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The structure of expanded mercury

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Abstract. The structure of expanded mercury along its liquid–vapour coexistence curve has been studied in detail by applying the reverse Monte Carlo modelling technique to the x-ray diffraction data of Tamura and Hosokawa (Tamura K and Hosokawa S 1994 *J. Phys.: Condens. Matter* **6** A241). The models suggest that as the density decreases there is an initial change from a more close-packed to a less close-packed structure. Whilst most atom pairs retain the same near-neighbour distance, of about 3.0 Å, a few change to having a slightly larger neighbour distance of about 3.7 Å. At the lower densities many atoms have a very low coordination, indicating that they are on the edges of clusters, or on 'pathways' between clusters.

1. Introduction

It is still not known exactly what causes a metallic element to transform into a non-metal, and whether this electronic phase transition is continuous or discontinuous (Hensel and Edwards 1996). Expanded metals form a testing ground for the various theories that are advanced. Expanded metals are metals near their critical points, where the temperature is too high to permit a liquid to be the stable state, and the pressure too high to sustain a gas. In expanded mercury the density is the dominant factor governing the metal–non-metal transition, and it is believed that fluctuations in density are important in determining the physical properties in the critical region (Hensel 1990).

Unfortunately the critical point of most metals is at such extremes of temperature and pressure that it is very difficult to make accurate measurements of any steady-state properties. For example for mercury the critical point is at 1478 °C, 1673 bar and occurs when the density is 5.8 g cm^{-3}. However, recently structural measurements have been made along the liquid–vapour coexistence curves for caesium, rubidium and mercury (Winter *et al* 1987, 1991, Tamura and Hosokawa 1992, 1993, 1994). The structure of the former monovalent metal was studied in detail by Nield *et al* (1991) using the reverse Monte Carlo technique. This study showed that as the critical point was approached the atoms formed clusters, with the critical point, and probably the metal–non-metal transition, corresponding to a bond percolation transition.

For mercury the conductivity can be described by a nearly free-electron model down to 11 g cm^{-3}, and below 9 g cm^{-3} it is essentially semiconducting. Hence the metal–non-metal transition does not coincide with the liquid–gas one in this case. It is found that many physical phenomena show anomalous behaviour in the region between 11 and 5.8 g cm^{-3}. It is important, therefore, to understand the structure of expanded mercury in this region, and useful to compare this with that of caesium.

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In the present paper we apply the reverse Monte Carlo technique to x-ray diffraction data measured by Tamura and Hosokawa (1994). The more advanced modelling that we employ enables more detailed information to be obtained about the structure than was available previously.

2. Reverse Monte Carlo modelling of expanded mercury

Reverse Monte Carlo (RMC) modelling was developed by McGreevy and Pusztai (1988) to allow detailed structural information to be obtained from diffraction data on liquids and amorphous materials. With this technique the positions of atoms in a configuration obeying periodic boundary conditions are altered until they give good agreement with experimentally obtained structure factors or pair distribution functions. The final atomic positions provide one possible model of the structure of the material under study. RMC modelling has been successfully applied to the room temperature structure of mercury by Petkov and Yunchov (1995).

In the present work the initial model at each density consisted of approximately 5000 atoms arranged at random, but moved a minimum distance apart, corresponding to the closest approach of two atomic centres. It was found, by inspection of the pair distribution functions during modelling, that a slightly larger closest-approach value was appropriate at room temperature as opposed to the higher-temperature (lower-density) data sets, since the atoms have sufficient energy to approach each other more closely at higher temperatures. The modelling was to the structure factors obtained by x-ray diffraction by Tamura and Hosokawa (1994). These data have a minimum Q of about 0.8 Å, and hence little small-angle scattering is included.

Table 1 gives information about each data set, including the closest-approach distance used in the modelling and the renormalization constants. The renormalization constant multiplies the data during fitting, and is determined by RMC modelling to enable a good fit to the data to be obtained. It was found that with the lower-density data sets, peaks occurred in the pair distribution function near the low-r cut-off, irrespective of what the cut-off was, unless such a renormalization factor was applied. The renormalization is close to one for the less extreme experimental conditions, but differs from these values at lower densities, i.e. higher temperatures and pressures. It is likely that either the density or the corrections or both are less accurately determined for these data sets. Figure 1 shows the quality of fit to the structure factor obtained for expanded mercury at 9.82 g cm^{-3}. The pair distribution functions obtained by averaging over eight model configurations produced by RMC modelling in each case are shown in figure 2. The spike at low r in the lowest-density data set shows that renormalization does not correct all of the problems with the data in this case.

Table 1. Information about the data sets, including the modelling parameters used in each case.

Density (g cm^{-3})	Temperature (°C)	Pressure (bar)	Closest approach (Å)	Renormalization constant
13.55	20	6	2.6	1.00
12.40	500	51	2.5	1.00
10.98	1000	420	2.5	1.09
9.82	1300	1166	2.5	1.17
9.24	1400	1559	2.5	1.19
3.43	1500	1585	2.5	0.82

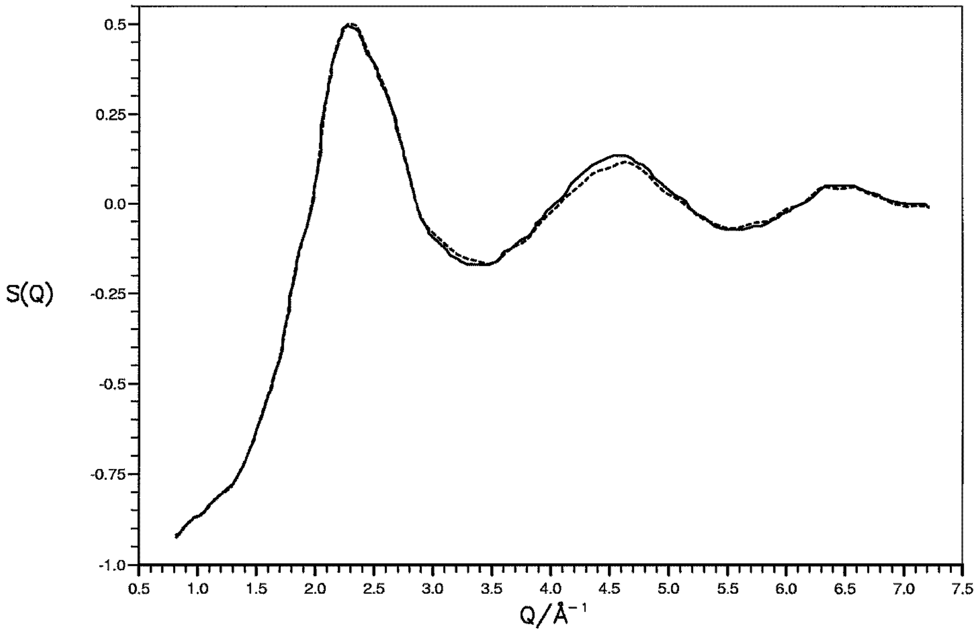

Figure 1. The RMC fit (dashed line) to the 9.82 g cm^{-3} experimental structure factor of expanded mercury (solid line).

3. Results and discussion

The pair distribution functions obtained from RMC modelling, shown in figure 2, can be compared to those obtained by direct transformation by Tamura and Hosokawa (1994). The two are in reasonable agreement at the higher densities, where no renormalization was necessary. At these higher densities, the pair distribution function shows significant structure, with the first peak at 3.0(1) Å, and the second at 5.8(2) Å. As the density of the liquid is decreased, the position of the first peak increases only slightly, to 3.1(1) Å. The lack of change in this peak position indicates that the bonding remains unchanged. However, from our models, a shoulder or side peak appears to be present on the high-r side of the first peak at the lower densities. This is most evident from the 9.82 and 9.24 g cm^{-3} data, and must indicate that there is a second separation between near neighbours, of approximately 3.7 Å. The first peak position increases to 3.5(1) Å in the lowest-density data set, which is in the dense-vapour region.

The average coordination number, Z, can be studied, together with the distribution of coordination numbers in the RMC model. The coordination number can be calculated in a number of ways, which take different account of the overlap of the second-neighbour shell of atoms with the first-neighbour shell. In figure 3 two methods have been used. The first integrates the radial distribution function up to the first maximum (3.0 Å) and then doubles this, hence giving an underestimate of the true coordination number. The second integrates up to the first minimum, giving a more realistic estimate. The first minimum was taken as 4.7 Å, since this is beyond the side peak. When integrating up to 3.0 Å, Z is found to be proportional to density at the higher densities, but there is an upturn from linearity at the lowest density, although less strong than that seen by Tamura and Hosokawa (1994).

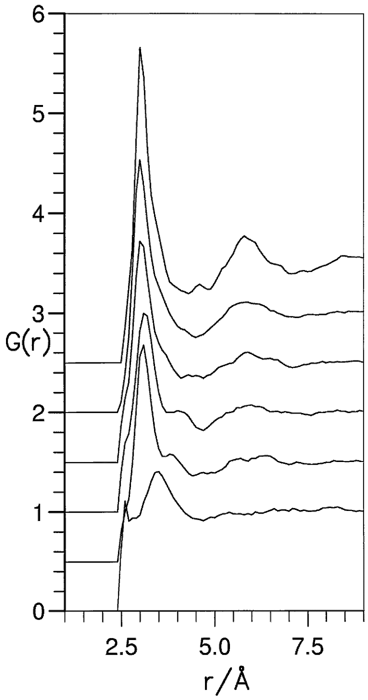

Figure 2. Pair distribution functions obtained from RMC modelling for expanded mercury. The curves correspond, from bottom to top, to the models for the 3.43, 9.24, 9.82, 10.98, 12.40 and 13.55 g cm^{-3} density structures, with successive densities displaced vertically by 0.5.

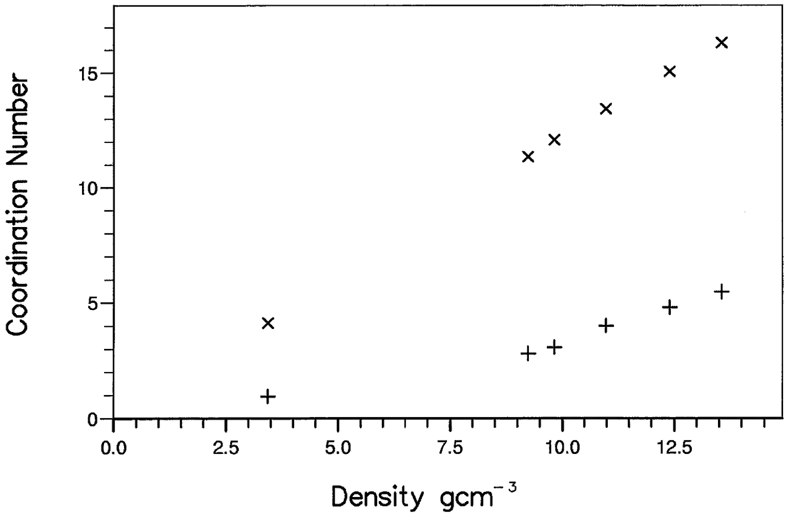

Figure 3. The average coordination number of expanded mercury, calculated by integrating the radial distribution function up to 3.0 Å and doubling (+) and by integrating it up to 4.7 Å (×).

However, when integrating to 4.7 Å the coordination number is proportional to the density over the complete range of densities. This integration limit is more meaningful, and hence

Table 2. The percentage of atoms with each coordination number at various densities. Neighbours were calculated up to 4.7 Å.

Number of neighbours	13.55 (g cm^{-3})	10.98 (g cm^{-3})	9.24 (g cm^{-3})	3.43 (g cm^{-3})
0	0	0	0	0.7
1	0	0	0	3.9
2	0	0	0	11.6
3	0	0	0	20.4
4	0	0	0	23.6
5	0	0	0	20.0
6	0	0	0.2	12.0
7	0	0	0.8	5.5
8	0	0.1	3.3	1.8
9	0	0.6	9.0	0.4
10	0	2.5	17.0	0.1
11	0	7.8	23.7	0
12	0.2	16.6	22.2	0
13	1.4	24.2	14.4	0
14	7.2	23.6	6.9	0
15	18.8	15.6	2.0	0
16	27.9	6.7	0.4	0
17	25.5	1.8	0.1	0
18	13.5	0.4	0	0
19	4.4	0	0	0
20	0.9	0	0	0
21	0.2	0	0	0
22	0	0	0	0

this is believed to be the true trend. Such a linear relationship was also seen for expanded caesium (see, for example, Nield *et al* 1991).

The coordination number decreases considerably with decreasing density, showing that although the near-neighbour distance is largely unchanged, on average each atom has fewer neighbours. This is mostly caused by the distribution of coordination numbers possessed by the atoms in the configuration shifting to lower values as the density decreases, as shown in table 2. (In this table the coordination numbers were calculated by integrating up to 4.7 Å, but very similar trends are seen with lower integration limits, except that there is a shift to lower coordination numbers for all densities.) In other words, the commonly mentioned clustering does not simply keep the local neighbour environment unchanged in the centre of clusters, while atoms on the outsides of the clusters have fewer neighbours because of their situation. At the higher densities it is more appropriate to think in terms of a gradual change from a more close-packed to a less close-packed structure. As the density decreases further, many atoms have a small number of neighbours, indicating that they are on the surface of clusters, or on ‘pathways’ between them. However, it should be borne in mind that the lack of low-Q scattering in the experimental data could mean that the model structure contains less clustering than is present in the real material.

For expanded caesium it was suggested that the metal–non-metal transition could be thought of as a bond percolation transition (Nield *et al* 1991). In such a transition the RMC configuration of atoms is best envisaged as a configuration of ‘bonds’ (a ‘bond’ being taken to exist whenever two atoms are within a certain distance of each other). As Z decreases, the number of ‘bonds’ does also, until a point is reached where there is no longer a pathway connecting the opposite sides of the configuration box: this is the bond percolation transition. The criterion for a bond percolation transition in a totally random configuration is for the coordination number, Z_c, to fall to 2.7 (Pike and Seager 1974). This criterion takes no account of clustering, which will increase Z_c slightly.

In caesium the liquid–gas and metal–non-metal transitions occur very close to one another (Winter *et al* 1988), and so it was unclear whether the bond percolation approach was more generally applicable to the liquid–gas transition near the critical point (Nield *et al* 1991). From figure 3 it can be seen that with the larger 'bond' length of 4.7 Å the coordination number for mercury is about 11 at a density of 9 g cm^{-3}, which is the density above which the material is semiconducting. (It is difficult to choose one 'bond' length as the most appropriate, but our conclusions are unaffected, provided that the choice is within the first-minimum region of the pair distribution function. In fact, at higher densities, where the metal can be described by a nearly free-electron model, the electron mean free path is closer to 7 Å (Hensel 1990)). At 5.8 g cm^{-3}, the critical-point density, Z has a value of close to 7. In fact, even if the coordination number at this density is only calculated up to 4.1 Å, it is still significantly larger than Z_c, with a value of 5.5. Hence we can conclude that the metal–non-metal transition is certainly not related to a bond percolation transition, and even near the liquid–gas critical point the structure seems too highly coordinated for this to be a realistic model.

4. Conclusions

The reverse Monte Carlo method has been successfully used to model the structure of mercury along its liquid–vapour coexistence curve. The modelling confirms that the first peak position in the pair distribution function, at 3.0 Å, changes very little until the dense-vapour region is reached. However, it is found that there is an additional peak in the pair distribution functions of the 9.82 and 9.24 g cm^{-3} density data, suggesting that some pairs have a different near-neighbour separation of approximately 3.7 Å. The coordination number changes linearly with density through the whole of the density region studied.

Hence, as the density decreases, there is a gradual change from a more to a less close-packed structure. As the density decreases further, some atoms adopt arrangements with a slightly larger near-neighbour distance, and many atoms have a small number of neighbours, indicating that they are on the surface of clusters, or on 'pathways' between them. The metal–non-metal transition cannot be considered in terms of a bond percolation transition, and it seems improbable that such an explanation is applicable to the liquid–gas critical point either.

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