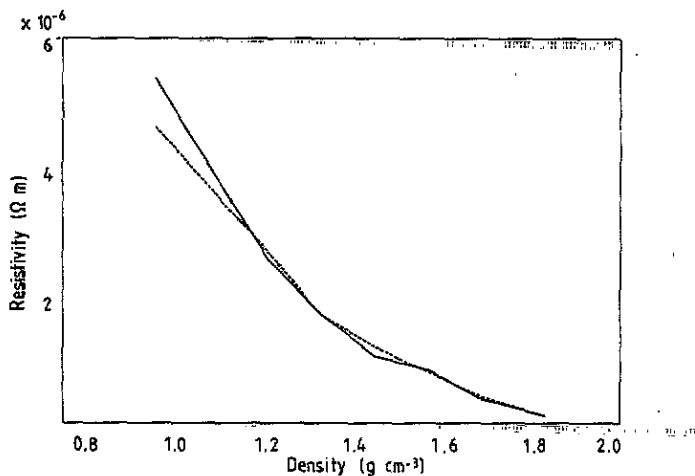

Figure 6. Comparison of the experimental resistivity (solid line) and that calculated using a random walk approach (dashed line).

5. Conclusion

It has been shown that as the density decreases towards the liquid–gas critical point the atoms in liquid caesium start to cluster, some of these clusters being finite close to the critical point. The resistivity has been calculated using only the RMC-produced atomic configurations, with multiplication by the temperature to take account of the effect of thermal motion. Since this correctly reproduces the experimentally determined density dependence, it must be concluded that structure is the major determining factor for the resistivity, and that any calculations which do not use a realistic model for it cannot succeed. Evidence has been presented which suggests that the metal–non-metal transition can be thought of as a bond percolation transition. Future work on an inert gas near its critical point should make clear whether the bond percolation approach is applicable to the liquid–gas transition, which might suggest that this occurs simultaneously with the MNM transition in the alkali metals.

Acknowledgments

References

Franz G, Freyland W and Hensel F 1980 *J. Physique Coll.* **41** C8 70
Hensel F 1990 *J. Phys.: Condens Matter* **2** SA33
Hensel F and Uchtmann H 1989 *Ann. Rev. Phys. Chem.* **40** 61
Jüngst S, Knuth B and Hensel F 1985 *Phys. Rev. Lett.* **55** 2160
McGreevy R L and Pusztai L 1988 *Mol. Simul.* **1** 359
Winter R, Bodensteiner T, Gläser W and Hensel F 1987 *Ber. Bunsenges. Phys. Chem.* **91** 1327
Winter R, Noll F, Bodensteiner T, Gläser W, Chieux P and Hensel F 1988 *Z. Phys. Chem.* **156** 145