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## The structure of molten CsAu: *ab initio* and Monte Carlo study

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**Abstract.** We report the results of a Monte Carlo simulation for the structure of the stoichiometric CsAu melt, based on an *ab initio* quantum mechanical calculation of the interionic potentials, which is in excellent agreement with experiment.

The structure of CsAu melts has been the subject of several experimental (Martin *et al* 1980a, b) and theoretical studies (Evans and Telo da Gama 1980, Copestake 1983, Sharma *et al* 1982). The first of these was based on the mean spherical approximation (MSA) for the restricted primitive model (RPM) of a molten salt. Despite the oversimplification of the model and the approximations involved in the calculation, the total structure factor  $S_t(k)$  was found to be in qualitative agreement with the measured  $S_t(k)$  for the stoichiometric melt. Subsequent generalizations of the model (including different sized ions or screened Coulomb interactions) and/or use of more sophisticated theories (e.g. the hypernetted chain) have not substantially improved the results of the original calculation (Copestake *et al* 1980, Copestake and Evans 1982, Copestake 1983).

Since the accuracy of these approximations is reasonable we believe that the discrepancies found between the measured and calculated structure factors of CsAu are due to the inadequacy of the interionic interactions. Indeed CsAu is a particularly interesting system exhibiting a wide range of behaviour as a function of concentration. While pure Cs and Au are metallic conductors, molten CsAu at the stoichiometric composition exhibits a very low conductivity and some structural features typical of ionic systems. In spite of this, no 'realistic models' have been proposed for the stoichiometric melt. This is due to the difficulty of modelling the  $\text{Au}^-\text{Au}^-$  and  $\text{Cs}^+\text{Au}^-$  interactions, since the interionic potential for  $\text{Cs}^+\text{Cs}^+$  is well known (Dixon and Sangster 1977).

Motivated by the partial success of previous studies based on simple ionic models (Evans and Telo da Gama 1980) we have used quantum-mechanical *ab initio* methods (Hehre *et al* 1986) based on effective core potentials (ECPs) (Kahn *et al* 1976, Bachelet *et al* 1982, Hay and Wadt 1985a, b, Wadt and Hay 1985) to construct the interionic interactions of this many-electrons system. In this paper we report the results of a Monte Carlo simulation for the structure of the stoichiometric melt using the *ab initio* interionic potentials which are in very good agreement with the experimental results. We interpret

Table 1. *Ab initio* ECP interionic potential for CsAu.

<i>ij</i>	$A_{ij}$ kcal mol <sup>-1</sup>	$B_{ij}$ Å <sup>-1</sup>	$C_{ij}$ kcal Å <sup>6</sup> mol <sup>-1</sup>	$D_{ij}$ kcal Å <sup>8</sup> mol <sup>-1</sup>
Au <sup>-</sup> Au <sup>-</sup>	1404489.1	3.867	-24995.9	-22318.3
Cs <sup>+</sup> Cs <sup>+</sup>	359920.0	3.802	-2200.3	-4000.1
Cs <sup>+</sup> Cs <sup>2+</sup>	359748.0	3.468	-2188.2	-4002.1
Cs <sup>+</sup> Au <sup>-</sup>	4668.8	1.810	633.0	0.0

<sup>a</sup> From Dixon and Sangster 1977.

this as an indication of the correctness of the interionic model used in this work since the structure is calculated 'exactly' by the Monte Carlo method.

The interionic potential for CsAu was constructed by a quantum mechanical valence electrons *ab initio* calculation based on effective core potential methods, which despite some limitations (Hay and Wadt 1985a, b) has been used successfully in the study of many-electron systems and is in excellent agreement with calculations including all the electrons (Wadt and Hay 1985, Hay and Wadt 1985a, b).

Our calculation uses a 'superionic approach' in which the interaction energy of an ion pair is calculated as the difference between the 'superion' and the energies of the isolated ions. The two main caveats of this method are; (i) basis-set superposition errors (Boys and Bernardi 1970, Kolos 1979), and (ii) the assumption that the interactions are pairwise additive (Ortega-Blake *et al* 1984). The former can be controlled by using a larger basis set (see below) and/or by applying counterpoise methods (Jaszunski *et al* 1977). The latter is a very useful approximation which could, in principle, be corrected by adding to the pair interactions, interactions between three, four etc, ions. Additionally, *ab initio* ECPs methods are not reliable (Wadt and Hay 1985a, b) when the distance between the ions in the 'superion' is less than the sum of the experimental ionic radii (3.38 Å, 3.86 Å and 3.62 Å for Cs<sup>+</sup>Cs<sup>+</sup>, Au<sup>-</sup>Au<sup>-</sup> and Cs<sup>+</sup>Au<sup>-</sup> respectively).

In the *ab initio* calculation, Cs<sup>+</sup> is described by the effective core (1s<sup>2</sup> . . . 5p<sup>6</sup>) while Au<sup>-</sup> includes in addition to the effective core (1s<sup>2</sup> . . . 4f<sup>14</sup>) outer electrons described by an STO-3G minimal basis set. Although no systematic study of the basis-set dependence was carried out, preliminary results with a larger basis set (double zeta for the valence electrons) are qualitatively the same for the Au<sup>-</sup>Au<sup>-</sup> and Cs<sup>+</sup>Au<sup>-</sup> interactions. We note that relativistic effects which may be important for elements with  $Z > 36$  are included in the ECPs (Wadt and Hay 1985).

The calculations were carried out using the GAUSSIAN 88 program (Frisch *et al* 1988) on a Convex-220 supercomputer. The final set of interaction energies (24 for Cs<sup>+</sup>Cs<sup>+</sup>, 53 for Cs<sup>+</sup>Au<sup>-</sup> and 36 for Au<sup>-</sup>Au<sup>-</sup>) was fitted to an analytic function of the form:

$$\varphi_{ij}(r) = A_{ij} e^{-B_{ij}r} + C_{ij}r^{-6} + D_{ij}r^{-8} + Q_{ij}r^{-1}$$

where  $Q_{ij}$  is  $\pm 1.0$  meaning that complete ionization was assumed. Thus,  $\varphi_{ij}(r)$  is a rigid ion (Fumi-Tosi-like) interionic potential. The full set of parameters is shown in table 1. In figure 1 are plotted the *ab initio* results as well as the fitted potentials. The quality of the fit is excellent for the Cs<sup>+</sup>Cs<sup>+</sup> interaction and acceptable for Cs<sup>+</sup>Au<sup>-</sup> and Au<sup>-</sup>Au<sup>-</sup>. Note that it is possible to obtain better fits by including additional terms, such as  $r^{-2}$  . . . , etc. We believe, however, that these long-ranged corrections should not be truncated, and thus the full expressions are not the most convenient to use in computer simulations.

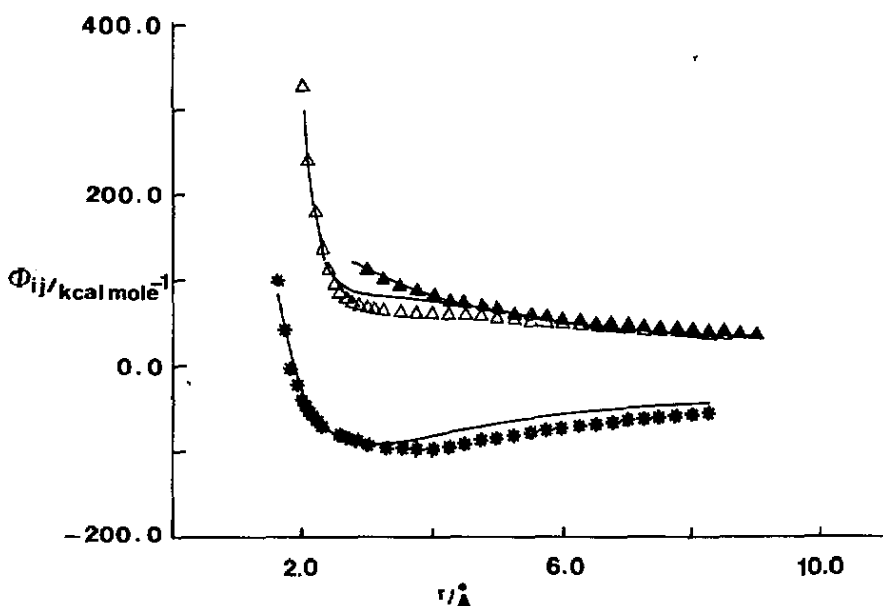


Figure 1. *Ab initio* interionic potentials between  $\text{Cs}^+\text{Cs}^+$  ( $\blacktriangle$ ),  $\text{Au}^-\text{Au}^-$  ( $\triangle$ ) and  $\text{Cs}^+\text{Au}^-$  ( $*$ ) pairs and corresponding analytic fits (curves).

There are two features of our interionic potentials that are worth noting: (1) the excellent agreement between our  $\text{Cs}^+\text{Cs}^+$  *ab initio* potential and the model reported by Dixon and Sangster (1977). This is an interesting result since our calculation for  $\text{Cs}^+\text{Cs}^+$  involves interactions between the cores only, suggesting that this ECP is accurate for Cs; (2) the significant differences between the  $\text{Cs}^+\text{Cs}^+$  and  $\text{Au}^-\text{Au}^-$  interactions, mainly in the short and intermediate ranges from 2.0–5.0 Å.

The Monte Carlo calculations were performed using the standard Metropolis algorithm. The ions (108  $\text{Au}^-$  and 108  $\text{Cs}^+$ ) were placed in a cubic cell of size 21.37 Å, which corresponds to the experimental number density of  $0.0221 \text{ \AA}^{-3}$  at a temperature of 913.15 K. Long-ranged Coulombic interactions were calculated using a 'modified Ewald sum', a practical and accurate procedure proposed by Adams and Dubey (1987). An equilibration run of  $10^6$  configurations was followed by the production run of  $10^6$  configurations when averages were taken.

The partial radial distribution functions (RDFs) for CsAu are shown in figure 2, where we also show the Monte Carlo RDFs of the RPM model (diameters 3.15 Å). The most striking point of the structure predicted using the *ab initio* interionic model is the marked difference between the  $\text{Au}^-\text{Au}^-$  and  $\text{Cs}^+\text{Cs}^+$  distribution functions. Thus, the  $\text{Au}^-\text{Au}^-$  RDF yields a distance of closest approach of about 2.5 Å, and it exhibits a first maximum (1.65) at 2.98 Å followed by a second maximum at roughly twice that distance (5.8–6.4 Å). Integration up to the first coordination shell, defined as usual by the first minimum of the RDF (3.6 Å) gives a value of 1.2. The  $\text{Cs}^+\text{Cs}^+$  ions, on the other hand, have a larger distance of closest approach of 2.95 Å. The  $\text{Cs}^+\text{Cs}^+$  RDF has a maximum (1.68) at 4.5 Å and a subsidiary broad maximum ( $\sim 1.1$ ) in the 6.2–7.1 Å range. Note that this feature, a shoulder in the RDFs at an intermediate distance between the first two maxima, is also exhibited by the RPM like-like RDFs but is absent in the *ab initio*  $\text{Au}^-\text{Au}^-$  correlations.

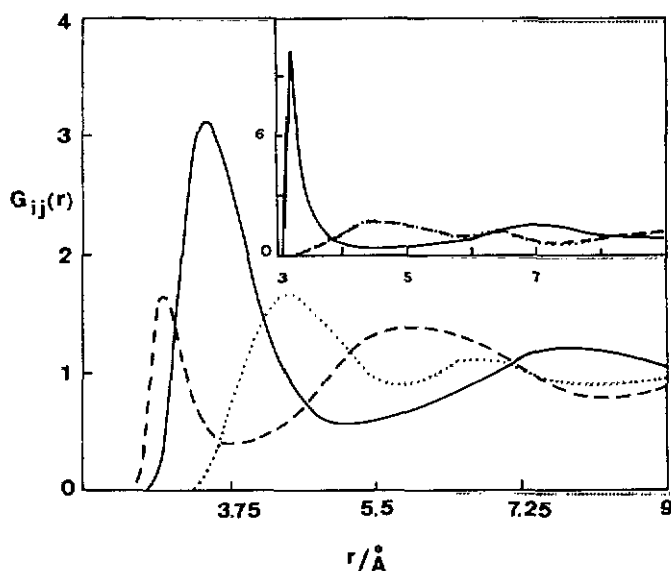


Figure 2. Partial radial distribution functions.  $G_{\text{Cs}^+\text{Au}^-}$  (full curve),  $G_{\text{Au}^-\text{Au}^-}$  (broken curve) and  $G_{\text{Cs}^+\text{Cs}^+}$  (dotted curve) of the *ab initio* and RPM (inset) models.

Integration up to the first coordination shell (5.85 Å) yields a value of 8.7. The  $\text{Cs}^+\text{Cs}^+$  and  $\text{Au}^-\text{Au}^-$  RPM RDFs are identical (1.7) at 4.5 Å followed by a subsidiary maximum ( $\sim 1.2$ ) at 6.3 Å which is due to  $+-+$  or  $-+-$  ordering. These RDFs are very similar to the *ab initio*  $\text{Cs}^+\text{Cs}^+$  structure. Finally for  $\text{Cs}^+\text{Au}^-$  the distance of closest approach is 2.55 Å. The first maximum (3.12) of the  $\text{Cs}^+\text{Au}^-$  RDF is at 3.5 Å. This is followed by a well defined first coordination shell, up to 5.16 Å, and integration of the RDF gives 7.3, a value close to the coordination number of alkali halides (6–7) (Rovere and Tosi 1986). The RPM  $\text{Cs}^+\text{Au}^-$  RDF exhibits a sharp peak (10.3) at 3.2 Å and integration up to the first coordination shell ( $\sim 4.4$  Å) yields 5.2.

The overall picture that emerges for the structure of equimolar molten CsAu suggests that a  $\text{Cs}^+$  ion is surrounded by a first group of four  $\text{Au}^-$  ions (this number is obtained by integration up to the position of the first maximum of the corresponding RDF). The  $\text{Au}^-$  ions, despite their strong repulsive Coulombic interactions, can approach each other relatively closer as a consequence of the important 'van der Waals'-like interactions (i.e. the  $C_{--}/r^6$  and  $D_{--}/r^8$  contributions to the interionic potential). This feature, unusual in ionic systems such as alkali halides, where the distances of closest approach are generally related by  $+- \langle ++ \rangle - -$ , is a direct consequence of the *ab initio* interionic model constructed in this work. The  $\text{Cs}^+\text{Cs}^+$  RDF, however, is very similar to those observed in other ionic systems (Dixon and Sangster 1977).

The main difference between the structure of our model and that of the RPM (in addition to differences due to the softness of the cores) is the extreme asymmetry of the  $++$  and  $--$  correlations due to a somewhat peculiar behaviour of the latter.

Unfortunately, the partial structure of CsAu is not experimentally accessible (Enderby and Barnes 1990); consequently a comparison with the available neutron scattering experiments (Martin *et al* 1980a, b) can only be made in terms of average

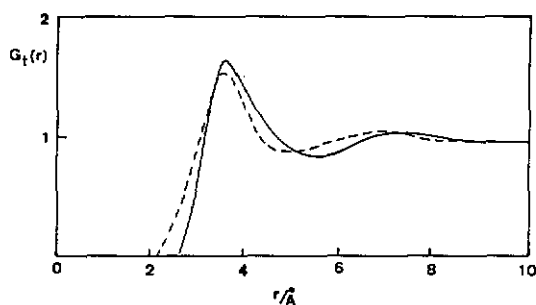


Figure 3. Experimental (broken curve) and *ab initio* (full curve) total radial distribution functions,  $G_t$  (see text).

functions. In figure 3 is plotted the computed total radial distribution function  $G_t(r)$  defined by:

$$G_t(r) = \frac{1}{2}(c_{\text{Cs}}b_{\text{Cs}}^2 G_{\text{CsCs}}(r) + c_{\text{Au}}b_{\text{Au}}^2 G_{\text{AuAu}}(r) + 2(c_{\text{Cs}}c_{\text{Au}})^{1/2} G_{\text{CsAu}}(r))$$

where  $c_{\text{Cs}}$  and  $c_{\text{Au}}$  are the molar concentrations of each species and  $b_{\text{Cs}}$  and  $b_{\text{Au}}$  are the corresponding neutron scattering lengths. In the same figure we include the experimental data of Martin *et al* (1980a, b). The agreement between the average structure functions of the *ab initio* model and experiment is very good. In particular, the position of the first maximum (3.5 Å) is exactly reproduced, although its value in the simulation (1.7) is slightly overestimated when compared with experiment (~1.6). The secondary maximum at ~7.1 Å is also nicely reproduced. The small discrepancies which are observed suggest some differences between the model and the real distances of closest approach of the  $\text{Au}^- \text{Au}^-$  and/or  $\text{Cs}^+ \text{Au}^-$  pairs. This means that there is room for improvement of the  $\text{Au}^- \text{Au}^-$  and/or  $\text{Cs}^+ \text{Au}^-$  interactions, at least at short range, which in view of the nature of the *ab initio* calculations is not surprising.

Finally in figure 4, is plotted the calculated (RPM and *ab initio*) as well as the measured total structure factor  $S_t(k)$  defined as:

$$S_t(k) = 1 + \frac{1}{2}\rho \int_0^\infty e^{ik \cdot r} (G_t(r) - 1) dr$$

where  $\rho$  is the total number density.

The agreement between the *ab initio*  $S_t(k)$  and experiment is very good. In particular, the positions and values of the first and second maxima at  $k = 1.98 \text{ \AA}^{-1}$  and  $3.9 \text{ \AA}^{-1}$ , respectively, as well as the intermediate and long-range behaviour are reproduced correctly suggesting that the overall description of the interactions is adequate. Although the agreement between the RPM and experimental  $S_t(k)$  is much worse, we note that both the RPM and *ab initio* models reproduce the position of the experimentally observed shoulder at low  $k$  (~1.2 Å<sup>-1</sup>). This shoulder, for  $k$  in the range from 0.8–1.3 Å<sup>-1</sup> is related to the long-ranged charge–charge correlations (Evans and Telo da Gama 1980, Enderby and Barnes 1990).

In conclusion, *ab initio* ECPs interionic potentials for CsAu correctly reproduce the experimental total structure factor of molten CsAu at equimolar composition. The calculated potentials include electrostatic interactions (due to fully ionized charge distributions) which are the dominant contribution of a Fumi–Tosi-like interionic model,

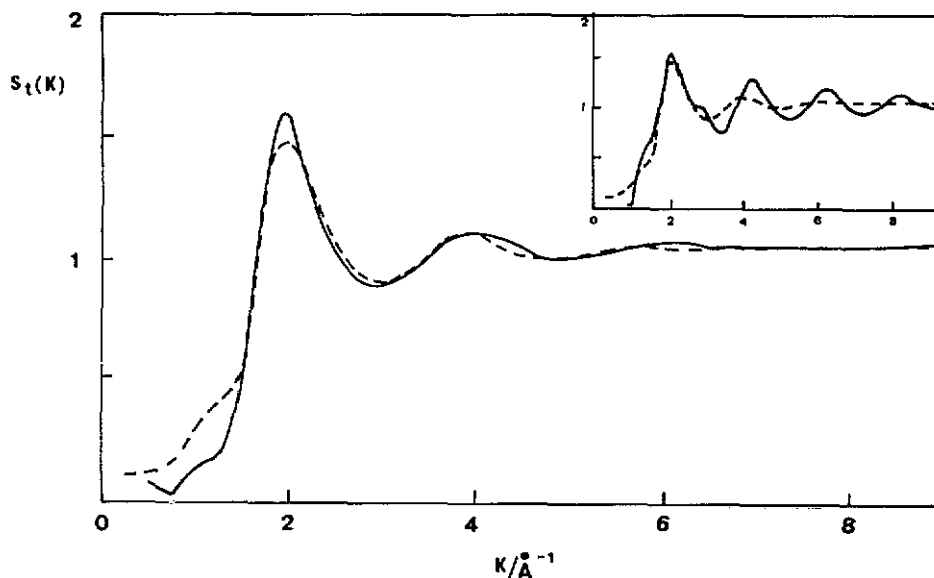


Figure 4. Experimental (broken curve) and *ab initio* (full curve) total structure factors,  $S_t$  (see text). Inset: experimental (broken curve) and RPM (full curve) total structure factors,  $S_t$ .

thus providing further theoretical evidence of the importance of Coulombic interactions in CsAu.

The introduction of a larger basis set for the construction of a refined interionic model and the study of the dynamics and thermal properties of this system is in progress.

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