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## A modified Van der Waals model for the coexistence curve of expanded metals

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**Abstract.** Recent measurements for expanded Hg, Cs and Rb have shown that the liquid–vapour coexistence curves for these metals do not obey the ‘law of rectilinear diameters’. It is shown here that a two-state Van der Waals equation with a density-dependent cohesive energy will lead to compositional fluctuations that result in a breakdown of the ‘law’. Calculations predict that Hg and the alkali metals will exhibit similar behaviour near the critical point. However, in the case of Hg the 6p–6s band-gap closure, which occurs at higher than critical densities, leads to an anomalous behaviour not observed in the alkali metals. The influence of this transition on the rectilinear behaviour is treated by introducing a further modification of the two-state model.

### 1. Introduction

The law of rectilinear diameters, formulated over a hundred years ago, states that as the critical temperature  $T_c$  is approached along the liquid–vapour coexistence curve, the rectilinear diameter (the mean density of a liquid ( $\rho_l$ ) and its equilibrium vapour ( $\rho_v$ )) is observed to deviate from the critical density  $\rho_c$  as a linear function of the temperature  $T$ . This is often expressed by the relationship:

$$\rho_d - 1 = A_1(T_c - T)/T_c + \dots$$

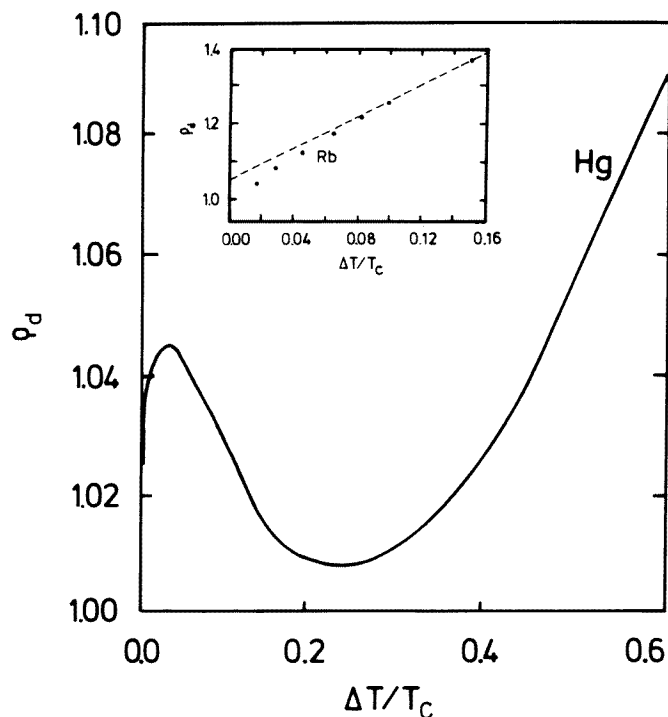
where  $\rho_d = (\rho_l + \rho_v)/2\rho_c$ . Terms of higher order in  $T$  are non-linear and represent a breakdown of the law [1]. This law, which is more correctly an empirical rule, was based on experimental data for simple insulating fluids. The possibility that the law could be violated has been anticipated in several theoretical papers [2–5].

Recently, measurements made for Hg [6], Rb and Cs [7] were found to exhibit a noticeably nonlinear behaviour. For these metals the two branches of the coexistence curve are strongly asymmetric and the law of rectilinear diameters breaks down. In the case of Cs and Rb the diameter anomalies are remarkably large (see figure 1). The figure includes also data for Hg with an accuracy comparable to that for the alkali metals. The following points are noteworthy.

(i) On the whole the coexistence curve for Hg is much more symmetric than those for Cs, Rb and Ar (see figure 2).

(ii) Starting from the critical temperature and with decreasing temperature,  $\rho_d$  for Hg first increases (see figure 1) then decreases to a minimum value, which is a behaviour opposite to that seen for molecular fluids and alkali metals.

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**Figure 1.** Rectilinear densities of rubidium and mercury plotted as functions of the reduced temperature.

(iii) Far below the critical temperature, the  $\rho_d$  for Hg regains a positive slope as observed for insulating fluids and the alkali metals. This implies that there are two competing variations of  $\rho_d$  with temperature which results in the observed minimum at intermediate  $\Delta T/T_c$ . The microscopic origin of the skewing toward higher densities far away from  $T_c$  may be a consequence of the presence of the metal–nonmetal transformation and the resultant change in the effective interparticle interaction and composition.

The equation of state, and the electrical and optical properties of these metals in the region of the vapour–liquid transition have been examined in considerable detail [8]. All of these elements show evidence for a nonmetal–metal transition over the two-phase region. While no specific mechanism for the transition has been assigned to the alkali metals it is known that caesium forms dimers and tetramers in the vapour and transforms to a nearly-free-electron metal in the liquid at densities greater than about two times the critical density. In the case of Hg it has been suggested that with increasing density there is a crossing of the filled 6s band and the empty 6p band in the two-phase region and that this filling is the origin of the nonmetal–metal transformation for Hg and the consequent change in the effective interparticle interaction. In contrast to the case for metals, the interatomic forces between insulating atoms, like xenon, are believed to be the same in the vapour and liquid, thereby leading to the rectilinear law over a very large range.

The purpose of this study is to show that a two-state Van der Waals (VdW) model which introduces compositional fluctuations will lead to an asymmetry in the calculated coexistence curve. For the present study we focus on Hg as the prototypical VdW substance because

it has a critical compressibility factor,  $Z_c = P_c V_c / RT_c = 0.39$ , which is quite close to the VdW value of 0.375. Although the model parameters are tuned to mercury it will be apparent that many of the critical features of Hg are common to the alkali metals, and that any comparisons for properties in which they differ provide important new information.

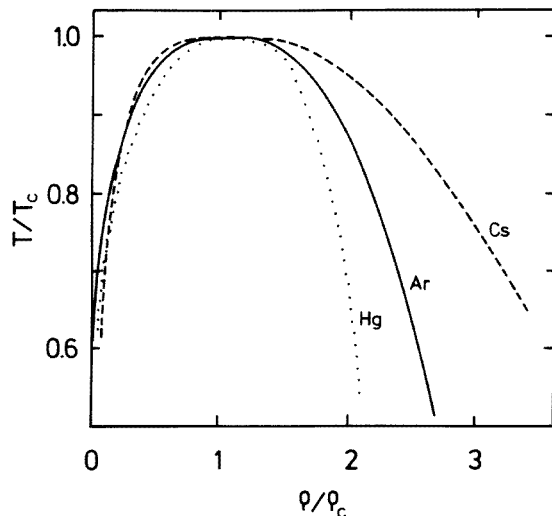


Figure 2. A comparison of  $T/T_c$ - $\rho/\rho_c$  coexistence curves for argon, caesium and mercury.

The paper is organized in the following manner. In this introductory section (1) we have presented a brief summary of the experimental results that need to be understood. To achieve this, a modified VdW model is constructed in section 2. First, the standard VdW model parameters are fitted to the critical temperature and density of Hg and it is shown that this model obeys the law of rectilinear diameters. Then, a two-state VdW model is constructed with parameters fitted to the same critical properties. This second model predicts a breakdown of the rectilinear law which is due to compositional fluctuations. The predictions show the same qualitative behaviour for Hg and the alkali metals near the critical point. However, in the case of Hg a nonmetal-metal transition which occurs at a density higher than the critical density leads to an anomalous behaviour not observed for the alkali metals. The influence of this transition on the rectilinear behaviour is treated in section 3 by introducing a further modification of the two-state model. The concluding section (4) summarizes our results.

## 2. The Van der Waals model

The Van der Waals (VdW) model is possibly the best understood model of the liquid-vapour critical region. Although not quantitatively accurate it is widely used for qualitative investigations and as the starting point for more advanced quantitative models, such as hard-sphere perturbation theory. The derivation of the VdW model is well known. Its simplicity makes it valuable for understanding the qualitative behaviour of the vapour-liquid coexistence curve.

### 2.1. The one-component VdW model

For clarity of presentation we provide the expression for the Helmholtz free energy ( $A$ ) per mole of a one-component fluid [9]:

$$A/RT = -\ln((V-b)/\Lambda^3) - a/VRT \quad (1)$$

and pressure:

$$P = RT/(V-b) - a/V^2 \quad (2)$$

where  $R$  is the gas constant,  $b$  is the excluded molar volume due to the finite size of molecules,  $a$  is a constant determined by the attractive forces between atoms and  $\Lambda$  is the thermal de Broglie wavelength. Isotherms calculated using this model show a sinuous loop corresponding to the separation of the fluid into liquid and vapour below a critical temperature, and above which  $P$  increases continuously as  $V$  decreases. At the critical temperature,  $\partial P/\partial V = \partial^2 P/\partial V^2 = 0$ . On calculating these derivatives one has, with the original equation, three equations from which to determine the model constants  $a$  and  $b$ .

The critical temperature, pressure and molar volume of Hg are, respectively, 1751 K, 1673 bar and  $34.6 \text{ cm}^3 \text{ mol}^{-1}$ . The VdW parameters  $a$  and  $b$  obtained by fitting to the critical temperature and volume are  $a = 5.67 \text{ l}^2 \text{ bar}$  and  $b = 11.53 \text{ cm}^3 \text{ mol}^{-1}$ . This leads to a predicted  $P_c = 1579 \text{ bar}$ , in reasonable agreement with the experimental value. The lower predicted value reflects the lower Van der Waals critical compressibility factor. The vapour-liquid equilibrium may be calculated by equating the Gibbs free energies ( $G = A + PV$ ) and pressure of the coexisting phases at constant temperature.

### 2.2. The two-state VdW model

Consider a VdW model for a system of two states or two components in a reacting fluid mixture. For the moment we leave the specific nature of the states or components undefined. These may be atoms in different thermally excited states, or a mixture of monomers and dimers, etc or clusters of differing sizes. We write the Helmholtz free energy as

$$A = -RT \ln((V-b)/\Lambda^3) - [(1-x)^2 a_1 + 2x(1-x)a_{12} + x^2 a_2]/V + xE^0 - TS_{mix}. \quad (3)$$

$a_1$  and  $a_2$  are the energy parameters of the pure states and  $a_{12}$  characterizes the mixture.  $x$  is the fraction of the state 2 species and the entropy of mixing is

$$S_{mix}/R = -(1-x) \ln(1-x) - x \ln x.$$

$E^0$  is a constant which sets the difference in energy of the two states at infinitely large volumes. Taking  $a_{12}$  as the simple arithmetic mean of the pure components,  $a_{12} = (a_1 + a_2)/2$ , the expression for the Helmholtz free energy becomes

$$A = -RT \ln((V-b)/\Lambda^3) - [(1-x)a_1 + xa_2]/V + xE^0 - TS_{mix}. \quad (4)$$

This equation is the same as that for ideal mixing. By varying the definition of  $a_{12}$  one can obtain results of varying degrees of sophistication. But, for this application, the present definition will suffice. The fraction of each fluid is obtained by minimizing the Helmholtz free energy and is given by the expression

$$x = \exp(-E_c/RT)/(1 + \exp(-E_c/RT)). \quad (5)$$

$E_c = (a_1 - a_2)/V + E_0$  is the difference in cohesive energy (or chemical potential) of the pure states and is volume dependent. At  $E_c = 0$ ,  $E^0 = (a_2 - a_1)/V_{cl}$ , where  $V_{cl}$  is referred to here as the closure volume.

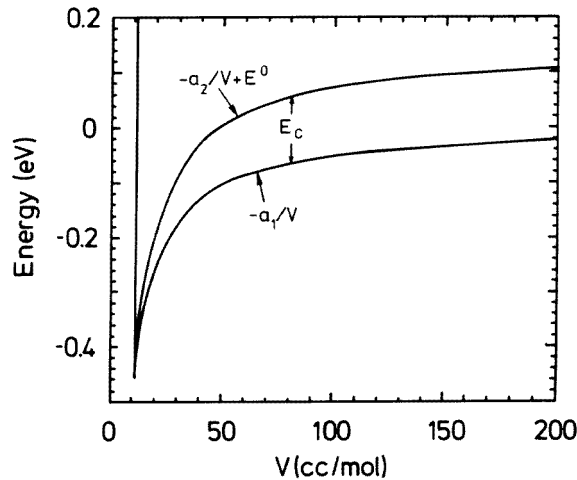
The expression for the pressure is obtained from equation (4):

$$P = RT/(V - b) - [(1 - x)a_1 + xa_2]/V^2. \quad (6)$$

It follows that since  $x = x(V, T)$  equation (6) can be written in a more general form:

$$P = RT/(V - b) - a(V, T)/V^2 \quad (7)$$

which is formally equivalent to one employing state-dependent interatomic forces.



**Figure 3.** The cohesive energies of the two pure states are  $-a_1/V$  and  $-a_2/V + E^0$  and are shown plotted versus volume. At volumes less than that of the hard sphere the energy becomes infinite.  $E_c = (a_1 - a_2)/V + E^0$ .

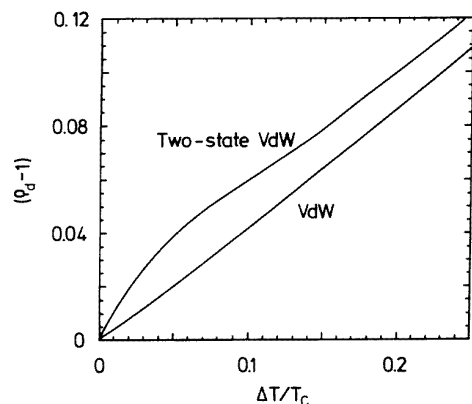
The parameters  $b$ ,  $a_1$  and  $a_2$  and  $V_{cl}$  were adjusted to predict the same value of the critical temperature and volume as the one-component model. In a rigorous treatment of the problem the values of  $b$  and  $V_{cl}$  would be composition dependent. However, given our meagre understanding of the microscopic properties of expanded fluids any choices for these parameters are likely to be arbitrary and incorrect. Therefore, since our primary purpose is to provide new insight we have resorted to the computationally simplest and most transparent approximations. For convenience we set the value of the excluded volume to be  $b = 11.53 \text{ cm}^3 \text{ mol}^{-1}$ , for both states. This is the same value of  $b$  as was used in section 2.1 and fixes the critical volume to the same experimental value. The volume ( $V_{cl}$ ), at which  $E_c = 0$ , was also set at  $b$ . Since  $V$  is always greater than  $b$  this choice of  $V_{cl}$  mainly adjusts the value of  $E^0$ . The values of  $a_1$ ,  $a_2$  and  $E^0$  so determined are, respectively,  $5.0 \text{ l}^2 \text{ bar}$ ,  $6.6 \text{ l}^2 \text{ bar}$  and  $0.14 \text{ eV}$ . The calculated critical pressure is  $1622 \text{ bar}$ . The cohesive energies of the two pure states are  $-a_1/V$  and  $-a_2/V + E^0$  and are shown plotted versus volume in figure 3. At volumes less than that of the hard sphere the energy becomes infinite.

There is now enough experimental and theoretical evidence for the presence of dimers and clusters in expanded metals to justify a multicomponent chemical reacting mixture as the basis for a model fluid. For example, it is well known that the diatomic molecule is the stable form of the alkali metals in the low-density gas phase [10]. Compressibility measurements of alkali metal vapours by Ewing *et al* [11] have shown that there exist substantial concentrations of dimers and tetramers at temperatures and pressures along the saturation line approaching the critical point. Redmer *et al* [12], on the basis of statistical mechanical calculations, have concluded that in the critical region the combined

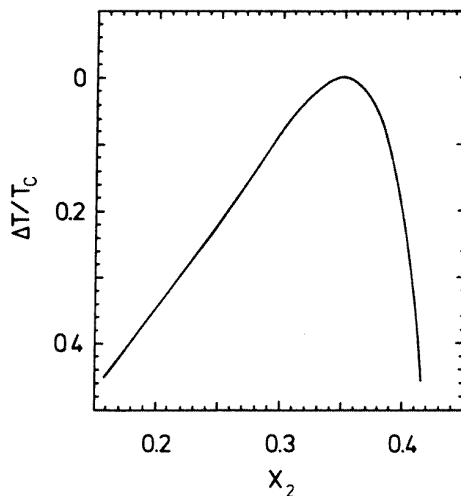
concentration of caesium dimers is of the order of 40%. Recently, measurements of the longitudinal current correlation functions of liquid rubidium by Pilgrim *et al* [13] along the liquid–vapour coexistence line were found to exhibit typical monatomic behaviour from normal liquid density down to twice the critical density. At this density a sequence of well defined peaks was observed which are characteristic of a harmonic oscillator. This has been interpreted as evidence for the passage of the expanded Rb from a monatomic to a molecular state.

However, more important than a knowledge of the precise species are the orders of magnitude of their energies. In the case of caesium the energy for dissociation of the dimer to free atoms is 0.43 eV. Total energy calculations [14] show that for densities near critical the energy separating a  $T = 0$  K lattice of diatomic molecules and a monatomic bcc lattice has decreased to about 0.2 eV, and they have equal energies near twice the critical density. Since these structures represent two extremes of bonding we can expect that over this density range the dense fluid will retain these qualitative features and have a continuous spectrum of species with energies in the thermal range.

In the case of Hg studies of bonding in clusters [15, 16] provide evidence for a continuous energy spectrum in which small  $Hg_n$  clusters ( $n < 13$ ) are Van der Waals bound and, after a transition region, sp hybridization leads to covalent bonding ( $30 \leq n \leq 70$ ). Between  $n = 95$  and  $n = 100$  a rapid decrease in the ionization potential is interpreted as the onset of metallization. This suggests that the cohesive energy term  $a(V, T)$ , in equation (7), may be written as an integral over an energy distribution function.



**Figure 4.** Calculated rectilinear densities of a Van der Waals and a two-state model plotted as functions of the reduced temperature.



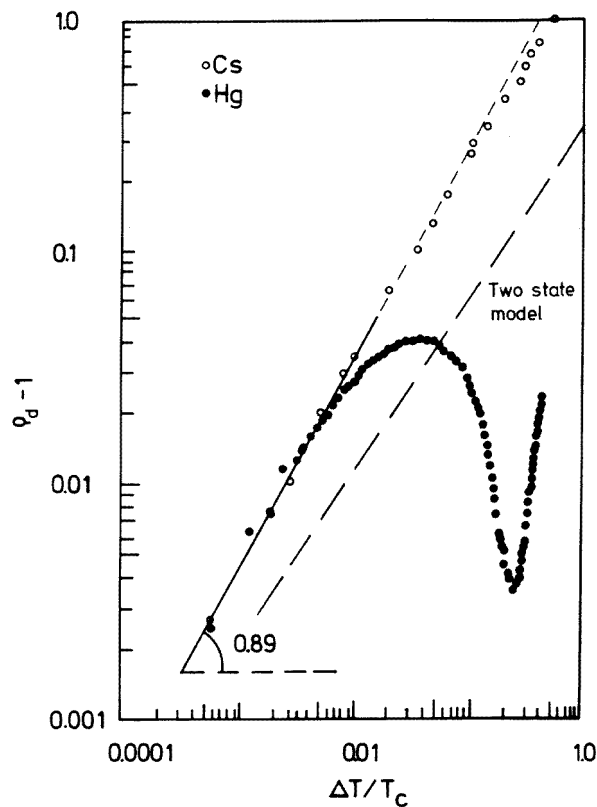
**Figure 5.** The calculated fraction of state 2 versus the reduced temperature.

### 2.3. Results of VdW calculations

Figure 4 shows the calculated rectilinear diameters obtained with the one-component and two-component VdW models. The one-component model predicts that the mean density of the liquid and its equilibrium vapour is a linear function of temperature in agreement with the law of rectilinear diameters. The Van der Waals value for the diameter slope is

$A_1 = 0.4$  as seen in the figure. In contrast, the introduction of composition dependence in the two-state model through a density-dependent cohesive energy leads to an asymmetry in the coexisting phases and as a result the law of rectilinear behaviour is not obeyed.

In order to place the present results in perspective, with those of previous workers, we recall that Widom and Rowlinson [2] speculated that a two-component model in which the pair potential between like species is zero, while the interaction between unlike species is strongly repulsive, would not obey the rectilinear law. More recently, Goldstein and co-workers [5] argued that the singularities observed in Cs and Rb arose from a strong density dependence of the screened ion-ion interactions. Clearly, the present model includes some features of both references with the exception that it ignores the role of density fluctuations by introducing a mean-field approximation. However, chemical intuition suggests that strong attractive many-body forces between metal atoms, in the presence of critical fluctuations, will favour clustering on some appropriate time-scale. Tarazona *et al* [17] introduced this crucial point into a lattice gas model of the alkali metals which took into account the strong inhomogeneities due to clustering and atom formation. Although their model is a very simple representation of a metal-atom fluid it does predict a nonlinear behaviour of the rectilinear law.

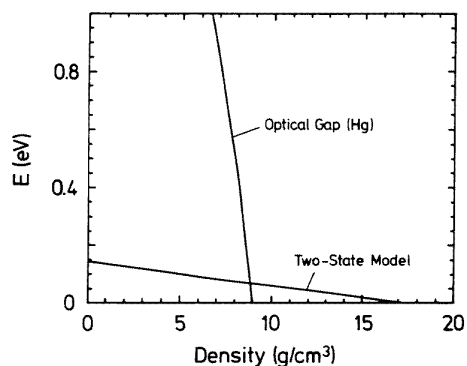


**Figure 6.** Rectilinear densities of caesium and mercury, and the two-state model plotted as functions of the reduced temperature.

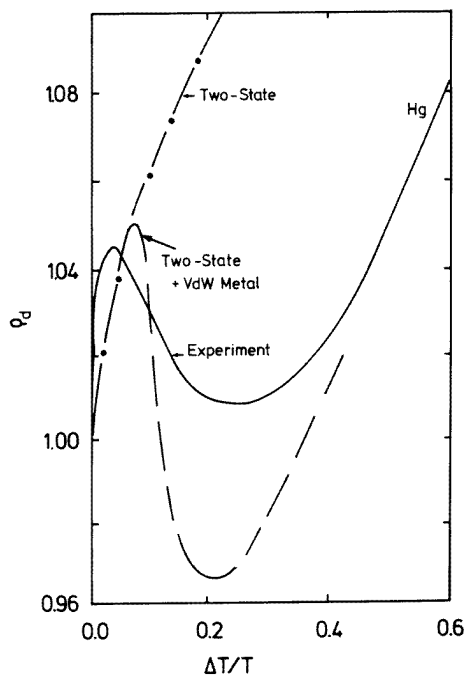
The nonlinear behaviour predicted by the present model stems from the variation of  $E_c$  (figure 3) with density which leads to values of  $x$  that are increasing with increasing



density. Figure 5 shows a plot of  $x$  versus reduced temperature along the coexistence curve. As a result, the negative contribution to the pressure from the larger  $a_2/V^2$ -term grows continuously at the expense of the smaller  $a_1/V^2$ -term going from vapour to liquid. This means that the pressure in the liquid is being lowered relative to that in the vapour. In order for the coexisting phases to equate their pressures the fluids must compress to higher densities. Since the compressibilities and thermal expansions of the two phases are considerably different this leads to an asymmetry in the rectilinear diameter when compared to the standard one-component model.



**Figure 7.** The model  $E_c$  versus the experimental optical gap for mercury.



**Figure 8.** Experimental and calculated rectilinear densities of mercury plotted as functions of the reduced temperature: experimental data (solid line); the two-state model (— · —); and the two-state model modified to include the VdW liquid metal with  $\rho > 9 \text{ g cm}^{-3}$  (— — —) (see the text).

A comparison of the calculated  $\rho_d$  (in figure 6) with those from the measurements shows a qualitative agreement for Cs. In the case of Hg the initial slope is similar to that for Cs and the present model, but then the slope diverges sharply at values of  $\Delta T/T_c$  greater than 0.01. The question as to why Hg is different can be at least partly addressed by comparing the density dependence of the model  $E_c$  with the experimental optical gap,  $E_c(V)$  being the energy needed to thermally excite state 2. Figure 7 shows that the model energies are much smaller than those of the experimentally determined optical gap, which closes at  $9 \text{ g cm}^{-3}$ , the metallic density. This suggests that there are a continuous series of relatively low energies of a thermal magnitude which determine thermodynamic properties for both Cs and Hg near the critical density. Above the gap closure density, Hg becomes metallic.

Calculations were also made with the present model using the experimentally determined optical gaps in place of  $E_c$ . But it was found that the resulting values of  $x$  were too small

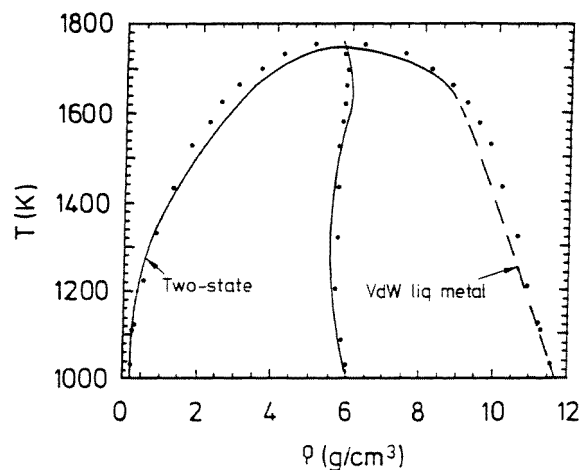
to influence the thermodynamic properties in the critical regime. A similar conclusion was reached by Nagel *et al* [18] based on a quantum statistical treatment of the metal–nonmetal and liquid–vapour transitions in Hg. Their model considered neutral and excited species of Hg atoms. They found that their calculated ionization potentials were in good agreement with measured optical gaps. However, they also found that ‘up to the Mott density, the composition is governed by the contribution of neutral atoms. The contribution of the singly charged mercury ions is small, and the partial density of  $\text{Hg}^{2+}$  is negligible. Therefore, mercury vapour can be considered as a nonmetallic dielectric system up to the metal density. The reason for this behaviour is found from the ionization energy the value of which is large compared with the temperature.’ In the next section we introduce a modification of the present model for Hg.

### 3. The nonmetal–metal transition in Hg

The most significant experiments relevant to the transformation of Hg from a metallic to a nonmetallic state are the electrical properties [8]. These show that from the highest density  $\rho = 13.6 \text{ g cm}^{-3}$  corresponding to the liquid at room temperature down to about  $11 \text{ g cm}^{-3}$  the properties of mercury can be described using the nearly-free-electron theory of metals but, with further expansion, a rather gradual diminution of metallic properties occurs in the density range between 11 and  $9 \text{ g cm}^{-3}$ . For still smaller densities the metallic behaviour as characterized by the Hall effect and electrical conductivity is no longer observed. On the basis of these considerations the model of section 2.2 is only applicable to Hg in the nonmetallic region,  $\rho < 9 \text{ g cm}^{-3}$ . Above  $9 \text{ g cm}^{-3}$  the model must be modified.

Let us assume that below  $9 \text{ g cm}^{-3}$  the two-state model remains applicable but that above this density liquid Hg is a homogeneous metal which can be represented as a one-component Van der Waals liquid (i.e. equations (1) and (2)). New values for the parameters  $a$  and  $b$  were obtained by extrapolating the lower-temperature values of  $\rho_d$  to  $T_c$  to determine a new critical density  $\rho'_c$  and fitting the  $T_c$  and  $\rho'_c$  to a VdW model of the metal phase. These parameters were found to be  $a = 6.8 \text{ l}^2 \text{ bar}$  and  $b = 13.8 \text{ cm}^3 \text{ mol}^{-1}$ . In order to ensure a continuous variation of the properties along the critical dome we assume that at  $\rho = 9 \text{ g cm}^{-3}$  and  $T = 1576 \text{ K}$  Hg undergoes an insulator–metal transition. This requires a matching of the pressure and Gibbs free energy of the two models. It is achieved by adjusting the  $a$ -parameter to  $7.27 \text{ l}^2 \text{ bar}$  and adding a constant to the metal free energy to establish a common reference energy.

The vapour–liquid equilibrium was recalculated at several temperatures for which the liquid density is  $\rho \geq 9 \text{ g cm}^{-3}$ . Figure 8 shows a plot of  $\rho_d$  versus  $\Delta T/T_c$  calculated using the two-state model and the modified version described in this section. The qualitative agreement between experiment and theory is striking. The model correctly predicts the reversal in  $\rho_d$  with decreasing temperature that occurs for  $\rho \geq 9 \text{ g cm}^{-3}$ . This is the result of introducing a larger value of  $b$  into the VdW equation which leads to stiffer liquid isotherms. Since the vapour two-state model is unaffected by this change the liquid must lower its density to satisfy the Gibbs equilibrium condition. Figure 9 shows the experimental and calculated coexistence curves, and especially noteworthy is the good agreement of the rectilinear lines. The matching leads to a small discontinuity that is smoothed. For densities  $\rho > 9 \text{ g cm}^{-3}$ , the liquid densities calculated using the metal isotherm are lower than those of the two-state model. The differences between the corresponding vapour densities are minimal. At much lower temperatures the diameter regains a positive slope as is observed for molecular fluids and alkali metals.



**Figure 9.** Calculated and experimental (dots) mercury vapour–liquid coexistence curves including rectilinear densities. The experimental data are from [6].

#### 4. Conclusions

The combined experimental and theoretical data suggest that there are two processes taking place in the critical region of Hg. One is a continuous change in composition characterized by a relatively small activation energy of the same magnitude as the critical temperature, leading to the asymmetry of the coexisting densities. This feature also appears to be present in expanded Cs as is evident from the agreement for small  $\Delta T/T_c$  for all three curves in figure 6. These changes near the critical region might involve the formation of dimers, trimers and clusters in their ground and low-lying excited states with larger units evolving with increasing density. The second process in Hg is the closing of the optical gap leading to metallization. Given the steepness of the optical gap curve we expect it to only influence the critical-point thermodynamics near the gap closure density of  $9 \text{ g cm}^{-3}$  and above.

The results suggest that the following picture can be used for expanded Hg. At high density (liquid-like near melting) the metallic bond network is dense and evenly distributed over the whole sample. Clustering occurs as the density decreases, keeping many atoms highly coordinated. However, the average coordination number decreases because the number of atoms on the surface of the clusters increases. This explains, on an atomic level, the steady decrease with decreasing density in the average coordination number at almost constant nearest-neighbour distance [8].

The two-state model employed here is clearly an oversimplification. However, because of its simplicity the VdW model has historically provided guidance for more quantitative theories. The excellent agreement between calculations and experiment for Hg (in figure 9) is due not only to the fortuitously appropriate nature of the VdW model for this element but also to the added modifications. Our results indicate that a careful examination of the nonlinearity of the rectilinear diameter has the potential for providing new insight into the nature of the vapour–liquid critical point. Improved microscopic models need to include species with energy differences comparable to the thermal energy.

## Acknowledgment

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