Molecular Conformation and Structural Correlations of Liquid D-*tert*-Butanol at Room Temperature by Neutron Diffraction

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An analysis of neutron diffraction data of liquid deuterated *tert*-butanol at room temperature to determine its molecular conformation is presented. Being a big molecule of 15 sites, the analysis is tricky and needs careful consideration. The resulting molecular parameters are compared with those obtained from other experimental data analysis and model calculations. The information about the intermolecular structural correlations, hydrogen-bonded molecular association in partcular is also obtained from the diffraction data analysis. – PACS number: 61.25

Key words: Conformation; Structure; Correlation; D-*tert*-Butanol; Neutron Diffraction.

1. Introduction

The present work is a continuation of our studies of hydrogen bonded liquids. *Tert*-butanol is the largest molecule in the series of monohydric alcohols which is miscible with water in all proportions. In the present study we have explored the molecular conformation and intermolecular correlations of liquid deuterated *tert*-butanol at room temperature by means of neutron diffraction measurements. The molecular conformation found by x-ray diffraction [1] was incomplete since the hydrogen positions could not be located separately. Neutrons can accurately see the hydrogen / deuterium positions, but because of the size of the molecule with its large number of atomic sites the separation of the intra- and inter-contributions is tricky [2]. To our knowledge there exists no neutron diffraction study on the complete molecular conformation of liquid *tert*-butanol. In [3] the structure and intermolecular correlations of this liquid were explored on the basis of [1]. For room temperature the proposition of a dominant cyclic hexamer ring molecular association by strong hydrogen bonding was quite successful. In [4] we have done a comperative study of the intermolecular correlations of the closely related (having almost similar molecular conformations) non hydrogen-bonded liquid neopentane and hydrogen bonded liquid *tert*-butanol (having one methyl group replaced by a hydroxyl group) at room temperature, which resulted in a dominant orientation correlation in the former and cluster correlation in the latter. Recently, in a preliminary report [5] we have shown that the neutron diffraction data also support the proposition of hexamer closed chain molecular association favourably representing the liquid structure of *tert*-butanol at room temperature. However, these conclusions depend on the accurate knowledge of the molecular conformation in the liquid state. Therefore in the present study we thoroughly analyse the detailed neutron data available to us. With a number of distances between different atomic sites being comparable with intermolecular distances, the separation of the intra- and intermolecular terms is quite difficult and therefore a modified and careful technique of data analysis has been adopted. In the following sections we describe the various aspects of our study.

2. Experimental

A careful neutron diffraction measurement of a fully deuterated liquid *tert*-butanol sample at room temperature was carried out on the high-Q diffractometer at Dhruva, BARC (India) in collaboration with the BARC group. The liquid used in the experiment consisted of a 99.8% deuterated sample available from Aldrich Ltd. (USA). It was held in a vanadium can of 6 mm diameter and 0.1 mm thickness. The conventional procedure was followed. The data

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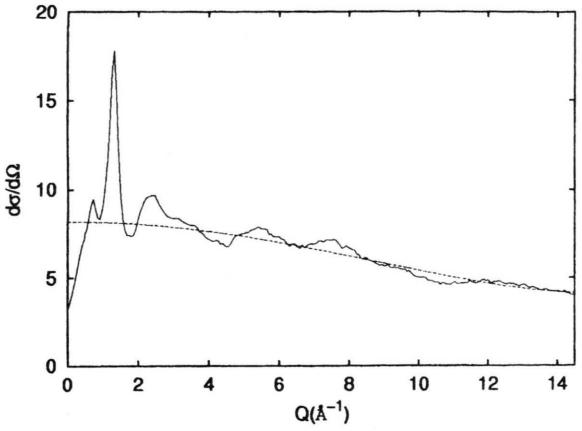

Fig. 1. Corrected cross-section data, $d\sigma/d\Omega$ vs. Q: — normalized experimental data, - - - self part.

collection and experimental corrections for container scattering, self-attenuation and multiple scattering were done in the usual manner, and the cross-section data were normalized using a standard vanadium rod. Incident wavelengths of 0.783 Å and 1.278 Å were used, and the data were recorded for an angular range of 3 to 125°. The corrected cross-section data show a strong pre-peak at a scattering vector Q of about 0.71 $Å^{-1}$, Fig. 1, similar to what is observed in x-ray diffraction data [1].

3. Method of Analysis

3.1. General

The corrected scattered data were extrapolated in the region $0 \leq Q \leq 0.3\,Å^{-1}$ and were normalized (on high-Q data as well) such that the graphical extrapolation to $Q \to 0$ yields an isothermal compressibility of 12.1×10^{-11} cm²/dyne. The data are then separated into "self" and "interference" terms,

$$\mathrm{d}\sigma/\mathrm{d}\Omega\big|_{\mathrm{expt}} = \mathrm{d}\sigma/\mathrm{d}\Omega\big|_{\mathrm{self}} + \mathrm{d}\sigma/\mathrm{d}\Omega\big|_{\mathrm{int}}. \quad (1)$$

At high-Q, the experimental cross-section data have a "fall-off" feature. This is due to interaction of incident neutrons with the vibrating scattering sites [2]. This part can be reproduced by the self scattering terms. For alcohols this can be represented [2, 6] by

$$\mathrm{d}\sigma/\mathrm{d}\Omega\big|_{\mathrm{self}} = [4b_{\mathrm{c}}^2 + b_{\mathrm{o}}^2 + 10b_{\mathrm{d}}^2 + 10(\sigma_{\mathrm{d}}^{\mathrm{i}}/4\pi)] \cdot (1 - aQ^2 + bQ^4), \quad (2)$$

Table 1. Inelasticity parameters: $a = (4.3118 \pm 0.002) \times 10^{-3}$ Å², $b = (9.3768 \pm 0.02) \times 10^{-6}$ Å⁴. Constant for Debye-Waller terms: $\lambda_0 = 0.10134$, $\chi^2 = 3.47979957 \times 10^{-5}$.

Molecular parameters	present	x-ray [1]	Electron diffraction [9] (Gas phase)	MOC[10] (Theoretical, gas phase)	MM2[9] (Theoretical, gas phase)
r_{CC} (Å)	1.54 ± 0.01	1.54 ± 0.01	1.529 ± 0.002	1.553	1.540
r_{CO} (Å)	1.43 ± 0.01	1.43 ± 0.01	1.446 ± 0.004	1.441	1.419
r_{CD} (Å)	1.094 ± 0.002	–	1.117 ± 0.002	1.085	1.114
r_{OD} (Å)	0.907 ± 0.02	–	1.016 ± 0.014	0.991	0.942
$\angle C_1OD_1$	(102.42 ± 2.0)°	–	(108.0 ± 3.0)°	104.3°	109.0°
ϕ_{OD_1}	(192.45 ± 5.0)°	–	*(3.1 ± 5.0)°	*3.2°	*0.6°
ϕ_1	(14.4 ± 2.0)°	–	$\phi_1 = \phi_2 = \phi_3$	$\phi_1 = \phi_2 = \phi_3$	$\phi_1 = \phi_2 = \phi_3$
ϕ_2	(9.45 ± 3.5)°	–	(12.0 ± 3.0)°	0.0°	0.8°
ϕ_3	(−12.0 ± 2.0)°	–	–	–	–

* Tilt angle of the *t*-butyl group.

where $\sigma_{\mathrm{d}}^{\mathrm{i}}$ is the incoherent scattering cross-section for deuterium and a, b are two inelasticity parameters. b_{c}, b_{o}, b_{d} are the coherent scattering lengths of carbon, oxygen, and deuterium respectively. The inelasticity parameters a and b, estimated by χ^2-fitting between the self-scattering term, and the experimental data at high-Q values (starting from $Q \simeq 5.5$ - 6.0 $Å^{-1}$) are listed in Table 1. The overall normalization constant, estimated from the isothermal compressibility limit, is taken as 0.228. Figure 1 shows the fitted results for the normalized $\mathrm{d}\sigma/\mathrm{d}\Omega\big|_{\mathrm{expt}}$ and $\mathrm{d}\sigma/\mathrm{d}\Omega\big|_{\mathrm{self}}$. $\mathrm{d}\sigma/\mathrm{d}\Omega\big|_{\mathrm{int}}$, obtained from (1), contains both intra- and intermolecular contributions. The total structure function, $H(Q)$, is defined as

$$H(Q) = \mathrm{d}\sigma/\mathrm{d}\Omega\big|_{\mathrm{int}} / \sum b_i^2$$

$H(Q)$ can be separated into intra- and intermolecular terms given by

$$H(Q) = H_{\mathrm{m}}(Q) + H_{\mathrm{d}}(Q), \quad (3)$$

where $H_{\mathrm{m}}(Q) = (\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{int}}^{\mathrm{intra}}/(\sum_i b_i)^2$ and $H_{\mathrm{d}}(Q) = (\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{int}}^{\mathrm{inter}}/(\sum_i b_i)^2$. In the literature a term often used is the molecular structure factor, $S_{\mathrm{m}}(Q)$, which is given by

$$S_{\mathrm{m}}(Q) = F_1(Q) + H_{\mathrm{d}}(Q), \quad (4)$$

where $F_1(Q) = \sum_i b_i^2/(\sum b_i)^2 + \sum_i \sum_{ji \neq j} b_i b_j j_0 (Qr_{ij}) \exp(-\gamma_{ij}Q^2)/(\sum_i b_i)^2$, r_{ij} being the mean distance between sites i and j. $2\gamma_{ij}$ is the mean square variation in the distance r_{ij}. $\gamma_{ij} = (1/2)\lambda_0^2 r_{ij}$, where

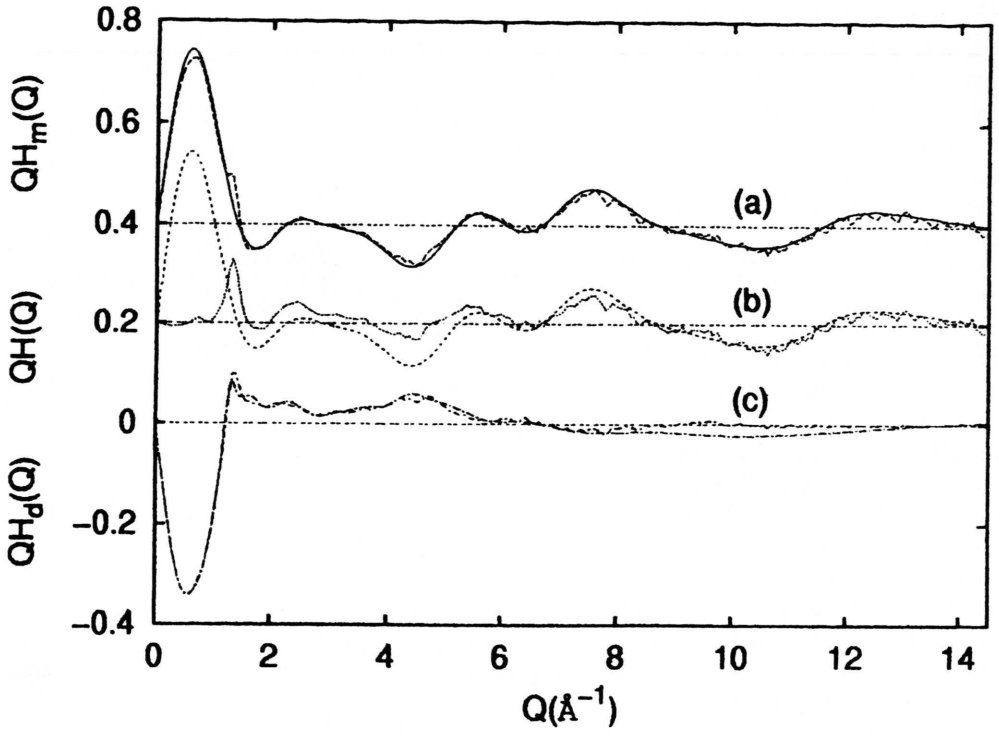

Fig. 2. Q-weighted structure functions vs. Q: (a) - - - $QH_m(Q)$ (corrected); — $QH_m(Q)$ (model), ordinate scale shifted by 0.4. (b) ··· $QH(Q)$ (experimental); - - - $QH_m(Q)$ (model), ordinate scale shifted by 0.2. (c) ····· $QH_d(Q)$ (from exptal data); -●-●- hexamer ring cluster model result.

λ_0 is taken to be a constant for all the pairs (similar to Prins relation [7]). i and j sum independently over 15 atomic sites within the *tert*-butanol molecule. $j_0(x) = \sin x/x$ is the zeroth order spherical Bessel function. $F_1(Q)$ infact contains a coherent self-term and intra interference term $H_m(Q)$. $H_m(Q)$ gives information about the structure of the molecule, while $H_d(Q)$, often also called 'distinct' structure function, gives information about the intermolecular or liquid structure. In terms of partial structure functions $H_{ij}(Q)$, $H_d(Q)$ can be written as

$$H_d(Q) = (\sum_i b_i)^{-2} \sum_i \sum_j (2 - \delta_{ij}) b_i b_j H_{ij}(Q).$$

The inverse Fourier transform (I. F. T.) of $H_d(Q)$ gives the liquid r-weighted intermolecular correlation function $d(r)$ and the radial distribution function (RDF), $G_d(r)$ given by

$$d(r) = \frac{2}{\pi} \int_0^\infty Q H_d(Q) \sin(Qr)\, dQ \qquad (5a)$$

$$G_d(r) = 1 + d(r)/4\pi\rho r, \qquad (5b)$$

where ρ is the density of *tert*-butanol at room temperature.

$G_d(r)$ is related to partial distribution functions, $g_{ij}(r)$ given by

$$G_d(r) = (\sum_i b_i)^{-2} \sum_i \sum_j b_i b_j g_{ij}(r)$$

where $g_{ij}(r) = 1 + \frac{1}{2\pi^2\rho r} \int_0^\infty Q H_{ij}(Q) \sin(Qr)\, dQ$.

3.2. Molecular Conformation

In hydrogen-bonded liquids, effects of intermolecular hydrogen bonding persists at high Q [1]. So $H_d(Q)$ continues to show oscillatory behaviour, positive and negative, and modulates $H_m(Q)$. $H_d(Q)$, however, tends to vanish gradually, and so $H(Q)$ almost equals to $H_m(Q)$ at large Q. This implies that for Q greater than some value Q_{min}, the value of the

total structure function comes primarily from the intermolecular part. Assuming a model of the molecule, we can find the atom-atom distances. By calculating $H_m(Q)$, using these distances, we can fit $QH_m(Q)$ to $QH(Q)$ for $Q > Q_{min}$ by the χ^2-fitting method. For this fit we use an initial set of intraparameters obtained from x-ray data analysis [1] and neutron data analysis of other alcohols [2, 6]. Now subtracting $H_m(Q)$ from $H(Q)$ in (3) we obtain a first estimate of $H_d(Q)$. The intermolecular radial distribution function is obtained from the I. F. T. of $H_d(Q)$ according to (5b). Because of the limited Q-range (Q_{max}) available in the experiment, a modification or window function, $W(Q) = \sin(\pi Q/Q_{max})/(\pi Q/Q_{max})$ [6], was used in the I. F. T. Further, we choose Q_{max} such that $G_d(r = 0)$ is almost zero and it is assumed that the contribution of the integral in (5a) beyond $Q = Q_{max}$ is almost zero. $G_d(r)$ is expected to be zero in the range $0 \leq r \leq r_0$ where r_0 is about 1.5 Å, because within the core region of the molecule there is little possibility of intermolecular interaction. Setting $G_d(r) = 0$ for this region, a Fourier transform (F. T.) of the resultant $G_d(r)$ would yield a new $QH_d(Q)$. Subtracting this $QH_d(Q)$ from QH(Q) we obtain the corrected $QH_m(Q)$. The difference between the corrected $QH_m(Q)$ and original $QH_m(Q)$ is however small. Varying molecular parameters, the subsequent iteration process gives a best fit to this corrected function. A χ^2-fitting is used for the whole range of Q-data in steps of 0.01 Å^{-1}. This method resembles the method applied by Bertagnolli et al. [8] for a neutron diffraction data analysis of liquid acetonitrile. The fitted curves are shown in Fig. 2(a). The agreement is very good. The molecular parameters are listed in Table 1.

4. Results of the Analysis

4.1. Model of the Molecule and Intra-molecular Structure

In the x-ray diffraction studies of liquid *tert*-butanol, Narten [1] used the group scattering concept. The methyl and hydroxyl groups were treated as single scattering sites. Since the x-ray measurements are dominated by scattering from the carbon and oxygen atoms, important information about hydrogen positions was not directly accessible. In [3], however, we considered the methyl group, oxygen and hydroxyl hydrogen as different scattering sites.

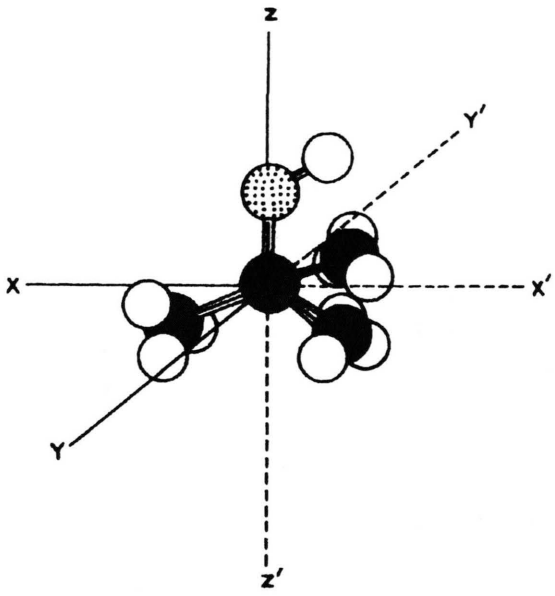

Fig. 3. Molecular conformation of liquid *tert*-butanol. Black circles: carbon atoms; white circles: deuterium atoms; dotted circle: oxygen atom.

In neutron diffraction, deuterium atoms scatter the neutron beam significantly. So diffraction by deuterium atoms must be considered. Considering all the scattering sites as scattering units, *tert*-butanol consists of 15 scattering sites. It is quite a big molecule, almost spherically symmetric with small asymmetry due to the hydroxyl group. Although *tert*-butanol is a big molecule, comparable with the glycerol molecule (having 14 sites) [2], there is an interesting feature in the structure of *tert*-butyl alcohol due to its almost symmetrical structure except due to methyl and hydroxyl groups.

The conformation of the molecule is represented in Figure 3. Considering its symmetric structure, one can minimize the number of parameters to describe its conformation. We assume C_1C_2 in the X-Z plane and C_1O along the Z-axis. The coordinates of C_3 and C_4 are obtained by 120° and 240° rotations of the C_2 coordinates about the Z-axis, respectively. We minimize the number of parameters by assuming that the CC distances (C_1-C_2, C_1-C_3, C_1-C_4) and also all the CD distances in the methyl groups are equal. The r_{CC} and r_{CO} distances are taken as obtained from the x-ray diffraction data analysis. Denoting D_1 as hydroxyl deuterium four rotational angles ϕ_{OD_1}, ϕ_1, ϕ_2, ϕ_3 (in addition to $\angle C_1OD_1$) and two internal distances r_{CD} and r_{OD} are treated as variable parameters, while the

methyl backbones are assumed to have tetrahedral geometry. The tilt angle of the methyl group, which is quite small in the vapour phase [9], is assumed to be zero in the liquid state as in the x-ray work [1]. We however consider ϕ_{OD_1}, the rotational angle of OD_1 measured from X-Z plane while ϕ_1, ϕ_2, ϕ_3 are the rotational angles of the CD_3 groups about C_1C lines.

Using the method stated earlier, the χ^2-fitting result depicted in Fig. 2(a) gives the molecular parameters (Table 1), which are all very reasonable. The parameters determined by the electron diffraction method [9], theoretical molecular orbital calculation (MOC) with the energy gradient method in the STO-3G level [10] and molecular mechanics calculation (MM2) [9] are also listed for comparison. In the orbital calculation the methyl and hydroxyl groups were almost symmetrically placed, and a precision in the estimation of bond lengths of the order of 0.03 Å was possible. The hydroxyl group OD_1 is almost at a staggered position, as expected. However, the hydroxyl OD_1 distance appears to be smaller than that obtained in liquid methanol [6], but this is much bigger than the one obtained for liquid isopropanol [11]. In crystalline ethanol this distance is found to be as small as 0.79 Å and 0.85 Å [12]. The error estimate for each parameter is done to allow a 1% incrase in the χ^2-value. The thermal vibrational factors were calculated as already stated, and the proportionality constant λ_0 was also obtained by χ^2-fitting and is listed in Table 1 along with other molecular parameters. In Fig. 2(b) we show the Q-weighted model intrastructure function $H_m(Q)$ along with the Q-weighted total structure function $H(Q)$. The agreement between the two data at large Q is almost similar to the one obtained in x-ray diffraction data analysis [1].

4.2. Intermolecular Contributions and Liquid Structure

We then use (3) to obtain the intermolecular structural contribution $H_d(Q)$. The determination of this function is important in the sense that the liquid structure is obtained thereby. The Q-weighted data $H_d(Q)$ are shown in Figure 2(c). The oscillatory behaviour gradually vanishes above 9.5 $Å^{-1}$, similar to the one in the x-ray case [1], and this indicates that our treatment to find out the molecular parameters is quite accurate. The intermolecular r-weighted correlation function $d(r)$ is determined using (5a) and is shown in Figure 4(a). The window function is used in the Fourier transform to reduce the undesirable ripples which arise due to truncation effects. A quadratic interpolation with Filon's quadrature has been used. The result obtained from x-ray data [1] is also shown in Fig. 4(a) for comparison. For obvious reason the OD peak is absent in the x-ray result. Anyway, the intermolecular atom-atom correlations can be clearly identified. The comparison also helps to identify the plausible hydrogen-bonded molecular association or cluster present in the liquid state at room temperature. The humps at 1.8 Å to 2.0 Å and at 3.0 Å are clearly due to distances associated with the intermolecular O-D and O-O distances, respectively, arising from an almost linear H-bond. The result exhibits a broad oscillatory pattern extending to about 16 Å. The main feature is a broad peak at $\sim$ 6 Å, which is similar to one observed in glycerol [2], whereas the main broad peak for methanol appears at $\sim$ 4.5 Å [6], signifying the largeness of the *tert*-butanol molecule. It is also interesting to note that the spurious oscillations in $d(r)$ around the density line in the low r (< 1.5 Å) region can be represented approximately by a damping oscillatory function (Fig. 4(a)). The corrected $d(r)$ function is shown in Figure 4(b). The OD and OO peaks are now clearly visible. The corrected RDF, $G_d(r)$ curve is shown in Figure 4(c). The various distances at which the peaks and humps occur, as in the x-ray data [1, 3], support the presence of specific molecular associations (preferably hexamer rings) in the liquid state.

5. General Remarks

In this analysis we have studied the molecular conformation of hydrogen-bonded liquid *tert*-butanol through neutron diffraction. Although it is a big molecule having 15 atoms, it has a structural beauty, being almost spherical with a small asymmetry due to the hydroxyl group. The analysis gives an average conformation of the molecule and shows the effect of intermolecular H-bonding. The basic liquid structure of alcohols is the H-bonding of neighbouring molecules resulting in the formatiom of clusters [13, 14].

To deduce the liquid structure, the x-ray data were analyzed [3] for two models – a closed chain hexamer and a linear chain tetramer cluster of neighbouring molecules. The hexamer chain model was

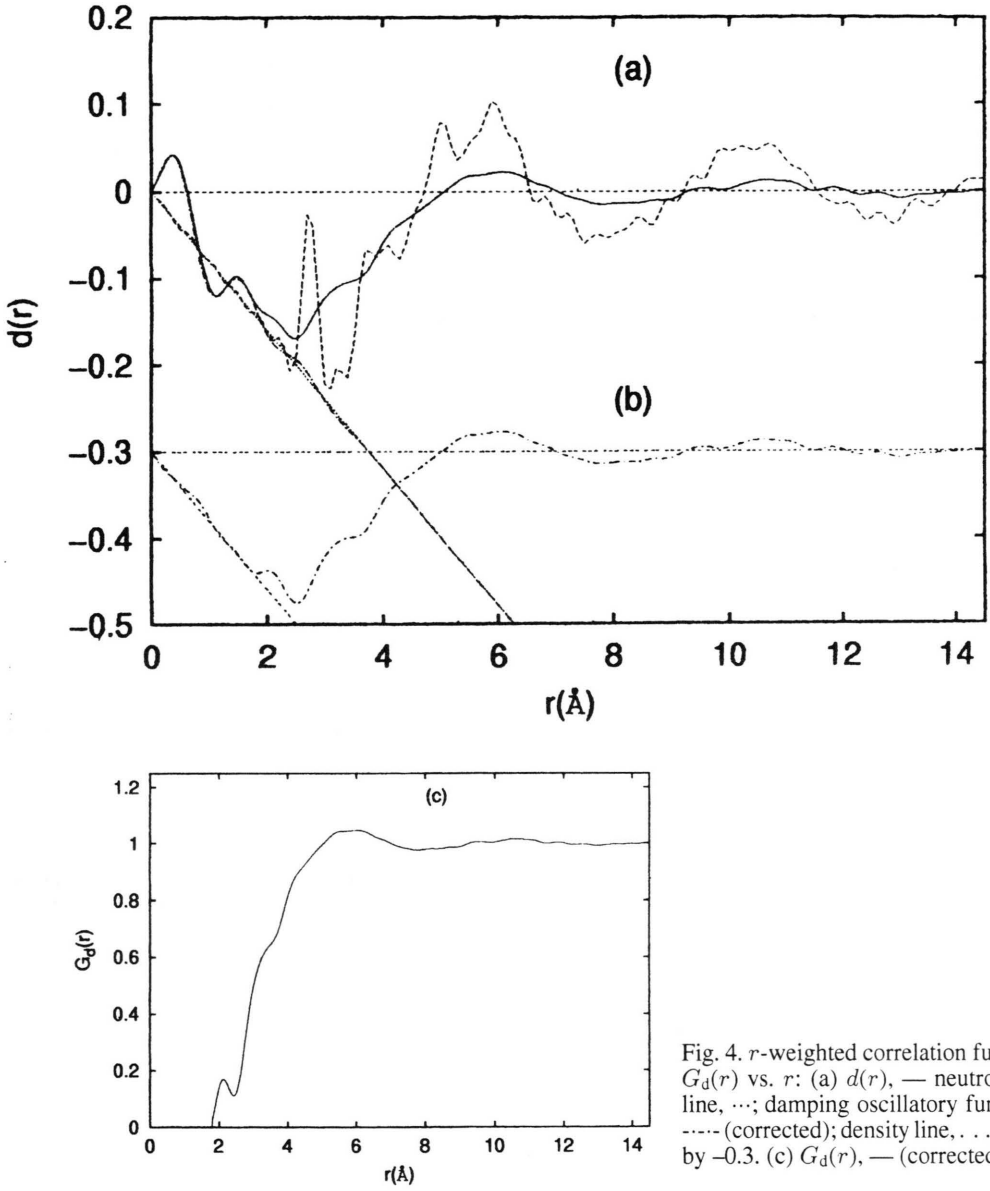

Fig. 4. r-weighted correlation function, $d(r)$ and RDF, $G_d(r)$ vs. r: (a) $d(r)$, — neutron; x-ray - - -; density line, ···; damping oscillatory function, -●-●-. (b) $d(r)$, -·-·- (corrected); density line, . . ., ordinate scale shifted by –0.3. (c) $G_d(r)$, — (corrected).

shown to be more probable. In a recent communication [4] a more crucial analysis of the structure of *tert*-butanol liquid in terms of the asymmetrical part of the intermolecular correlation was presented. This analysis too suggests that the hexamer ring cluster model is a plausible model for the liquid structure. The intermolecular H-bonded hexamer closed chain cluster model reproduces well the pre-peak in the x-ray diffraction data [3], and so does also the preliminary work with neutron diffraction data [5] of liquid *tert*-butanol. Detailed work on model analysis is in progress and will be reported soon. One such result for the hexamer ring cluster model, as assumed in [5], is shown in Figure 2(c).

In the analysis of heats of vaporization and other allied data [13] of the organic alcohols there is a strong support in favour of small cyclic rings mostly tetramers for intermolecular structure. In vapor phase of alcohols the existence of closed tetramer rings are known for long while in solid phase a linear chain of infinite length is well known [14]. In pure liquids the actual structural association is not still very clear

but the diffraction data strongly favours the dominant presence of cyclic hexamer rings.

Neutron diffraction data of liquid *tert*-butanol based on isotopic substitution method [15] has been analyzed by empirical potential structure refinement model. The results however suggest the intermolecular H-bonding to be of less extent than generally accepted. The actual conformation of the molecule was however not known by this analysis.

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