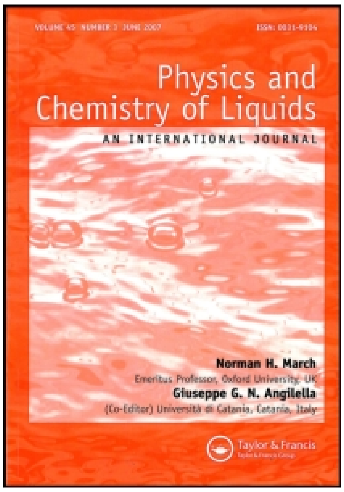

**Physics and Chemistry of Liquids**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

# Structural differences between Ionic and molecular fluid models of liquid $UO_2$

L. B. Bhuiyan[a]; P. J. Grout[a]; N. H. March[a]
[a] Department of Physics, The Blackett LaboratoryImperial College, London

**To cite this Article** Bhuiyan, L. B. , Grout, P. J. and March, N. H.(1977) 'Structural differences between Ionic and molecular fluid models of liquid $UO_2$', Physics and Chemistry of Liquids, 6: 4, 291 — 300
**To link to this Article: DOI:** 10.1080/00319107708084147
**URL:** http://dx.doi.org/10.1080/00319107708084147

*Phys. Chem. Liq.*, 1977, Vol. 6, 291–300

Printed in Holland

# Structural Differences Between Ionic and Molecular Fluid Models of Liquid $UO_2$

L. B. BHUIYAN, P. J. GROUT, and N. H. MARCH

*Department of Physics, The Blackett Laboratory, Imperial College, London SW7 2BZ*

(*Received May 2, 1977*)

Though present evidence favours an ionic model of liquid $UO_2$, it seems of interest to compare and contrast structural predictions of such a model with those of a molecular fluid model.

Therefore, in this paper, we present partial structure factors on the basis of the reference interaction site model for liquid $UO_2$ just above its melting temperature. In this treatment, the "molecules" consist of rigid (linear) clusters of hard spheres.

In the absence of experimental information on the structure of liquid $UO_2$, comparison is made with the earlier work of Bhuiyan *et al*, for the mean spherical approximation (MSA) to the ionic model. Considerable resemblance with the MSA results appropriate to zero coupling constant is found.

## 1 INTRODUCTION

The properties of liquid $UO_2$ are of considerable interest in connection with testing and safety aspects of nuclear reactors. But little is known, so far, about the structure of this liquid. Therefore, in a previous paper by Bhuiyan *et al.*[1] we have studied the partial structure factors of an ionic model of liquid $UO_2$, based primarily on a mixture of $U^{4+}$ and $O^{--}$, though the variation of structure with degree of ionicity was also explored.

The model underlying the above work was that of charged hard spheres. Unfortunately, the exact solution of even such a simple model is currently not possible except by computer experiments and we therefore employed the mean spherical approximation (MSA) to the ionic model. This leaves uncertainties, because the theory is valid for intermediate coupling constants, whereas in $UO_2$ with a fully ionic model the coupling constant is rather large.

In view of this, we thought it of interest to compare and contrast the partial structure factors obtained by the above route with the opposite model which takes liquid $UO_2$ as a molecular fluid. We want to make it clear from the outset that the weight of evidence is in favour of the ionic model of $UO_2$. However, the evidence is for the solid, and since cases are known (e.g. $AlCl_3$)[2] for which ionic materials in the solid state show negligible ionic conductivity in the liquid, this is not decisive. Regarding the evidence for the ionicity of solid $UO_2$ we may cite:[3]

i) the fact that the cohesive energy is correctly given by the Born–Mayer model with ionic charges $Z_U = 4$, $Z_O = 2$.[4]

ii) the phonon dispersion curves are well described in terms of a shell model with an ionic charge of the same magnitude as in (i) above.[5]

The unresolved problem of the structure of liquid $UO_2$ seemed to us of sufficient practical importance to examine what common features, if any, might exist between two such different models as ionic and molecular.

## 2 STRUCTURE IN MOLECULAR FLUID MODEL

As in the ionic case, so in the molecular fluid model it is necessary to either employ approximate theories, or go to full computer simulation. It is the former approach we choose to adopt in the present work. Over the last few years, the so-called reference interaction site model (RISM) theory for molecular liquids proposed by Andersen and Chandler[6] has been widely used to study the equilibrium structural and thermodynamic properties of such systems. For example, Lowden and Chandler[7,8] have studied liquid $N_2$, $CCl_4$, $CS_2$, $CSe_2$ and $C_6H_6$, while Hsu *et al.*[9] report results for $N_2$, $O_2$ and $Br_2$. These authors show that with an appropriate choice of diameters for the hard spheres, the predictions of the RISM theory are in good agreement with neutron diffraction experiments, as well as with computer simulation of these liquids.

None of the above liquids is ionic whereas we remarked above that the ionicity of solid $UO_2$ would point towards an ionic model of the liquid. However, recently Powles[10] and Gillan[11] have studied the structure of liquid CuCl by treating it as a molecular fluid. In particular, Gillan has reported results from the RISM theory, and has thereby obtained fair agreement with the partial structure factors as measured by Page and Mika[12] for liquid CuCl.

It appears, therefore, that in spite of the fact that in the liquid state CuCl has observable ionic character, as demonstrated by nuclear magnetic resonance[13] and by high ionic conductivity, comparable to that of the molten alkali halides, a useful structural description seems still to be afforded by a molecular fluid picture. Therefore we shall present results below for the RISM for liquid $UO_2$ and compare them with our earlier structural predictions from an ionic model.[1]

## 3 REFERENCE INTERACTION SITE MODEL

The physical assumptions made, and the mathematical formalism employed, in the RISM have been summarized in several places by now.[6,7,11] Therefore we restrict ourselves below to a statement of the basic equations underlying the model, and we shall then concentrate on presenting the numerical results for the model when applied to molten $UO_2$.

Working with total correlation functions $h_{\alpha\beta}(r)$ related to the site–site radial distribution functions $g_{\alpha\beta}(r)$ by

$$h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1 \tag{3.1}$$

it is then important to the approach to introduce a site–site direct correlation function $c_{\alpha\beta}(r)$ through the Ornstein–Zernike like matrix equation:

$$\tilde{h}(q) = \tilde{w}(q)\tilde{c}(q)[I - \rho\tilde{w}(q)\tilde{c}(q)]^{-1}\tilde{w}(q) \tag{3.2}$$

As usual, $\tilde{h}(q)$ denotes the Fourier transform of $h(r)$ etc., $\rho$ is the mean molecular number density while $\tilde{w}_{\alpha\beta}(q)$ is the Fourier transform of the intramolecular correlation function

$$w_{\alpha\beta}(|\mathbf{r} - \mathbf{r}'|) = \frac{1}{\rho^2}\left\langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i^\alpha)\delta(\mathbf{r} - \mathbf{r}_i^\beta) \right\rangle. \tag{3.3}$$

In Eq. (3.3), $\langle \ldots \rangle$ denotes an ensemble average while $\mathbf{r}_i^\alpha$ is the position of the $\alpha$th interaction site in the $i$th molecule.

Assuming the molecules to be rigid, we have explicitly, with $l_{\alpha\beta} = |\mathbf{r}_i^\alpha - \mathbf{r}_i^\beta|$,

$$\tilde{w}_{\alpha\beta}(q) = \frac{\sin ql_{\alpha\beta}}{ql_{\alpha\beta}}. \tag{3.4}$$

Equation (3.2), together with the relations

$$g_{\alpha\beta}(r) = 0 \qquad r < \sigma_{\alpha\beta} \tag{3.5a}$$

$$c_{\alpha\beta}(r) = 0 \qquad r > \sigma_{\alpha\beta} \tag{3.5b}$$

where $\sigma_{\alpha\beta}$ denotes the hard sphere diameter for the interaction between site $\alpha$ on one molecule and $\beta$ on another, are the equations defining the RISM. Naturally Eq. (3.5a) is an exact consequence of a hard-sphere interaction, whereas approximations are involved in writing Eq. (3.5b).

Thus the problem the RISM presents is the solution of the coupled nonlinear integral equations (3.2) and (3.5) for $g_{\alpha\beta}(r)$ and $c_{\alpha\beta}(r)$.

### 3.1 Partial structure factors

The liquid partial structure factors, our particular concern in this work, are defined by

$$S_{\alpha\beta}(q) = \frac{1}{N} \langle \exp[i\mathbf{q} \cdot (\mathbf{r}_i^\alpha - \mathbf{r}_j^\beta)] \rangle \tag{3.6}$$

where $N$ is the total number of particles in the liquid. If the sites $\mathbf{r}_i^\alpha$ and $\mathbf{r}_j^\beta$ coincide with the nuclei, these are precisely the quantities determined by neutron scattering experiments.[12]

It is straightforward from the above equations of the RISM to express (3.6) as

$$S_{\alpha\beta}(q) = \tilde{w}_{\alpha\beta}(q) + \rho\tilde{h}_{\alpha\beta}(q), \tag{3.7}$$

$\tilde{w}$ and $\tilde{h}$ being given by (3.4) and (3.2).

### 3.2 Numerical solution

For parameters appropriate to the two cases discussed below, the RISM Eqs. (3.2) and (3.4) were solved by making use of the computer program[14] and an independent verification of the solutions was carried out using programs which treated the problem as one in non-linear optimization theory. The radial distribution functions $g_{\alpha\beta}(r)$ were obtained by the Fourier inversion of Eq. (3.2).

## 4 MODEL OF $UO_2$ MOLECULE

We are not aware of direct experimental data on the geometry and bond lengths of the $UO_2$ "molecule" in the liquid state. We therefore assume at the outset that based on the crystalline structure,[15] each uranium atom associated with its two nearest neighbour oxygen atoms forms a linear $UO_2$ molecule, the identity of which is preserved in the liquid. Consequently, the "bond-length" used in the calculation is just the crystalline U–O distance.

Two sets of calculations were carried out:

i) with the Pauling diameters for uranium and oxygen and

ii) with the hard sphere diameters that reproduced the experimentally observed compressibility,[16] in the ionic model of Ref. 1.

In both cases (i) and (ii) the hard sphere diameters were assumed to be additive

$$\sigma_{\alpha\beta} = \tfrac{1}{2}(\sigma_\alpha + \sigma_\beta) \tag{4.1}$$

The constants employed in (i) and (ii) are collected in the Table.

TABLE I

Parameters used in two cases studied

| | (i) | (ii) |
|---|---|---|
| U–O bond length | 2.37 | 2.37 |
| $\sigma_U$ | 1.94 | 1.63 |
| $\sigma_O$ | 2.80 | 2.36 |
| $\rho$ | 0.0195 | 0.0194 |

*N.B. Lengths are in Å, and densities in Å$^{-3}$*

## 5 RESULTS

The partial structure factors $S_{ij}(q)$ and the pair correlation functions $g_{ij}(r)$ are shown in Figures 1 to 4. Figures 1 and 2 correspond to case (i), the others to case (ii). The variable $q$ has been expressed in terms of the dimensionless quantity $y = q\sigma_O$, while in $r$ space we have also measured distances in units of $\sigma_O$.

The most striking feature of the partial structure factors $S_{ij}(y)$ is the presence of the troughs on the long wavelength side of the first peak in $S_{ii}(y)$. Such troughs are not found in the corresponding structure factors given by

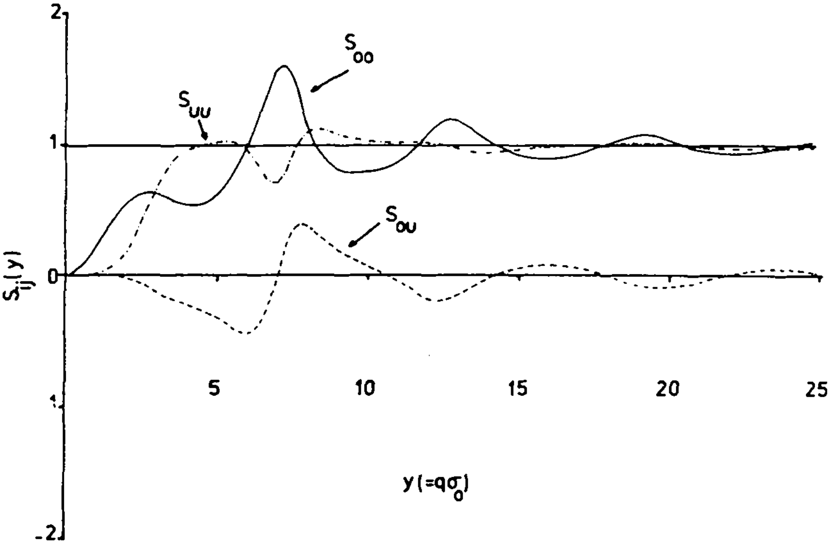

FIGURE 1 Partial structure factors for molecular fluid model using Pauling diameters (model i).

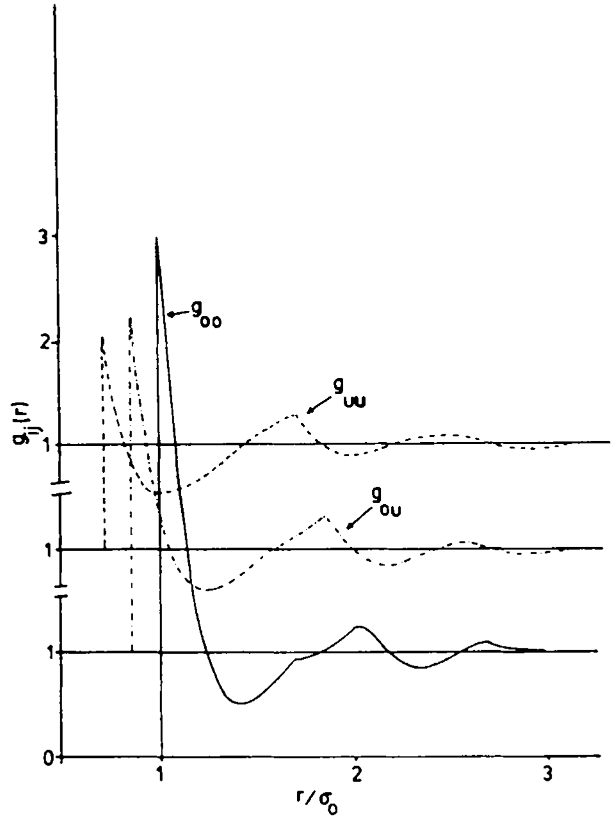

FIGURE 2 Radial distribution functions for model i.

the MSA to an ionic model.[1] It should be noted though that in this work on CuCl using the RISM, Gillan[11] observed such a trough in $S_{CuCu}$.

Comparing the partial structure factors in more detail with those corresponding to the partially ionic case reported in (1), the following features are observed:

i) the amplitudes and phases of $S_{ij}(y)$ are different; the height of the first peak in $S_{OO}$ is nearly the same, but the $S_{UU}$ peak is lower in the molecular fluid picture than in the MSA to the ionic model.

ii) the shoulder observed in the $S_{OO}$ in the MSA is absent in the RISM, and, in the MSA, for large $y$ the oscillations are less pronounced.

iii) apart from the trough at $y \sim 7$, $S_{UU}$ is relatively structureless.

iv) in the cross-correlation function $S_{UO}(y)$, although the positions of the first minimum and maximum are the same in both models, their widths are

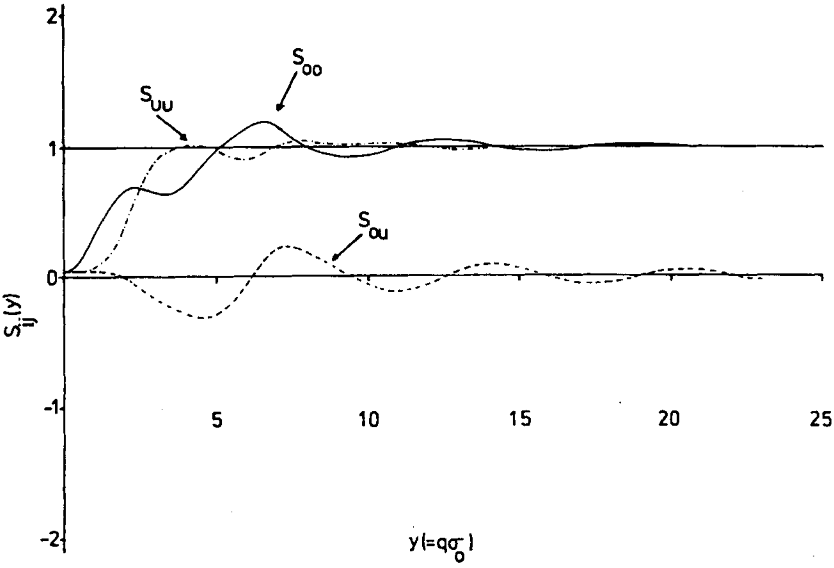

FIGURE 3 Partial structure factors for model ii (sizes summarized in Table).

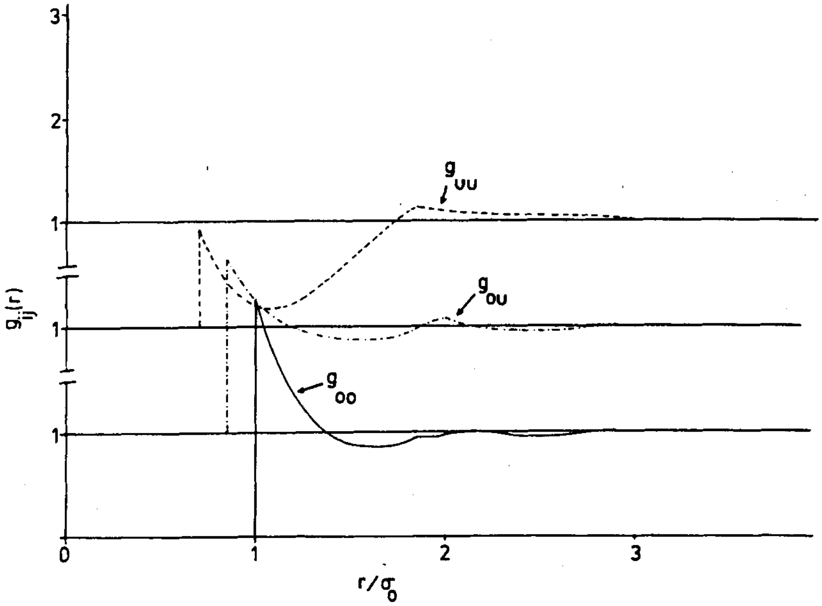

FIGURE 4 Radial distribution function for model ii.

not and in general the results differ beyond $y \gtrsim 10$, both in phase and amplitude.

v) the depth of the first minimum in $S_{UO}$ is smaller in the RISM than in the MSA and the width of the trough is large.

The points (iii) and (v) suggest that the correlations for U-U and U-O in the MSA to the ionic model extending well into r-space are much weaker in the molecular fluid picture; we might say that the O atoms are effectively "shielding" the U-atom in the RISM. This point of view is consistent with the fact that the oscillations in $g_{ij}(r)$ are much more damped than in the MSA to the ionic model.

Another feature which supports the above discussion is the similarity between the molecular fluid picture and the structure of neutral hard sphere results for liquid $UO_2$. Thus, in both $S_{ij}(y)$ and $g_{ij}(r)$ the peak positions and the phases are the same although in the RISM the oscillations in $g_{ij}(r)$ are somewhat more damped; the contact values of $g_{ij}(r)$ are also lowered.

However, a major difference occurs between the molecular fluid results and the neutral hard sphere case in the long wavelength limit. Thus, for neutral hard spheres, $S_{UU}(q = 0)$ is $\sim 1$ while $S_{UO}(0) < 0$, only $S_{OO}(0)$ being very small and positive. But in the RISM, the $S_{ij}(0)$ are all positive and tend to values $\sim 10^{-2}$.

In our case (ii), we chose for the diameters of oxygen and uranium the values which reproduced the experimental compressibility in the MSA;[1] it is noteworthy that in the RISM we regain the correct long wavelength behaviour of $S_{ij}(y)$. Also in case (ii), the oscillations in $S_{ij}(y)$ are more heavily damped than in case (i), while the troughs in $S_{ii}(y)$ are broadened out.

In both sets of calculations, cusps, i.e. discontinuities in slopes are observed in $g_{ij}(r)$; these appear to be a general feature in the RISM, due to hard-core interactions among the molecules.

## 6 CONCLUSION

One obvious conclusion from the present work on the molecular fluid model of $UO_2$ is that the considerable short-range order given by the MSA to the ionic model of molten $UO_2$ (Ref. 1) is no longer present. Indeed, one very characteristic feature of an ionic model is the charge neutrality condition, which relates the phases in the oscillations of the three partial structure factors.

In contrast, the "shielding" of the U atom by the O atoms is done in the RISM, it would seem, too effectively. Similarities between the molecular fluid results for $S_{ij}(y)$ and $g_{ij}(r)$ with those from neutral hard sphere theory support this point of view. The presence of troughs in $S_{ij}(y)$ is not, as far as we can see, easily discussed in simple physical terms.

From the previous work on the RISM[7–9] it has been shown that by varying the size of the atoms it is possible to bring theory and either experiment or computer simulation into agreement. The absence of such information for liquid $UO_2$ precludes such a procedure, with the consequence that, in all likelihood, the present structural calculations can at best be semiquantitative.

It is important to re-emphasize that, while modelling the structure has been the prime interest of our present program, we are well aware that the weight of evidence is in favour of an ionic picture of liquid $UO_2$. A difficult point in any simulation of structure by a molecular fluid model must therefore be that made immediately above; i.e. the choice of sizes of the O and U "atoms." There is considerable uncertainty on the "best" way to make this choice on a priori grounds in a molecular fluid model; and yet comparison of cases (i) and (ii) of the present paper shows that the structure is very appreciably influenced by the choice of sizes.

Nonetheless, the results of Ref. (1), in conjunction with those presented here, ought to be useful in interpreting structural properties of liquid $UO_2$ when eventually neutron diffraction data and/or computer simulation results become available.

## Acknowledgements

We are very grateful to Drs. Lidiard, Gillan and Rae of the Theoretical Physics Division, AERE, Harwell, for their continuing interest and helpful discussions concerning our programme on liquid $UO_2$. Thanks are also due to our colleague at Imperial College, Dr. P. J. Dobson, who drew our attention to the work on $AlCl_3$.

One of us (L. B. B.) wishes to thank Prof. D. Chandler and Dr. L. J. Lowden for helpful correspondence and for supplying a copy of the programs.[14] L. B. B. also acknowledges the award of a Commonwealth Scholarship (U.K.) during the course of this work.

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