

## Metal-Nonmetal Transition in Expanded Liquid Mercury

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At the anomalously high density of  $\sim 9 \text{ g/cm}^3$ , expanded liquid mercury is found to undergo a metal-nonmetal transition which is associated with the formation of a gap in the density of states at the Fermi energy. Although previous calculations have all yielded values of the density for the metal-nonmetal transition that are too low ( $\sim 5.5 \text{ g/cm}^3$ ), it is shown that a simple model emphasizing fluctuations in the local coordination number produces the correct value.

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During the last ten years, considerable effort has been put into investigating the properties of metals near their critical points. Much of this effort has focused on mercury, one of the few metals whose critical point is accessible under laboratory conditions. A comprehensive understanding of the electron structure of liquid Hg at high temperatures and pressures has so far been lacking. Experimental measurements such as those of the Knight shift,<sup>1,2</sup> conductivity,<sup>3</sup> and optical properties<sup>4</sup> have indicated that as the density is lowered, a gap in the density of states appears to develop between the  $6s$  and  $6p$  bands (and thus at the Fermi energy,  $E_F$ ) at a density,  $\rho$ , of  $\sim 9 \text{ g/cm}^3$ . The opening of this gap is associated with a metal-nonmetal (M-NM) transition at the same density. On the other hand, most theoretical calculations<sup>5,6</sup> indicate that a gap should not open until a density in the region of the critical point is reached ( $\rho_c \sim 5.5 \text{ g/cm}^3$ ).

To explain the anomalous behavior of Hg in both the liquid and vapor phases near the critical point, Turkevich and Cohen<sup>7</sup> have postulated the existence of an excitonic insulator phase. They argue that no single-particle picture, with or without disorder, can produce a real gap at  $\rho \sim 9 \text{ g/cm}^3$  and therefore a collective effect must be occurring. In this paper, I propose a single-particle model that produces a real gap at the correct density. Central to this model is the fluctuation in local coordination numbers caused by the disordered structure of an expanded fluid.

The strongest evidence that a real gap in the density of states opens at  $\rho \sim 9 \text{ g/cm}^3$  comes from the NMR measurements of El-Hanany and Warren,<sup>1</sup> which show that the Knight shift vanishes at this density,<sup>2</sup> indicating that the density of  $s$  states at  $E_F$  becomes negligible. As already noted by others,<sup>7,8</sup> these measurements are inconsistent with a pseudogap model. In an attempt to understand the vanishing of the Knight shift, Mattheiss and Warren<sup>5</sup> carried out band-structure calculations for Hg. To simulate the change in density they performed their calculations for crystal-line structures of different coordination number. The justification for this is as follows: Neutron-diffraction measurements<sup>9</sup> on expanded liquid Rb for densities

down to  $\sim \frac{1}{3}$  of the melting-point density indicate that the expansion of metals occurs in a way that is similar to that of the rare-gas liquids.<sup>10</sup> In these systems the structural data show that the nearest-neighbor distance remains roughly constant as the density is reduced; the coordination number, however, decreases. For liquid Hg a similar analysis of the x-ray measurements yields a constant nearest-neighbor value of  $3.07 \text{ \AA}$  in the limited density range  $13.68\text{--}12.87 \text{ g/cm}^3$ .<sup>11</sup> The fact that the interatomic distance of the Hg dimer<sup>12</sup> is very similar ( $\sim 3.2 \text{ \AA}$  vs  $\sim 3.1 \text{ \AA}$ ) to that of the liquid<sup>11</sup> indicates that if changes do occur at lower densities, they should be quite small. The average coordination number,  $\bar{Z}$ , is then nearly proportional to the density. Matheiss and Warren<sup>5</sup> showed that as  $\bar{Z}$  (and thus  $\rho$ ) decreased by a factor of  $\sim 3$ , the bandwidth of filled states decreased by a factor of  $\sim 2$ . However, a real gap developed only at  $Z \sim 4$  (or  $\rho \sim 5.5 \text{ g/cm}^3$ ) in agreement with other calculations but *not* with experiments.

The model discussed here is also based on the assumption of a linear decrease in average coordination number with decreasing density, but in addition it takes into account the fact that the actual local coordination numbers will be distributed randomly over a range of values surrounding the mean value. As the density is reduced, some atoms will have such low coordination numbers that interactions with their neighbors are insufficient to cause overlap between their  $s$  and  $p$  states; they will thus have an "energy gap" between their  $s$  and  $p$  states. From previous calculations<sup>5,13</sup> on fluid Hg with uniform density, one can estimate that for  $Z = 4$  ( $\rho \sim 5.5 \text{ g/cm}^3$ ) a gap is just on the verge of opening, while for  $Z = 3$  ( $\rho \sim 4.1 \text{ g/cm}^3$ ) a gap of  $2\text{--}3 \text{ eV}$  should exist. Thus although the strong disorder in the random fluid will produce band-tailing effects that will smear out local effects for atoms with  $Z = 4$ , we expect that for those with  $Z \leq 3$  the band tails will be insignificant near  $E_F$  and shall assume that a real gap remains. We find that at a well-defined density, the local gap of these low-coordinated atoms "percolates" throughout the liquid, creating a real gap in the total density of states. It should be not-

ed that this random model is completely unrelated to that of Cohen and Jortner<sup>14</sup> in which *classical* percolation theory was applied to a system assumed to have microscopic inhomogeneities.

The physical basis of this model of the M-NM transition is illustrated in Fig. 1 for a cluster of atoms on a two-dimensional lattice representing an instantaneous configuration. For the example shown, the maximum value of  $Z$  for each atom is 6, but because the average density is somewhat reduced, "vacancies" are present and  $\bar{Z} = 4.9$ . Now consider a tight-binding picture in which transport occurs by means of nearest-neighbor hopping. We assume as above that atoms with  $Z \geq 4$  have a continuous density of states, while those with  $Z \leq 3$  have a gap at  $E_F$  in their local density of states as shown in Fig. 2. In Fig. 1(a) all of the atoms in the configuration shown have  $Z \geq 4$ , and thus all take part in conduction; the system is a good conductor. In Fig. 1(b) an additional atom has been removed, causing one atom (the shaded one) to have  $Z = 3$ . This atom now has no states with energy near  $E_F$  which deters electrons having energies near  $E_F$  from hopping onto it from neighboring atoms. These neighboring atoms, indicated by thicker lines, thus have their effective coordination number,  $Z_{\text{eff}}$ , reduced by 1 throughout a range of energy near  $E_F$ . Since this reduction in  $Z_{\text{eff}}$  is sufficient that an additional atom (labeled 1) now has  $Z_{\text{eff}} \leq 3$ , the above effect begins to propagate. From Fig. 1(b), it can be seen that the removal of just one atom from the original configuration is sufficient for an effective energy gap to spread cooperatively throughout the entire cluster, leading now to a M-NM transition. The numbers show the progression of the spread of the energy gap; those with lower numbers helping to create gaps for those of higher numbers. In this example, the gap "percolates" throughout the system when the density is reduced by a moderately small 15%–20%, whereas with the alternative assumption of uniform coordination number, a reduction of ~ 40% is required to achieve the same result.

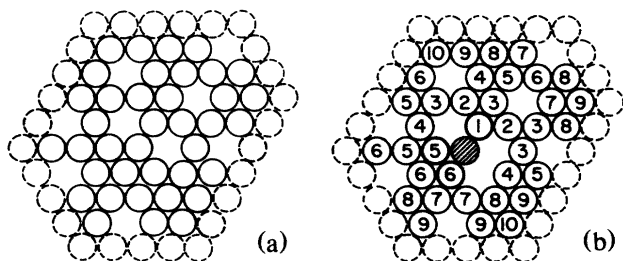


FIG. 1. Atoms in a two-dimensional cluster. The complete border of dashed circles that surround the cluster shows that no vacancies lie on the edge of the cluster. (a) The cluster with nine vacancies. (b) The cluster with ten vacancies. The additional vacancy causes the shaded atom to have only three nearest neighbors.

Although the above example is oversimplified, it illustrates the main aspects of the model. The local-density fluctuations drive the M-NM transition to occur at an average density considerably higher than that predicted for a uniform system. In addition, because the transition depends on the formation of a gap that is governed by probabilistic relations similar to those of the "percolation probability" of percolation theory, it is continuous but very sharp.

The physical effect demonstrated in Fig. 1 can be investigated in a random, three-dimensional system with a simple, tight-binding quantum percolation Hamiltonian:

$$H = \sum_i^Z t_{ij} c_j^\dagger c_i$$

in which the hopping parameter,  $t_{ij}$ , has only two possible values; namely  $t$  if a hop to a particular neighboring site is possible and zero otherwise. We use a standard, single-particle Green's-function method, with a Bethe lattice to represent the disordered system and a Monte Carlo technique (which has been described previously<sup>15</sup>) to produce the random local environment. Since within this model the local atomic configurations play the dominant role in causing the M-NM transition, the use of a Bethe lattice, which produces the correct local atomic environments, should give a good approximation to the density at the transition, even though it ignores closed loop paths.

We take liquid Hg to be a random alloy of Hg atoms and vacancies with the concentration,  $x$ , of Hg proportional to  $\bar{Z}$  and equal to 1.0 at the melting point. We follow Mattheiss and Warren<sup>5</sup> and take  $\bar{Z} \propto \rho$  with  $\bar{Z} = 10$  for  $\rho = \rho_m$ , the density at the melting point, which leads to  $x = \bar{Z}/10$ . We assume that atoms with  $Z_{\text{eff}} \geq 4$  are accessible at all energies near  $E_F$  but take

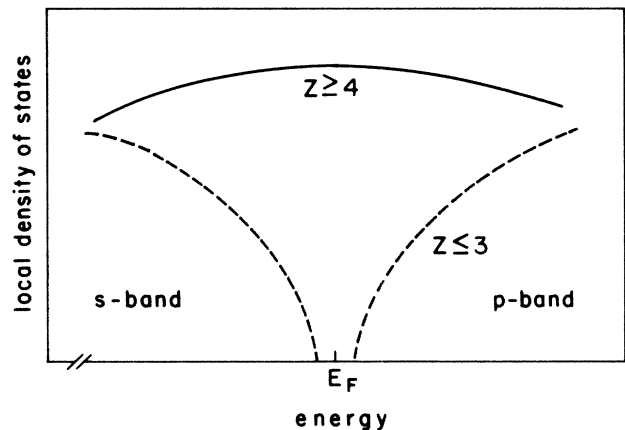


FIG. 2. A schematic representation of the local density of states in the neighborhood of  $E_F$ . The solid curve pertains to atoms with  $Z \geq 4$ . The dashed curve indicates that for  $Z \leq 3$ , a gap occurs at  $E_F$ .

atoms with  $Z$  or  $Z_{\text{eff}} \leq 3$  to have a real gap in the region of  $E_F$ . Since, in actuality, a very small band tail is always present and such band-tailing effects are cumulative, one would not expect the effect of a low-coordinated atom in reducing the  $Z_{\text{eff}}$  of its neighbors to propagate infinitely far, even near the M-NM transition. To make sure that the model does not depend on such an unphysical assumption, I examined the effect of imposing a reasonable cutoff on the propagation of  $Z_{\text{eff}} < Z$ . The calculations show that a cutoff at the sixth nearest neighbor has little effect on the density at which we predict the M-NM transition should take place, but a more severe cutoff does affect our results.

The calculated density of states per atom at  $E_F$ ,  $n(E_F)$ , is shown in Fig. 3 together with the Knight-shift measurements,<sup>2</sup> which are proportional to the density of  $s$  states at  $E_F$ . It can be seen that  $n(E_F)$  drops sharply to zero at  $x = 0.67$  which corresponds to  $Z = 6.7$  and  $\rho \sim 9 \text{ g/cm}^3$  in excellent agreement with experiment. Although at this concentration, only  $\sim 4\%$  of the atoms have  $Z \leq 3$ , this number is sufficiently large to create a gap in the density of states in the system.

The sharpness of the transition is, of course, exaggerated by the simplicity of the model. In the first place, the nearest neighbors of an atom in a liquid do not all lie at the nearest-neighbor distance but instead have a range of interatomic distances  $d$ . Since the overlap integral, which is represented by the hopping parameter  $t$  falls off exponentially with  $d$ , hopping occurs only over some small spread in  $d$  values. Nevertheless, this spread in  $d$  will introduce a range of  $t$  values and broaden the transition somewhat. In addition, the cumulative band-tailing effects mentioned

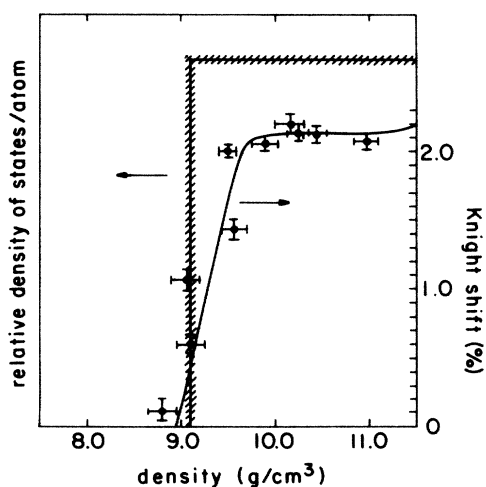


FIG. 3. The calculated density of states of  $E_F$  as a function of density shown on a relative scale (the shaded line). Also shown are the Knight-shift measurements from Ref. 2 (experimental points with connecting line).

above cause atoms that are further from those with  $Z \leq 3$  to have reduced gap widths. Just at the M-NM transition, an effective gap, one that averages over band-tailing effects of all the atoms, forms. As the density is reduced further, the number of atoms with low coordination number grows very rapidly, increasing the effective gap width. These effects, taken together, should account for the gradual increase in gap width deduced from conductivity measurements.<sup>3</sup> Of course, the conductivity measurements themselves show an additional broadening caused by thermal activation across the gap.

The very close agreement between the calculated density for the M-NM transition and its measured value must be somewhat fortuitous considering the approximations that have been made. Of crucial importance for the model considered is, for example, the assumption that the nearest-neighbor distance,  $d$ , remains constant as the density is reduced. For instance, an increase of 1% in  $d$  would reduce the density at the M-NM transition by  $\sim 4\%$ . (An increase of 10% in  $d$  would allow other theoretical models<sup>5</sup> to account for the M-NM transition, but such a large change in  $d$  is very unlikely as discussed above.) The use of a different constant of proportionality between  $\bar{Z}$  and  $\rho$  can also cause a small shift in the calculated density for the M-NM transition.

Within the framework of the above model it is tempting to speculate about the nature of fluid Hg at densities just below the M-NM transition. As  $\rho$  falls below  $9 \text{ g/cm}^3$ , the conductivity falls rapidly and the metallic contribution to the cohesive energy falls correspondingly. In this region, atoms can recapture some of this cohesive energy, provided that the random density fluctuations place them in clusters that are sufficiently large and dense. Thus large, dense clusters are expected to occur with more than random probability. In this region the microscopic inhomogeneities proposed by Cohen and Jortner<sup>14</sup> may well exist. Since large, dense clusters have also been postulated to exist in the vapor phase above  $3 \text{ g/cm}^3$ ,<sup>16,17</sup> the structures of the two phases would approach each other in the region of the critical point. The large separation between the density at which the M-NM transition occurs and that at the critical point can be understood in terms of the thermally activated conductivity. This persists well beyond the M-NM transition<sup>3</sup> (the conductivity falls off much more slowly than the Knight shift with decreasing density), and contributes sufficiently to the cohesive energy to retain the liquid state.

Our simple model shows that it is quite reasonable that a gap in the density of states of Hg opens as the density is lowered to  $\rho \sim 9 \text{ g/cm}^3$ ; it is not necessary to invoke collective effects. Other calculations have not found a gap because they have ignored the random

fluctuations in the atomic coordination number. That the expanded alkali metals behave quite differently from expanded Hg can also be understood easily in terms of this model. Random fluctuations in  $Z$  are also expected to occur in the alkali metals, but  $E_F$  for these systems lies in the middle of the  $s$  band. If a gap were to open between the  $s$  and  $p$  bands, as in Hg, it would have little effect. Much lower particle densities are required to open a gap in the middle of the  $s$  band, and it is observed that M-NM transitions in the alkali metals occur only when densities near the critical density are reached.<sup>18</sup>

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