

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

The Reference Interaction Site Model and the Structure of Liquid Germanium Tetrabromide

K. N. Swamy^a; L. B. Bhuiyan^b

^a School of Chemistry, University of Hyderabad, Hyderabad, India ^b Department of Applied Mathematics and Computing Science, The University, Sheffield, U.K

To cite this Article Swamy, K. N. and Bhuiyan, L. B.(1980) 'The Reference Interaction Site Model and the Structure of Liquid Germanium Tetrabromide', *Physics and Chemistry of Liquids*, 9: 2, 169 – 174

To link to this Article: DOI: 10.1080/00319108008084774

URL: <http://dx.doi.org/10.1080/00319108008084774>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Reference Interaction Site Model and the Structure of Liquid Germanium Tetrabromide

K. N. SWAMY

School of Chemistry, University of Hyderabad, Hyderabad 500001, India

and

L. B. BHUIYAN

*Department of Applied Mathematics and Computing Science,
The University, Sheffield S10 2TN, U.K.*

(Received July 1, 1979)

The reference interaction site model of Chandler *et al.* has been used to study the structure of liquid Germanium tetrabromide. The molecular structure factor is in fair agreement with the Neutron scattering experiments. The inter-molecular atomic distribution functions were also determined and the calculations tend to support the view that the local structure of liquid Germanium tetrabromide is one in which GeBr_4 molecules form an interlocking structure.

1 INTRODUCTION

Exploiting the physical idea that the structure of a dense fluid is primarily due to the shape of the molecules in the fluid and is governed by the short range, quickly varying portions of the intermolecular potential and the effect of the weak attractive interactions are of the mean field type, Chandler *et al.*¹⁻⁴ have developed a theory known as the Reference Interaction Site Model (RISM) to generate the structure of molecular fluids. The predictions of this theory are in good agreement with the Monte Carlo calculations.⁵ Narten^{6,7} and Sandler and Narten⁸ have applied the RISM to predict the structure of Benzene, Carbon tetrachloride and Carbondisulphide; the agreement with experimental structure factors is near quantitative. Recently Hsu and Chandler⁹ have shown that the RISM theory predicts the local structure of

molecules having large electric dipole moments and calculated the molecular structure factors of liquid acetonitrile and deuterated acetonitrile, again with very good correspondence with experimental results.

We were motivated by the above successes of the RISM to apply the theory to estimate the neutron scattering structure factor (and the intermolecular atom-atom distribution functions) of liquid GeBr_4 . Neutron diffraction experiments on this liquid have been performed by Egelstaff *et al.*¹⁰ The interesting feature in the structure factor $S(k)$ is the appearance of two closely spaced peaks around $k \sim 1.7 \text{ \AA}^{-1}$. We thought it of interest in particular to see whether such a feature is predicted by the RISM.

2 THE REFERENCE INTERACTION SITE MODEL (RISM)

The theory of the RISM has been discussed extensively in the earlier references; we therefore confine ourselves to giving only a brief outline of the theory. In this molecular fluid picture each molecule contains m interaction sites and the location of the α th interaction site in the j th molecule is given by

$$\mathbf{r}_j^\alpha = \mathbf{R}_j + \mathbf{l}_j^\alpha \quad (2.1)$$

where \mathbf{R}_j denotes the location of the centre of the j th molecule and \mathbf{l}_j is the vector displacement of the α th site from the centre. We consider the molecule to be rigid and the total potential energy between molecules 1 and 2 is

$$W(12) = \sum_{\alpha=1}^m \sum_{\gamma=1}^m \Phi_{\alpha\gamma}(|\mathbf{r}_1^\alpha - \mathbf{r}_2^\gamma|) \quad (2.2)$$

where $\Phi_{\alpha\gamma}(r)$ is a hard sphere interaction

$$\begin{aligned} \Phi_{\alpha\gamma}(r) &= \infty & r < \sigma_{\alpha\gamma} \\ &= 0 & r > \sigma_{\alpha\gamma} \end{aligned} \quad (2.3)$$

with $\sigma_{\alpha\gamma}$ denoting the sphere diameter for the interaction between site α on one molecule and site γ on the other and we assume that diameters are additive (i.e.)

$$\sigma_{\alpha\gamma} = \frac{1}{2}(\sigma_\alpha + \sigma_\gamma) \quad (2.4)$$

Considering the site-site intermolecular pair correlation function $g_{\alpha\gamma}(r) = (h_{\alpha\gamma}(r) + 1)$, a site-site direct correlation function $c_{\alpha\gamma}(r)$ is defined by the equation

$$\hat{h}(k) = \hat{w}(k)\hat{c}(k)[I - \rho\hat{w}(k)\hat{c}(k)]^{-1}\hat{w}(k) \quad (2.5)$$

where ρ is the molecular number density and $\hat{h}(k)$, $\hat{c}(k)$ denote matrices of elements $\hat{h}_{\alpha\gamma}(k)$ and $\hat{c}_{\alpha\gamma}(k)$ respectively and the caret denotes the spatial

Fourier transform given by

$$\hat{c}_{\alpha\gamma}(k) = \int dr \exp[-ik \cdot r] c_{\alpha\gamma}(r) \quad (2.6)$$

The elements of the $\hat{c}(k)$ matrix are the Fourier transform of the intramolecular correlation functions

$$\hat{w}_{\alpha\gamma}(k) = \langle \exp[ik \cdot (I_1^\alpha - I_1^\gamma)] \rangle \quad (2.7)$$

and the brackets denote an equilibrium ensemble average. Equation (5) is solved using the closure relations

$$h_{\alpha\gamma}(r) = -1 \quad r < \sigma_{\alpha\gamma} \quad (2.8a)$$

and

$$c_{\alpha\gamma}(r) = 0 \quad r > \sigma_{\alpha\gamma} \quad (2.8b)$$

The coupled nonlinear integral Eqs. (2.5) and (2.8) were solved for $c_{\alpha\gamma}(r)$ for $r < \sigma_{\alpha\gamma}$ and for $h_{\alpha\gamma}(r)$ for $r > \sigma_{\alpha\gamma}$.¹¹ Using the site-site correlation functions the molecular structure factor was calculated using the equation

$$S(k) = \left(\sum_{\alpha=1}^m b_\alpha^2 \right)^{-1} \sum_{\alpha,\gamma=1}^m b_\alpha b_\gamma [\hat{w}_{\alpha\gamma}(k) + \rho \hat{h}_{\alpha\gamma}(k)] \quad (2.9)$$

The ideal gas structure factor is obtained by setting $h_{\alpha\gamma}(r) = 0$ in Eq. (2.9) and is given by

$$S_{\text{ideal}}(k) = \left(\sum_{\alpha=1}^m b_\alpha^2 \right)^{-1} \sum_{\alpha,\gamma=1}^m b_\alpha b_\gamma \hat{w}_{\alpha\gamma}(k) \quad (2.10)$$

where b_α are the coherent neutron scattering amplitude for a nucleus of type α .

3 THE MODEL FOR GeBr₄

Our RISM picture of GeBr₄ molecule is shown in Figure 1. The molecule is assumed to be rigid with the following intramolecular atom-atom lengths¹²

$${}^L\text{Ge} - \text{Br} = 2.29 \text{ \AA}$$

$${}^L\text{Br} - \text{Br} = 3.82 \text{ \AA}$$

Sidgwick and Laubengayer¹³ have reported the liquid densities at 30°C and 50°C and we have extrapolated density to 60°C from their data, this is

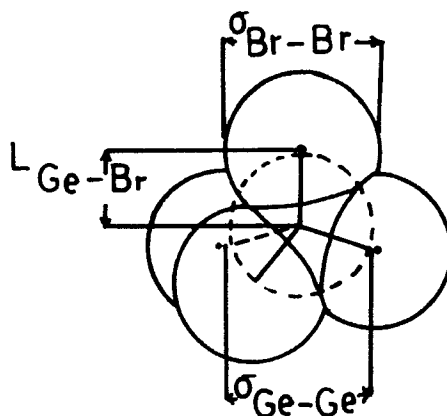
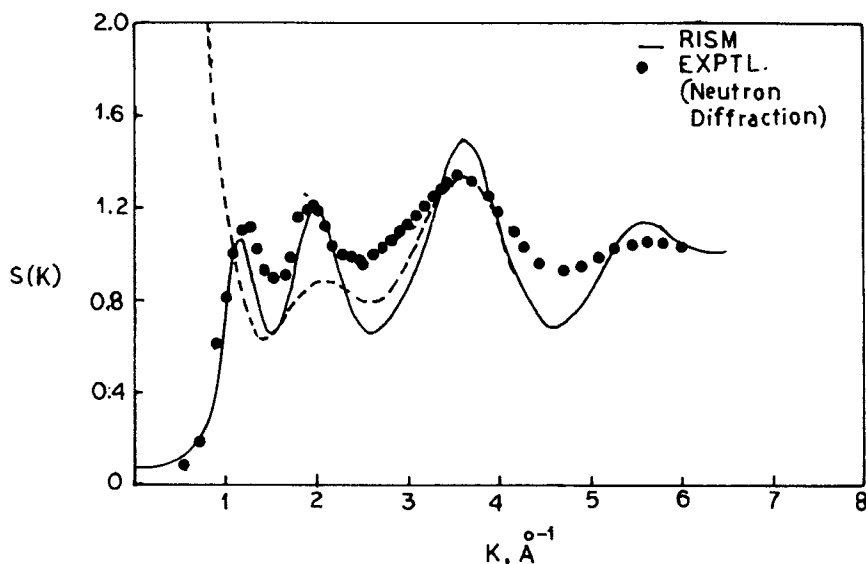


FIGURE 1 RISM picture of Germanium tetrabromide molecule.

because the neutron diffraction experiments were carried out at this temperature. We have solved the RISM on IRIS 55 computer. The sphere diameters chosen (to give the best "fit" to experiment) are $\sigma_{Ge} = 2.44 \text{ \AA}$ and $\sigma_{Br} = 3.4 \text{ \AA}$. The values of the Vander Waals radii¹⁴ are $Ge = 1.22 \text{ \AA}$ and $Br = 1.9 \text{ \AA}$ and our value for Bromine is close to the Vanderwaals radius. The molecular structure factor calculated for this model is shown in Figure 2, and is compared with the Neutron diffraction results of Egelstaff

FIGURE 2 The molecular structure factor of liquid $GeBr_4$ at $60^\circ C$. The full curve is from the RISM. The dots are the experimental points. The chain curve is $S_{ideal}(k)$.

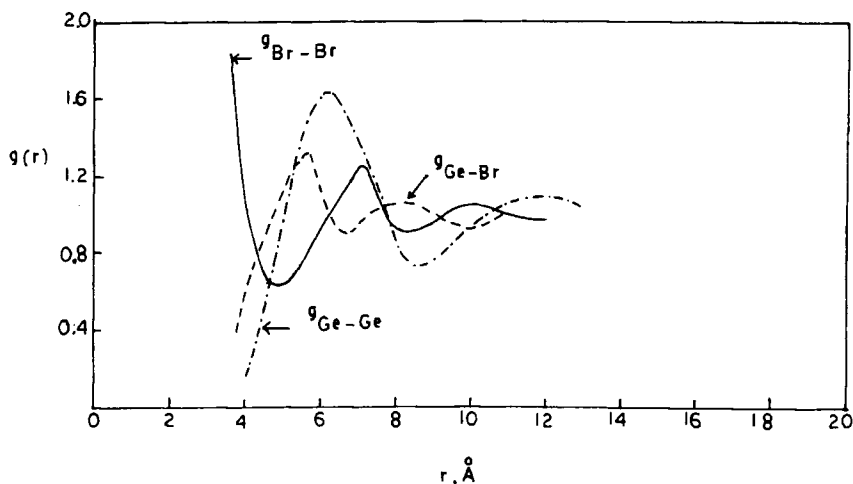


FIGURE 3 The atom atom distribution functions of liquid GeBr_4 , ——— $g_{\text{Br-Br}}$, - - - - $g_{\text{Ge-Br}}$ and - · - · - $g_{\text{Ge-Ge}}$.

*et al.*¹⁰ The intermolecular atom-atom distribution functions $g_{\alpha\gamma}(r)$ obtained from the RISM are shown in Figure 3.

4 RESULTS

From Figure 2 it is evident that the RISM predicts the main peaks in the molecular structure factor quite well but the RISM theory minima in the structure factor are too shallow. In this connection it is important to mention that Egelstaff *et al.*¹⁵ assumed liquid GeBr_4 expands in similar manner as CCl_4 and scaled up the 30°C density data whereas we have taken the density data at 30°C and 50°C and extrapolated it up to 60°C. The first and second peaks in $g_{\text{Ge-Ge}}$ occur at 6.1 Å and 12 Å respectively. The locations of the maxima in $g_{\text{Ge-Br}}$ coincide roughly with the locations of minima in $g_{\text{Br-Br}}$. The Ge-Br radial distribution function has its main peak at 5.3 Å. These features seem to indicate that the local structure of liquid GeBr_4 is one similar to liquid CCl_4 as proposed by Narten⁷ in which a central molecule is interlocked with four of its near neighbours thus giving rise to angular correlations. Egelstaff *et al.*¹⁰ proposed their "Apollo model" in which the Ge-Br bond of one molecule is in line with that of the other molecule and the Bromine atom lies in the hollow formed by three off-axis Bromines of the other molecule. According to this model the main peak in $g_{\text{Ge-Ge}}$ should

occur at a distance not less than the Ge-Br distance (2.3 Å) plus the shell radius within which the coordination number

$$n_{\text{Ge-Br}}(r) = 4\pi\rho \int_0^r r^2 g_{\text{Ge-Br}}(r) dr \quad (4.1)$$

predicts a germanium has four Bromine neighbours (4.9 Å). Thus for the Apollo model the main peak of $g_{\text{Ge-Ge}}$ should occur at no smaller distance than 7.2 Å. But in fact $g_{\text{Ge-Ge}}$ peaks at 6.1 Å. This would appear to suggest that the Apollo model of Egelstaff *et al.* is inadequate for the present case and that the structure of liquid GeBr_4 is better approximated by the one suggested for liquid CCl_4 by Narten.⁷

References

1. D. Chandler and H. C. Andersen, *J. Chem. Phys.*, **57**, 1930 (1970).
2. D. Chandler, *J. Chem. Phys.*, **59**, 2742 (1973).
3. L. J. Lowden and D. Chandler, *J. Chem. Phys.*, **61**, 6587 (1974).
4. L. J. Lowden and D. Chandler, *J. Chem. Phys.*, **61**, 5228 (1974).
5. D. Chandler, C. S. Hsu, and W. B. Street, *J. Chem. Phys.*, **66**, 5231 (1977).
6. A. H. Narten, *J. Chem. Phys.*, **67**, 2102 (1977).
7. A. H. Narten, *J. Chem. Phys.*, **65**, 573 (1977).
8. S. I. Sandler and A. H. Narten, *Mol. Phys.*, **32**, 1543 (1976).
9. C. S. Hsu and D. Chandler, *Mol. Phys.*, **36**, 215 (1978).
10. P. A. Egelstaff, D. I. Page, and J. G. Powles, *Mol. Phys.*, **20**, 881 (1970).
11. We are grateful to Dr. L. J. Lowden for supplying the computer programs for solving the RISM equations.
12. A. F. Trotman-Dickenson, Ed., *Comprehensive Inorganic Chemistry*, Vol. 2, Pergamon Press, Oxford (1973).
13. N. V. Sidgwick and A. W. Laubengayer, *J. Am. Chem. Soc.*, **54**, 948 (1932).
14. L. Pauling, *The nature of the chemical bond*, third edition (Ithaca, Cornell University Press, 1960).
15. D. I. Page, Private communication.