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LIQUID STRUCTURE OF AMMONIA—A CASE OF APOLLO MODEL OF ORIENTATION FOR PYRAMIDAL MOLECULES*

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The Apollo model of Egelstaff *et al.* (1971) for the orientation of tetrahedral AB₃ type molecules has been extended to study the liquid structure of AB₃ type pyramidal molecules like ammonia. With a suitable choice of diameter to calculate the centre structure function through a hard sphere potential, the molecular structure function has been evaluated and compared with experimental X-ray diffraction results. The agreement is satisfactory. From the experimental molecular structure function, the intermolecular angle-averaged potential and other centre correlation functions have been evaluated.

Keywords : Apollo Model; Liquid Structure; Molecular Structure Function; Centre Correlation Functions; Inter-Molecular Angle-averaged Potential

INTRODUCTION

ORIENTATIONAL correlations play a significant role in molecular liquids (Egelstaff *et al.*, 1971; Powles, 1973; and Sandler *et al.*, 1974), and thus it has been tried by various workers (Page & Powles, 1971; Suzuki & Egelstaff, 1974; Murad *et al.*, 1979; Gopala Rao & Murthy, 1976; Gopala Rao & Joarder, 1979, 1980, 1981; and Gopala Rao & Satpathy, 1982) to explain liquid structures through orientational models. The concept of parallel and perpendicular orientations has been applied to linear di- and tri-atomic molecules successfully (Gopala Rao & Joarder, 1979, 1980). Egelstaff *et al.* (1971) proposed the Apollo Model of orientation for tetrahedral molecules. Several tetrahedral liquids have been studied with this model and it has been observed to give good results (Murad *et al.*, 1979; Gopala Rao & Murthy, 1976; and Gopala Rao & Joarder, 1981), unless the sphericity of the molecule has been lost substantially (Gopala Rao & Satpathy, 1981). In such cases, the orientational correlations are large enough to allow separation of the radial and angular part of the correlations.

In this work, the concept of Apollo model of orientation has been applied to the pyramidal liquid molecule, ammonia, where orientational correlations between neighbouring molecules is expected to play an important role due to associations (Narten, 1968, 1977). It has been assumed that the nitrogen nucleus situated at the apex of one molecule lies in the hollow formed by the three hydrogen nuclei of

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another molecule, the nitrogen of whose in turn lies in between the hollow of the three hydrogens of a third molecule and so on; the nitrogen nuclei forming an axis, around which the molecules may rotate. As has been done by Egelstaff *et al.* (1971), the orientation of one molecule with respect to another is assumed to be statistically independent of their relative separation. This assumption has been found to be good in case of quite a few liquid molecules (Gopala Rao & Murthy, 1976; and Gopala Rao & Joarder, 1979, 1980, 1981).

We have two objectives in the present work :

- (i) Using an angle independent potential for the centre structure function and the Apollo model of orientation for the orientational form factor, the molecular structure function, $S_m(Q)$ is to be generated and compared with X-ray diffraction results of Narten (1968).
- (ii) The experimental $S_m(Q)$ is to be used to evaluate the various centre correlation functions within the framework of the orientational model discussed above, through a method given by Rao and Joarder (1978).

THEORY

The molecular structure function, $S_m(Q)$, is given by

$$S_m(Q) = N_m [\sum b_i(Q)]^{-2} \langle \sum_i \sum_j b_i(Q) b_j(Q) \exp (i \bar{Q} \cdot \bar{r}_{ij}) \rangle, \quad \dots(1)$$

where N_m = the number of molecules in the system, $b_i(Q)$ and $b_j(Q)$ are the coherent scattering factors of the i th and j th nuclei, which are separated by a distance r_{ij} . The angular bracket indicates ensemble average and the summation extends over all pairs of nuclei in the system.

The contributions to the summation in eqn. (1) arising from atoms within the same molecule may be separated out from $S_m(Q)$, so that

$$S_m(Q) = f_1(Q) + D_m(Q), \quad \dots(2)$$

where $f_1(Q)$ is the molecular form factor and is defined by

$$f_1(Q) = [\sum b_n(Q)]^{-2} \langle | \sum_n b_n(Q) \exp (i \bar{Q} \cdot \bar{r}_{cn}) |^2 \rangle, \quad \dots(3)$$

where n ranges over all the nuclei in the molecule and c denotes the centre of the molecule.

In eqn. (2), $D_m(Q)$ corresponds to the intermolecular contributions and at small Q values it gives information about the liquid structure.

Following Egelstaff *et al.* (1971), we write eqn. (2) as

$$S_m(Q) = f_1(Q) + f_2(Q) [S_o(Q) - 1], \quad \dots(4)$$

where $f_2(Q)$ is the orientational form factor.

Eqn. (4) is exact only in case of purely spherical molecules. However, in the case of liquid ammonia, the peripheral hydrogen atoms being small in size, the molecule may be treated as fairly spherical to enable us to apply the above theory.

The terms $f_1(Q)$ and $f_2(Q)$ may now be expressed in the present case of AB_3 type of molecules as

$$f_1(Q) = [b_A(Q) + 3b_B(Q)]^{-2} [b_A^2(Q) + 3b_B^2(Q) + 6b_B^2(Q) \times \frac{\sin Qr_{B-B}}{Qr_{B-B}} + 6b_A(Q)b_B(Q) \frac{\sin Qr_{A-B}}{Qr_{A-B}}], \quad \dots(5)$$

and

$$f_2(Q) = [b_A(Q) + 3b_B(Q)]^{-2} [b_A^2(Q) + 6b_A(Q)b_B(Q) \times \frac{\sin Qr_{A-B}}{Qr_{A-B}} + 9b_B^2(Q)I(Qr_t)], \quad \dots(6)$$

where,
$$I(Qr_t) = \int_0^{\pi/2} J_0^2(Qr_t \sin \theta) \sin \theta d\theta, \quad \dots(7)$$

r_t being the radius of the circle through the three B nuclei and is given by

$$r_t = \frac{r_{B-B}}{2 \cos (\pi/6)} \quad \dots(8)$$

For the $S_c(Q)$ term in eqn. (4), we take the Percus-Yevick solution of a simple hard sphere potential with a suitable choice of the hard sphere diameter.

Since the present work yields good result, especially in the first peak region, for $S_m(Q)$ showing the usefulness of eqn. (4), this equation can be employed to obtain $S_c(Q)$ from the experimental $S_m(Q)$. From the $S_c(Q)$ so obtained, the centre direct correlation function, $C_c(r)$, centre radial distribution, $g_c(r)$ and the centre-centre angle averaged potential function, $\phi_c(r)$ can be obtained (Gopala Rao & Joarder, 1978).

RESULTS AND DISCUSSION

Sufficiently accurate X-ray diffraction result of liquid ammonia at 4 °C has been obtained by Narten (1968). The molecular correlation functions have been obtained by Narten (1977) by expanding the scattering density about the molecular centre as prescribed by Blum (1971).

The nearly sphere shape of the ammonia molecule allows one to obtain a good account of the $S_c(Q)$ function from a simple hard sphere potential. The hard sphere diameter is chosen so as to get the best account for the molecular structure function. This $S_c(Q)$ compares very well with the centre structure function given by Narten (1977), as can be seen from Fig. 1. The other molecular parameters

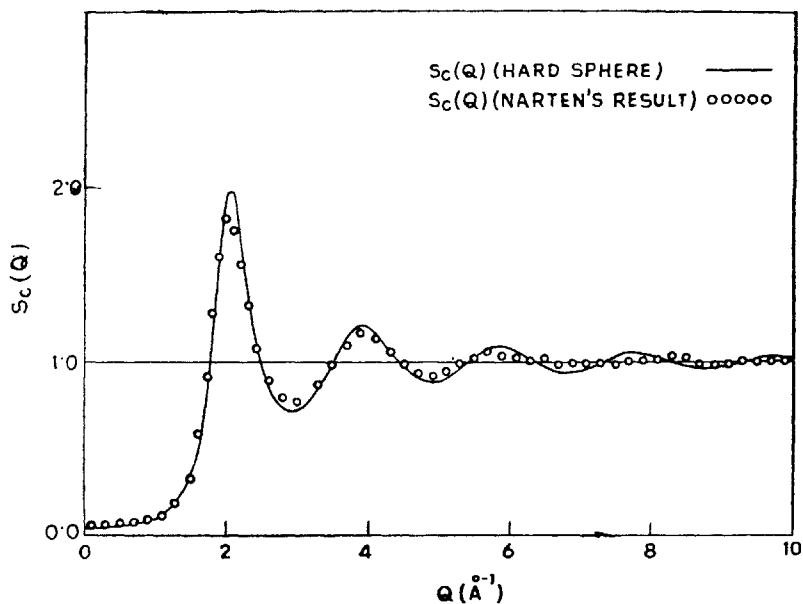


FIG. 1. Centre structure function, $S_c(Q)$, obtained from hard sphere potential (—) compared with Narten's results ($\circ \circ \circ \circ \circ$).

taken, like r_{N-H} and r_{H-H} , are those given by Moelwyn-Hughes (1961). The following are the various molecular parameters used in the calculations :

$$r_{N-H} = 1.014\text{\AA}$$

$$r_{H-H} = 1.628\text{\AA}$$

$$\text{Temperature, } T = 277 \text{ }^\circ\text{K}$$

$$\text{Hard sphere diameter, } \sigma = 3.23\text{\AA}$$

$$\text{Molecular number density, } \rho = 0.02237\text{\AA}^{-3}$$

The $S_m(Q)$ so obtained is compared with the experimental result of Narten (1968) in Fig. 2. It compares well. The theoretically obtained $S_m(Q)$ shows almost all the characteristics of the experimental one, except that in the experimental $S_m(Q)$, the oscillations damp out rapidly and the peak heights beyond the first peak are always less than the theoretical results. However, it may be pointed out here that in calculating the experimental $S_m(Q)$, the theoretically obtained form factors of Blum (1971) have been assumed to be correct. In Fig. 2 also given is the $S_m(Q)$ for ideal gas molecules or $f_1(Q)$.

When the experimental $S_m(Q)$ is available, eqn. (4) provides a method to find out the $S_c(Q)$ function within the framework of the Apollo model of orientation for these molecules. The $S_c(Q)$ so obtained has been used to obtain the various centre correlation functions. Now, if the nitrogen nucleus be taken as the centre of the

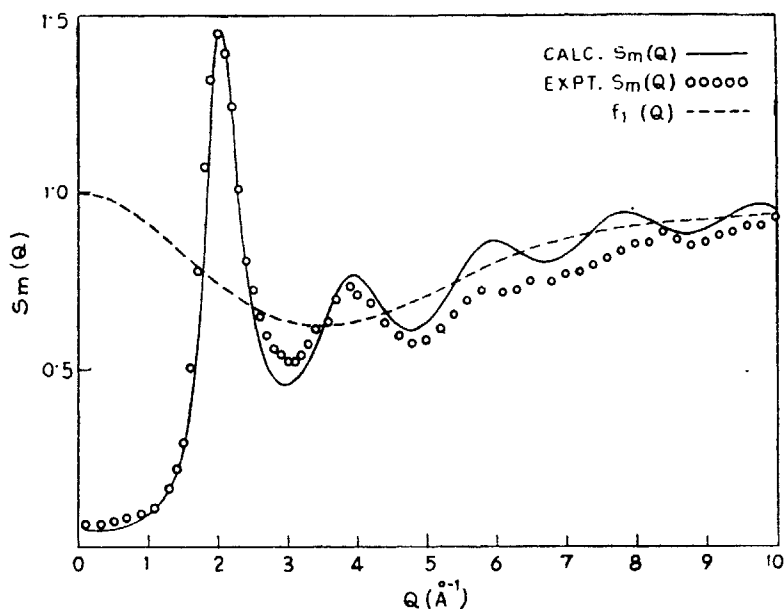


FIG. 2. Molecular structure function, $S_m(Q)$: Calculated results (—) compared with experimental results of Narten (○ ○ ○ ○ ○) and the intramolecular form factor, $f_1(Q)$ (---).

ammonia molecule, as has been done by Narten (1977), then the $S_c(Q)$ becomes identical to the partial structures for nitrogen, i.e., $S_{N-N}(Q)$ and the correlation function obtained for it stands for the partial nitrogen-nitrogen correlation functions.

In Fig. 3, we present the $C_c(r)$ and $g_c(r)$ functions. The $g_c(r)$ so obtained has been compared with that obtained by Narten (1977) from a different method and the agreement is excellent. The first peak in $g_c(r)$ is found at 3.45\AA , there being a shoulder at 3.75\AA and another peak at 4.65\AA showing the first coordination sphere of an ammonia molecule to be complex. Since the shoulder at 3.75\AA is very close to the sum of the van der Waal's radii of nitrogen (1.5\AA) and hydrogen (1.2\AA) atoms (Pauling, 1960) and their intramolecular separation (1.014\AA) (Moelwyn-Hughes, 1961), namely, 3.72\AA , it shows that some neighbouring molecules are in van der Waal's contact distance, some other remaining at an average distance of 4.65\AA . The first peak-position in $g_c(r)$ i.e., 3.45\AA perhaps corresponds to the distance between hydrogen bonded molecules. The second neighbour rests only at around 7\AA .

Fig. 4 shows the angle averaged intermolecular centre-centre potential function, $\phi_c(r)$. From this, it can be seen that the neighbouring molecules at 3.45\AA rest at a higher potential than the ones in van der waal contact at 3.75\AA , the minimum of the potential of 0.024eV being at 3.85\AA and there being only a small hump at 3.45\AA in the potential function curve. A subsidiary minimum in the potential function curve is found at 4.60\AA for the neighbouring molecule located around that distance, as seen from the $g_c(r)$ curve.

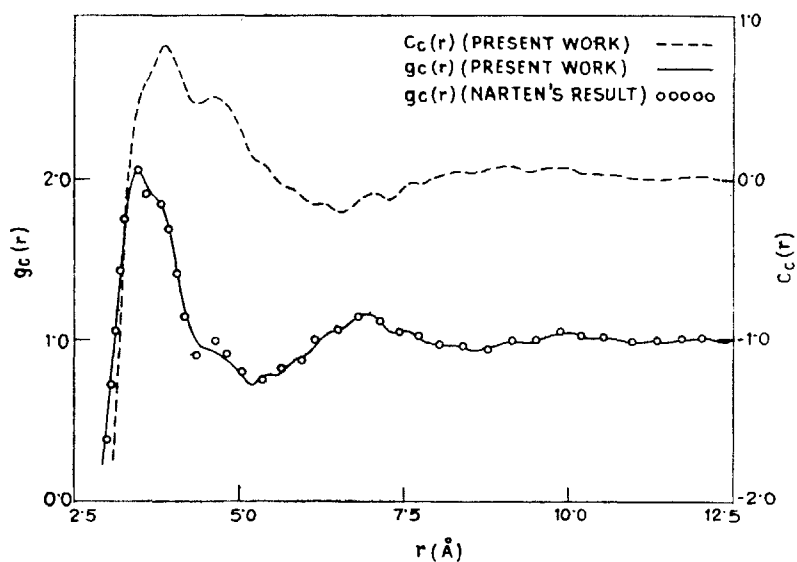


FIG. 3. Centre pair distribution function, $g_c(r)$: Results of present work (—) compared with Narten's results ($\circ \circ \circ \circ \circ$), and the calculated centre direct correlation function, $C_c(r)$, (---)

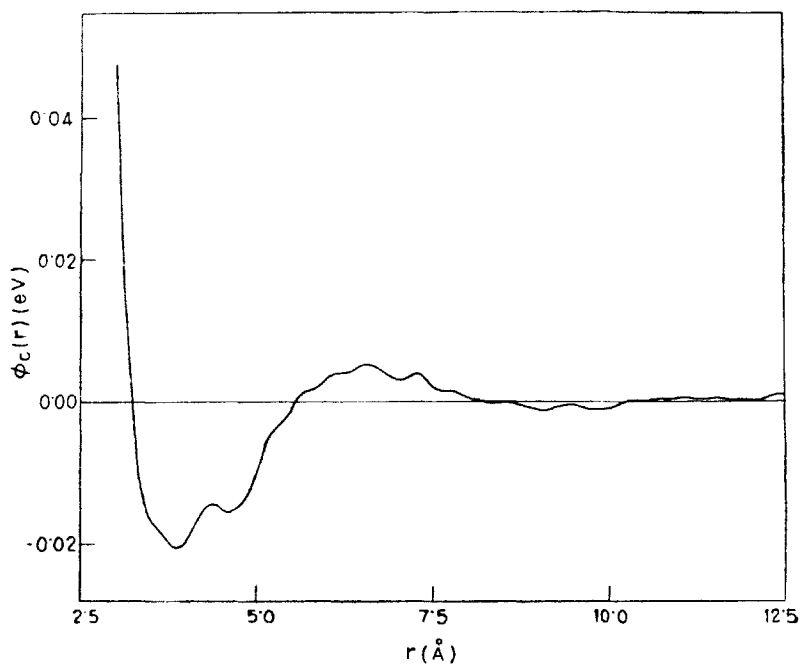


FIG. 4. Angle-averaged intermolecular pair potential, $\phi_c(r)$ in eV.

Thus, in conclusion it is seen that the present model of orientational correlation for AB_3 type of pyramidal molecules, like NH_3 , gives a proper account for the liquid structure. It may be pointed out here that this is not the only model and it is possible that some other model for the liquid may give equally good agreement with experiments.

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