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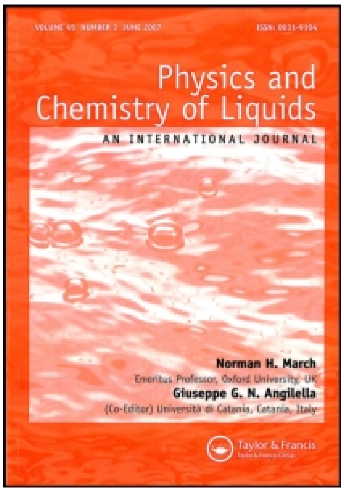

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Partial Structure Factors of Molten $HgCl_2$ in a Molecular Fluid Model

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Electrical conductivity measurements show that liquid $HgCl_2$ has a conductivity which is about 10^{-4}–10^{-5} times smaller than that of a molten alkali halide. This has prompted us to study the partial structure factors assuming a molecular picture for molten $HgCl_2$ (at slightly above melting temperature) based on the "Reference Interaction Site Model" RISM. According to this theory, the molecules consist of clusters of hard-spheres rigidly fused together, the equilibrium pair correlations being determined by the hard-core repulsive interactions.

From the partial structure factors $S_{\alpha\beta}(q)$ and the corresponding radial distribution functions $g_{\alpha\beta}(r)$, the most important feature that emerges is the dominance of the structure by the correlations among chlorine atoms, $S_{\mathrm{Hg-Hg}}$ being almost structureless. This is interpreted as being due to strong shielding of mercury atoms by the chlorine atoms.

1 INTRODUCTION

There is currently a good deal of interest in the way in which liquid structure is influenced by covalency versus ionicity. To take a recent example, CuCl, various approaches have been studied: for example, an ionic model in the limit of a very large difference in ionic diameters,[1] and with the appropriate ratio of diameters for CuCl[2] and, in contrast, a molecular fluid.[3,4] In both types of model, the partial structure factors exhibit some of the main features of those determined experimentally.[5] This situation obtains in spite of firm evidence for ionicity in molten CuCl from nuclear magnetic resonance[6] and from electrical conductivity results which show a conductivity comparable to that in molten alkali halides.

It therefore seemed of some interest to examine the case of molten $HgCl_2$, for which the electrical conductivity has been measured and is found to be about 10^{-4}–10^{-5} smaller than that in molten alkali halides.[7,8,9]† This

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† There is, however, evidence that with increasing pressure, this conductivity increases. (see Ref. 10).

suggests that the liquid might well be molecular, and this is therefore the picture adopted in the present paper.

Although such a molecular fluid model could in principle be solved exactly, by computer simulation, given the force laws, in this work we have used the "Reference Interaction Site Model" (RISM) for molecular fluids developed by Chandler and Anderson.[11] In support of the RISM, we can cite its success in predicting structures of molecular fluids in several publications before.[12,13,14]

The layout of the paper is as follow: in the next section we briefly summarize the basic equations that define the RISM theory, in Section 3 the method of solution and the physical parameters used are given. The results are represented in 4 and finally in 5 some conclusions are drawn from the results.

2 THE RISM THEORY

Detailed discussion of the RISM theory can be found in.[11,12,13] In this section we merely give the basic equations.

The RISM theory is defined by the following three equations

$$\tilde{h}(q) = \tilde{\omega}(q)\tilde{c}(q)[I - \rho\tilde{\omega}(q)\tilde{c}(q)]^{-1}\tilde{\omega}(q) \tag{2.1}$$

$$g_{\alpha\beta}(r) = 0, \ldots, r < \sigma_{\alpha\beta} \tag{2.2}$$

$$c_{\alpha\beta}(r) = 0, \ldots, r > \sigma_{\alpha\beta} \tag{2.3}$$

where the hard sphere diameter $\sigma_{\alpha\beta}$ is usually taken to satisfy the additivity condition

$$\sigma_{\alpha\beta} = \tfrac{1}{2}(\sigma_\alpha + \sigma_\beta) \tag{2.4}$$

In Eq. (2.1) $\tilde{h}(q)$, $\tilde{\omega}(q)$, $\tilde{c}(q)$ are matrices with elements $\tilde{h}_{\alpha\beta}(q)$ etc. where

$$\tilde{h}_{\alpha\beta}(q) = \int d^3\mathbf{r}e^{-i\mathbf{q}\cdot\mathbf{r}}h_{\alpha\beta}(r) \tag{2.5}$$

with

$$h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1 \tag{2.6}$$

Here $g_{\alpha\beta}(r)$ is the usual site-site[†] (α, β on different molecules) radial distribution function: $\omega_{\alpha\beta}(r)$ is the intra-molecular correlation function and

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[†] An RISM molecule consists of clusters of hard spheres fused together — the interaction sites of the theory.

for rigid molecules it is shown,[13] that

$$\tilde{\omega}_{\alpha\beta}(q) = \frac{\sin ql_{\alpha\beta}}{ql_{\alpha\beta}}; \tag{2.7}$$

where $l_{\alpha\beta} = |\mathbf{r}_i^\alpha - \mathbf{r}_j^\beta|$, the distance between sites of α and β on a molecule. $\mathbf{r}_i^\alpha$ denotes the position of the αth interaction site on the αth molecule. ρ is the mean molecular number density.

In (2.3), $c_{\alpha\beta}(r)$ is the site-site inter-molecular direct correlation function. Equation (2.2) is an exact consequence of repulsive hard-core interaction, (2.3) involves approximation. The problem of solving the RISM consists of finding solutions for the coupled non-linear Equations (2.1) to (2.3) to $g_{\alpha\beta}(r)$ and $c_{\alpha\beta}(r)$.

2.1 Partial structure factors

Neutron diffraction experiments measure partial structure factors defined by

$$S_{\alpha\beta}(q) = \frac{1}{N}\sum_{i,j}\langle e^{i\mathbf{q}\cdot(\mathbf{r}_i^\alpha - \mathbf{r}_j^\beta)}\rangle$$

where now $\mathbf{r}_i^\alpha$, $\mathbf{r}_j^\beta$ are the nuclei, $\langle\cdots\rangle$ denotes an ensemble average, and N is the total number of molecules. In terms of $\tilde{\omega}_{\alpha\beta}(q)$ and $\tilde{h}_{\alpha\beta}(q)$, the above equation is

$$S_{\alpha\beta}(q) = \tilde{\omega}_{\alpha\beta}(q) + \rho\tilde{h}_{\alpha\beta}(q) \tag{2.9}$$

The partial radial distribution functions were obtained by a straightforward fourier transform of (2.1):

3 METHOD OF SOLUTION

The RISM Eqs. (2.1) to (2.3) were solved numerically using the computer programs.[15] For details the reader is referred to Ref. (13).

The physical parameters used in the theory were as follow; for hard-sphere diameters $\sigma^{H}{}_{g}$ and σ_{Cl} we took values 2.2 Å and 3.62 Å respectively,[16] these are the Pauling diameters for these ions; the mean molecular number density ρ was taken as 0.00985 Å^{-3} (having been calculated from the liquid density of 4.44 gm/cm^3 at 280°C):[16] electron-diffraction experiments on gaseous $HgCl_2$ show it to be a linear molecule with mercury-chlorine bond-length $l_{Hg-Cl} = 2.29$ Å,[17] and thus $l_{Cl-Cl} = 4.58$ Å.

4 RESULTS

The partial structure factors and the site-site radial distribution (pair correlation) functions are shown in Figures 1 and 2 respectively. For

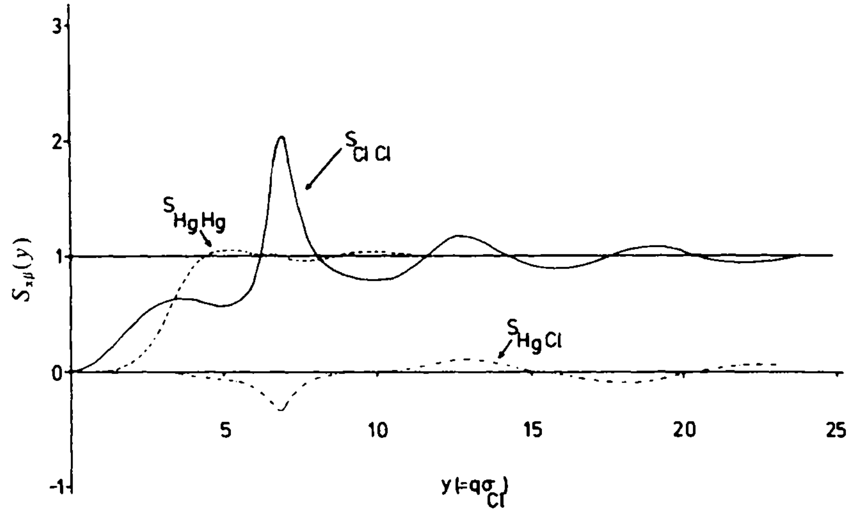

FIGURE 1 Partial structure factors for liquid $HgCl_2$ at 280°C. The dimensionless wave vect space variable plotted is $y = g\sigma_{Cl}$ where σ_{Cl} is the hard sphere diameter of chlorine.

the $S_{\alpha\beta}$'s the actual variable plotted is $y = q\sigma_{Cl}$ while in r-space lengths are expressed in units of σ_{Cl}.

The most important features we notice in the above curves are the following:

a) Apart from the presence of a broad shoulder on the long wave-length side of the first peak at $y \simeq 7$, the S_{Cl-Cl} resembles that for a simple liquid. In both $S_{\alpha\beta}(y)$ and $g_{\alpha\beta}(r)$, the oscillations in S_{Cl-Cl} and g_{Cl-Cl} are more pronounced than the other two correlations: in g_{Cl-Cl} in particular, oscillations extending well out in r-space are observed.

b) In S_{Hg-Cl}, the depth of the first minimum is rather small and the width of the trough large; the oscillations in g_{Hg-Cl} are damped and beyond $r/\sigma_{Cl} \gtrsim 3.5$ these are barely perceptible.

c) S_{Hg-Hg} is almost structureless: also g_{Hg-Hg} is the most damped of the three g's going very rapidly to its asymptotic value of unity.

In all the $g_{\alpha\beta}(r)$'s "cusps" (discontinuities in derivatives) are seen; these are due to repulsive hard-core interactions among the molecules in the RISM theory. (See for instance Ref. 13). The presence of the broad shoulder in S_{Cl-Cl}, on the other hand, is not immediately explicable physically.

It would seem from the above discussion that in a molecular fluid model, the structure in liquid $HgCl_2$ is dominated by correlations among chlorine atoms, the other correlations, viz those among Hg—Cl and Hg—Hg being

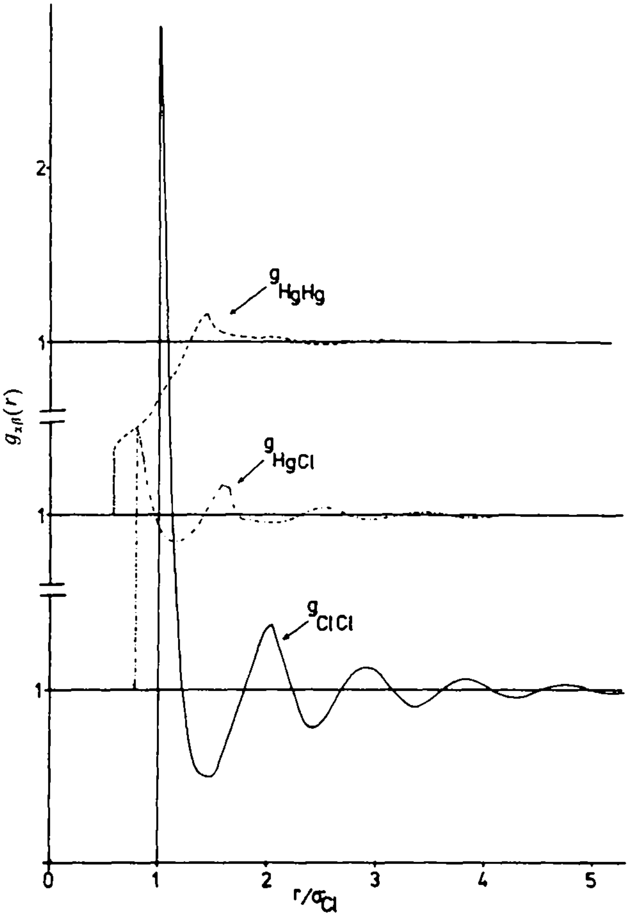

FIGURE 2 Partial radial distribution (pair correlation) functions for liquid $HgCl_2$ at 280°C obtained by Fourier transform of Eq. (2.1). σ_{Cl} is the unit of length.

rather weak. A plausible explanation might be in this RISM theory that the Hg-atom is very strongly shielded by the Cl-atom; in a picture of a linear symmetrical $HgCl_2$ molecule, this shielding is built into the theory. It is worthwhile to mention here that, in their work on liquid UO_2, Bhuiyan *et al.*[18] also observed relatively weak U-U and U-O correlations, in this case, too, the UO_2 molecule was assumed linear and symmetric.

5 CONCLUSIONS

Our main conclusion from this work is the dominance of the structure in liquid $HgCl_2$ by the Cl—Cl correlations; the shielding of the Hg-atoms by the Cl-atoms as we have seen, is to a certain extent inherent in a molecular fluid model.

Appropriate choice of diameters for the constituent hard-spheres in the molecule is a crucial feature of the RISM theory: indeed in most of its previous applications[13,14] after varying the sizes of the atoms, the best RISM molecule was considered as the one which gave closest agreement with the experiment (diffraction or computer simulation). There is also evidence that this choice of sizes considerably affects structure.[18] Absence of such information of $HgCl_2$ is clearly a disadvantage in this connection. Our results must therefore be viewed in this light and at this stage can only be qualitative. Subsequently, when experimental results do become available it might be necessary to supplement this work by a more detailed study which takes into account this variation of sizes of Hg and Cl atoms.

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References

1. M. Gillan, B. Larsen, M. P. Tosi, and N. H. March, *J. Phys.*, **C9**, 889 (1976).
2. M. C. Abramo, C. Caccamo, G. Pizzimenti, M. Parrinello, and M. P. Tosi, *J. Phys.*, **C9**, L593 (1976).
3. M. J. Gillan, *J. Phys.*, **C9**, 2261 (1976).
4. J. G. Powles, *J. Phys.*, **C8**, 895 (1975).
5. D. I. Page and K. Mika, *J. Phys.*, **C4**, 3034 (1971).
6. J. B. Boyce and J. C. Mikkelsen, *J. Phys.*, **C10**, L41 (1977).
7. Landolt-Bornstein, 6th edition 1960, Vol. II, Pt. 7, pp. 4 (Springer-Verlag, Berlin).
8. L. F. Grantham and S. J. Yosim, *J. Chem. Phys.*, **45**, 1192 (1966).
9. J. O'M. Bockris, E. H. Crook, H. Bloom, and N. E. Richards, *Proc. Roy. Soc. (London)*, **A255**, 558, (1960).
10. A. J. Darnell and W. A. McCollum, *J. Chem. Phys.*, **55**, 116 (1971).
11. D. Chandler and H. C. Andersen, *J. Chem. Phys.*, **57**, 1930 (1972).
12. L. J. Lowden and D. Chandler, *J. Chem. Phys.*, **59**, 6587 (1973).
13. L. J. Lowden and D. Chandler, *J. Chem. Phys.*, **61**, 5228 (1974).
14. C. S. Hsu, D. Chandler, and L. J. Lowden, *Chem. Phys.*, **14**, 213 (1976).
15. L. J. Lowden: RISM, RISMGR, RISMSK, Program no. QCPE 306, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana 47401, U.S.A.
16. Handbook of Chemistry and Physics: 53rd edition, 1972-1973 (Cleveland Ohio: Chemical Rubber Company).
17. Tables of interatomic distances and configuration in molecules and ions—supplement 1956-1959. Special publication no. 18, the Chemical Society, London.
18. L. B. Bhuiyan, P. J. Grout, and N. H. March, *Phys. and Chem. of Liquids* (1977) (in press).