

The partial distribution functions and effective pair potentials of some H-bonded liquids from diffraction data

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Abstract. The partial structures and distribution functions are directly linked to structural model of molecular liquids. The comparative study of partial distribution function of different hydrogen-bonded liquids gives the information that hydrogen-bonding is stronger in alcohols than in water and ammonia. The effective pair potential is directly related to the pair correlation function. The comparative study of such potentials for different hydrogen-bonded liquids gives some characteristic features.

Keywords. H-bonded liquid; partial distribution function; pair potential.

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1. Introduction

In our previous laboratory studies, investigations were carried out on the intermolecular structural association of strongly H-bonded liquids, water [1], alcohols [2] and weakly H-bonded liquid ammonia [3]. Devoid of intramolecular terms, the diffraction profile is essentially due to interference in the scattering from different atomic sites present on neighboring molecules so that description in terms of pair correlation functions is more directly linked to the observations. In the present study, the emphasis concerns on the method of evaluating the intermolecular partial structures and correlations in relation to the intermolecular structural association or cluster models of the H-bonded liquids studied earlier. These computed partial structures and correlations provide not only the crucial test [1] of the various association or cluster models but also clearly exhibit the structural distinction from other molecular liquids which are non H-bonded with van der Waals' forces dominating the intermolecular interaction. Like other liquids the pair correlation or distribution functions are directly related to the pair potentials. So if one knows these functions, in principle, the effective pair potential can be evaluated.

Though the intermolecular atom–atom pair distribution function $g_{\alpha\beta}(r)$'s are useful to define the detailed structure of the liquid and these functions have the advantage that their 'definition' do not involve any approximation, the actual extraction of these functions from experimental data is possible only in limited cases [4]. In the case of liquids which consist of two non-equivalent atoms e.g. water and ammonia there are three pair distribution functions and a minimum of three independent scattering experiments (x-ray, neutron, electron or isotopic substitution neutron experiments) are necessary to determine

these distribution functions. The number rapidly increases for molecules with more than two non-equivalent atoms e.g. methanol or acetonitrile [5, 6]. Many organic liquids of considerable importance consist of three or more atomic species, a full description in terms of $g_{\alpha\beta}(r)$ becomes extremely difficult.

The intermolecular atomic site-site pair distribution functions are also obtainable in Monte Carlo (MC) or molecular dynamics (MD) simulations based on effective pair potential models of H-bonded liquids [7]. However, a direct comparison of the partial $g_{\alpha\beta}(r)$ functions with experimentally evaluated values will give a proper test of the potential model [8] used in computation. Evidently the success of this method depends on the modelling of the potential function which itself is a problem for large H-bonded molecules.

In the light of such a situation, the present approach is relevant. The method is based on the assumption that on average, there exist in the liquid one or two types of distinct H-bonded clusters in dominant form. Using a combined analysis of x-ray and neutron diffraction data, we have evaluated [1–3] the center structure factors of several H-bonded liquids through geometrical cluster models. These models then readily yield the intermolecular structures and pair distribution functions. Further, the intermolecular center radial distribution function (CRDF), $g_c(r)$ and center direct correlation function (CDCF) $C_c(r)$ are obtained by Fourier transform of the center structure factor computed from diffraction data. These functions give the average intermolecular picture of the liquid systems with characteristic H-bonding features. From the knowledge of $g_c(r)$ and $C_c(r)$ it is possible to evaluate the average effective pair potentials for several H-bonded liquids using various approximate theories available in the literature [9].

2. Theoretical background

(a) *Partial structures and correlations*

The partial structure factors [9] for a molecule containing several atom types α and β can be expressed as

$$a_{\alpha\beta}(k) = 1 + \rho \int (g_{\alpha\beta}(r) - 1) \exp(ik \cdot r) dr, \quad (1)$$

where $g_{\alpha\beta}(r)$ is defined as follows. The total radial distribution function $g(r)$ consists of a number of independent partial distribution functions $g_{\alpha\beta}(r)$. In a molecular liquid, we can define atom pair distributions $g_{\alpha\beta}(r)$ so that $\rho g_{\alpha\beta}(r) dr$ is the number of β sites in a volume element dr at a distance r from an α site on another molecule in a fluid of bulk number density ρ . The function $g_{\alpha\beta}(r)$ are obtained from experimentally accessible partial structure factors $a_{\alpha\beta}(k)$ by Fourier inversion relation, i.e.

$$g_{\alpha\beta}(r) = 1 + \frac{1}{(2\pi)^3 \rho} \int_0^\infty (a_{\alpha\beta}(k) - \delta_{\alpha\beta}) j_0(kr) dk. \quad (2)$$

The atom–atom pair correlation functions $h_{\alpha\beta}(r)$ are given by $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$. In general, for molecular liquids the intermolecular distinct structure function $H_d(k)$ which

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is experimentally accessible contains a weighted sum of the partial functions [10] and is written as

$$H_d(k) = M(k) \sum_{\alpha} \sum_{\beta} f_{\alpha} f_{\beta} H_{\alpha\beta}(k), \quad (3)$$

where f'_{α} s are k -dependent x-ray atomic scattering factors or k independent neutron scattering lengths and $M(k) = [\sum_{\alpha} f_{\alpha}]^{-2}$, the summation extending over all atoms of a molecule. In (3) the partial structure function $H_{\alpha\beta}(k) = \rho h_{\alpha\beta}(k)$ and $\rho h_{\alpha\beta}(k) = a_{\alpha\beta}(k) - \delta_{\alpha\beta}$ for α site on one molecule and β site on another. The diffraction experiments on molecular liquids are interpreted in terms of atom-atom pair distribution functions $g_{\alpha\beta}(r)$. But they do not contain enough information to give the angular dependent pair distribution function.

The estimate of the number of neighboring β site of one molecule surrounding α site of another molecule [9] is obtained by integrating $g_{\alpha\beta}(r)$ as follows

$$n_{\alpha\beta} = 4\pi\rho \int_0^{r_{\min}} g_{\alpha\beta}(r)r^2 dr, \quad (4)$$

where r_{\min} is the value of the first minimum of $g_{\alpha\beta}(r)$ distribution function.

Partial structures and pair distribution functions via cluster model: In ref. [1, 2] it was shown on the basis of assumptions that the liquid contains distinct molecular clusters due to H-bonding and that these clusters are orientationally uncorrelated as

$$H_d(k) = H_c(k) + F_{2u}(k)[S_c(k) - f_3(k) - 1], \quad (5)$$

where $H_c(k)$ is the intermolecular cluster structure function defined by

$$H_c(k) = M(k)N_c^{-1} \sum_{1 \neq 1'} \sum_{\alpha, \beta} f_{\alpha_1} f_{\beta_{1'}} j_0(kr_{\alpha_1\beta_{1'}}) \exp(-\lambda_{\alpha_1\beta_{1'}}^2 k^2/2) \quad (5a)$$

with N_c , the number of molecules in a cluster, α, β denote the atoms while $1, 1'$ denote molecules, $\lambda_{\alpha_1\beta_{1'}}$, the root-mean-square deviation of the local instantaneous atom-atom separation distance $r_{\alpha_1\beta_{1'}}$, and $j_0(x) = x^{-1} \sin x$.

The uncorrelated molecular form factor $F_{2u}(k)$ is given by

$$F_{2u}(k) = M(k) \left[\sum_{\alpha} f_{\alpha} j_0(kr_{c_{\alpha}}) \exp(-\lambda_{c_{\alpha}}^2 k^2/2) \right]^2, \quad (5b)$$

where c refer to the center of a molecule.

The center structure $S_c(k)$ of the liquid is

$$S_c(k) = 1 + N_m^{-1} \sum_{1 \neq 1'} j_0(kr_{c_{11'}}) \exp(-\lambda_{c_{11'}}^2 k^2/2) \quad (5c)$$

with N_m the number of molecules in the system, $f_3(k)$, the structure factor resulting from molecular center pairs within a cluster defined as

$$f_3(k) = N_c^{-1} \sum_{1 \neq 1'} j_0(kr_{c_{11'}}) \exp(-\lambda_{c_{11'}}^2 k^2/2). \quad (5d)$$

We have in general $H_c(k) \rightarrow H_d(k)$ for moderate to large k values and geometrical modelling of $H_c(k)$ provides information about the existence of dominant molecular clusters [1–3]. Once the dominant clusters are identified it is straightforward to evaluate the partial structures and distribution functions via cluster model. In order to do that we follow the method of Orton [11] and Ohtomo *et al* [12] depicted in ref. [1]. We assume that $H_{\alpha\beta}(k)$'s in (3) are given by the term involving $\alpha - \beta$ interactions from functions $H_c(k)$ and $F_{2u}(k)$ of (5). Thus

$$H_{\alpha\beta}(k) = H_c^{(\alpha\beta)}(k) + F_{2u}^{(\alpha\beta)}(k)[S_c(k) - f_3(k) - 1], \quad (6)$$

where

$$H_c^{(\alpha\beta)}(k) = N_c^{-1} \sum_{1 \neq 1'} \sum_{\alpha, \beta} j_0(kr_{\alpha_1\beta_{1'}}) \exp(-\lambda_{\alpha_1\beta_{1'}}^2 k^2 / 2) \quad (6a)$$

and

$$F_{2u}^{(\alpha\beta)}(k) = (2 - \delta_{\alpha\beta}) j_0(kr_{c\alpha}) j_0(kr_{c\beta}) \exp[-(\lambda_{c\alpha}^2 + \lambda_{c\beta}^2) k^2 / 2]. \quad (6b)$$

The function $g_{\alpha\beta}(r)$'s are then given by

$$g_{\alpha\beta}(r) = 1 + \frac{1}{2\pi^2 \rho r} \int_0^\infty k H_{\alpha\beta}(k) \sin(kr) dk. \quad (7)$$

Thus, a knowledge of model cluster can yield the required partial structure factors and pair distribution functions from the experimental $H_d(k)$ data. If, however, $S_c(k)$ is calculable theoretically, then the model cluster can generate all the partial structure factors and pair distribution functions for the given molecular system. The results of our calculations are shown in figures 1–4.

(b) Intermolecular center–center correlations

The CRDF, $g_c(r)$ and CDCF, $C_c(r)$ are important average correlation functions between two molecules and these are obtained by Fourier inverse transform of center structure factor, $S_c(k)$ using the standard procedure [1]. Thus

$$g_c(r) = 1 + \frac{1}{2\pi^2 \rho r} \int_0^\infty k [S_c(k) - 1] \sin(kr) dk \quad (8)$$

and

$$C_c(r) = \frac{1}{2\pi^2 \rho r} \int_0^\infty \frac{S_c(k) - 1}{S_c(k)} \sin(kr) dk. \quad (9)$$

The accuracy of $g_c(r)$ can be checked by evaluating the isothermal compressibility of liquid at room temperature using the compressibility equation [9]

$$\rho k_B T \chi_T = 1 + \rho \int [g_c(r) - 1] dr. \quad (10)$$

The evaluation of $C_c(r)$ is important because it is intimately related to the average intermolecular potential energy function $\phi(r)$ [9]. The computed $C_c(r)$'s are shown in figure 5.

(c) Evaluation of effective pair potential of H-bonded liquids through diffraction data

The center structure factors evaluated from the combined analysis of x-ray and neutron data [1–3] can be used to compute the average effective intermolecular pair potential of

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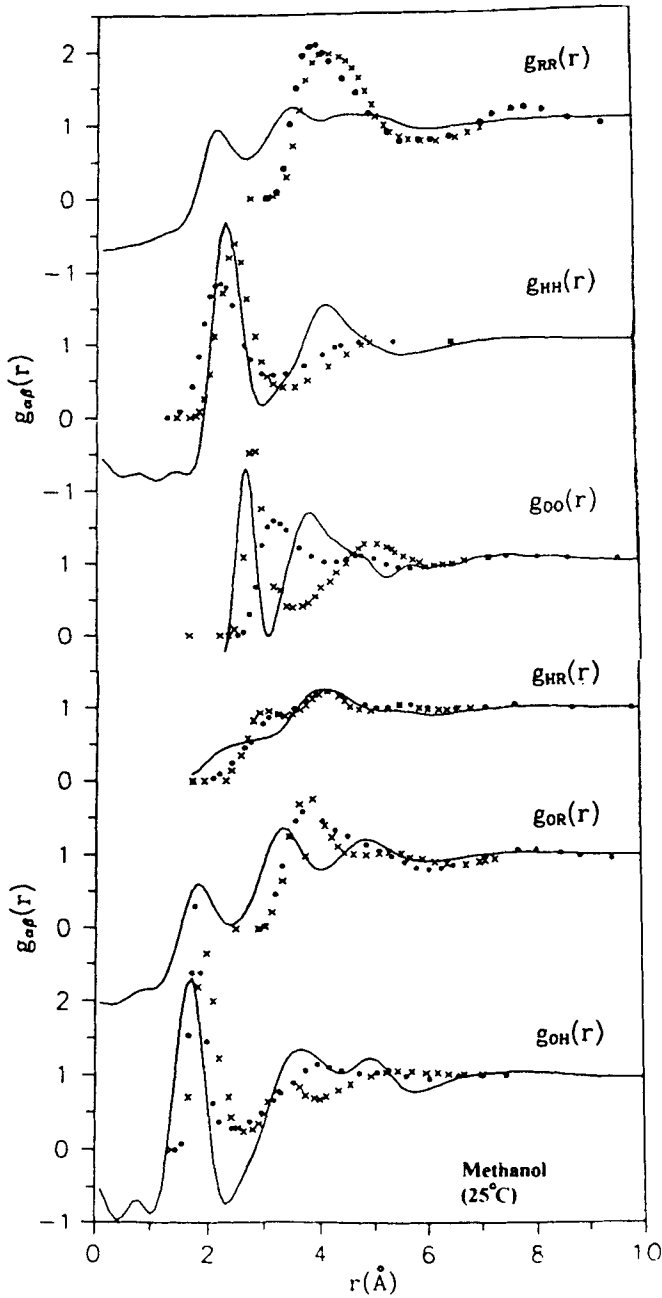


Figure 1. $g_{\alpha\beta}(r)$ for liquid methanol at 25°C. — Hexamer model, x x x simulation results, ••• RISM results.

H-bonded liquids. In [13] average effective intermolecular pair potential of water at room temperature was determined by modified hypernetted chain (MHNC) theory [9]. In the present case we do the computation for liquid ammonia at 4°C (weakly H-bonded) using

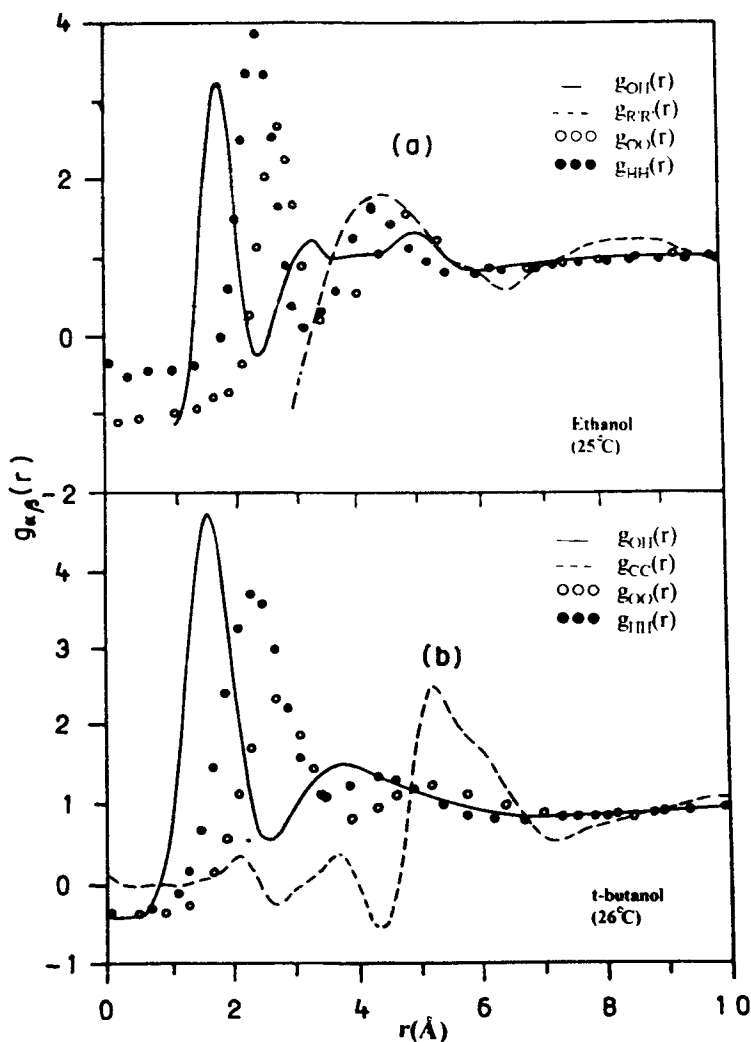


Figure 2. (a) Hexamer model $g_{\alpha\beta}(r)$ for liquid ethanol at 25°C; (b) Hexamer model $g_{\alpha\beta}(r)$ for liquid *tert*-butanol at 26°C.

the same procedure to bring out the characteristic difference from room temperature water (strongly H-bonded). The MHNC [9] theory of Rosenfeld and Ashcroft is known to be very accurate, quite universal in applications and many recent calculations are based on this theory [14].

The assumption of the existence of an effective pair potential, $\phi_{\text{eff}}(r)$ allows one to write the pair distribution function $g(r)$ as

$$g(r) = \exp[-\beta\phi_{\text{eff}}(r) + h(r) - C(r) + B(r)], \quad (11)$$

where $h(r) = g(r) - 1$, $C(r)$ and $B(r)$ are respectively the DCF and the 'Bridge function'. We have $g(r)$ and $C(r)$ obtainable from center structure factor data. $B(r)$ is not known. It

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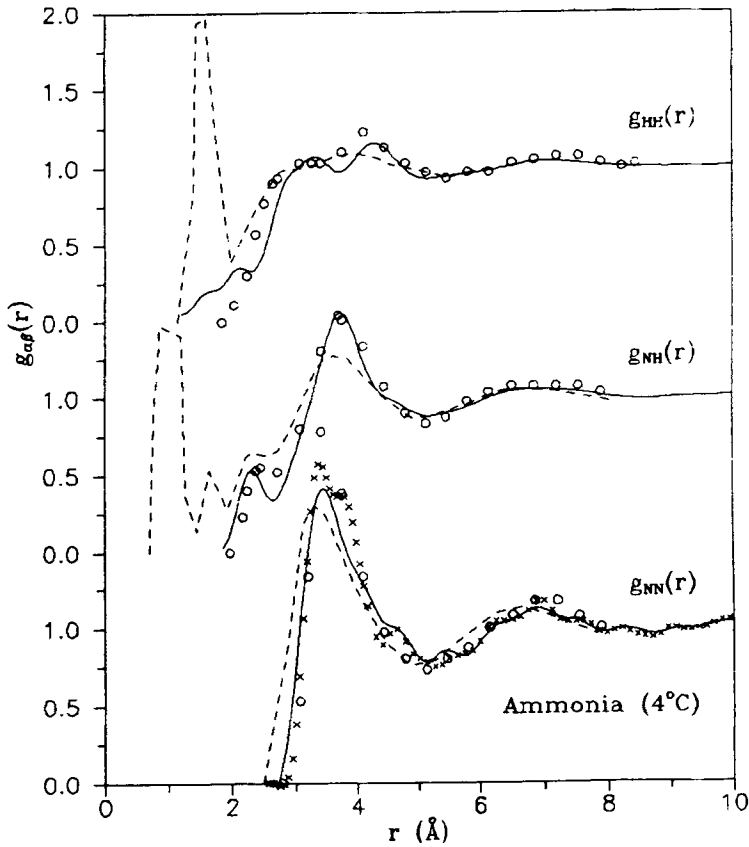


Figure 3. $g_{\alpha\beta}(r)$ for liquid ammonia at 4°C . ——— Symmetrical model, x x x $g_{\text{NN}}(r)$ from Narten; o o o simulation results, - - - - - experimental results.

is however known that for small r , $B(r) \cong B_{\text{hs}}(r)$ where $B_{\text{hs}}(r, \eta)$ is the Bridge function of hard sphere system with a packing density η . For large r , since $C(r) \sim -\beta\phi_{\text{eff}}(r)$ it is easy to show that

$$B(r) \cong B_{\text{hs}}(r, \eta) + \frac{1}{2}[h^2(r) - h_{\text{hs}}^2(r)]. \quad (12)$$

In the MHNC for all r one assumes $B(r)$ to be equal to $B_{\text{hs}}(r, \eta)$ with packing density η given by the Lado criterion [15]

$$\int [g(r) - g_{\text{hs}}(r, \eta)] \frac{\partial B_{\text{hs}}(r, \eta)}{(\partial \eta)} dr = 0. \quad (13)$$

Thus, in the MHNC $\phi_{\text{eff}}(r)$ is given by

$$\phi_{\text{eff}}(r) = -k_{\text{B}}T [\ln g(r) + C(r) - h(r) - B_{\text{hs}}(r, \eta)]. \quad (14)$$

The computed $\phi_{\text{eff}}(r)$ for liquid ammonia (4°C) is shown in figure 6 together with the result for water at room temperature [13]. For comparison we depict the results too for other approximate theories e.g., hypernetted chain (HNC) and Percus–Yeivick (PY) [9].

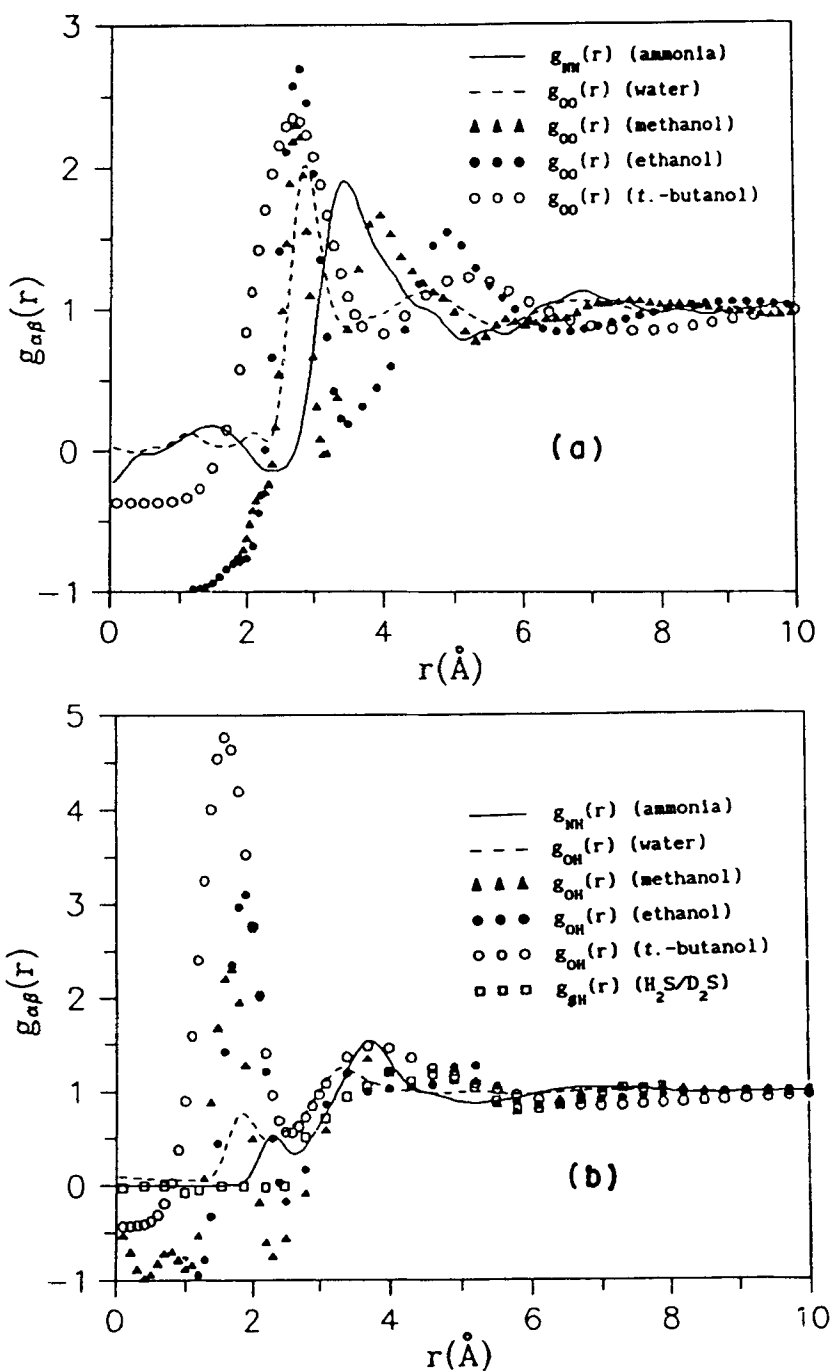


Figure 4a, b.

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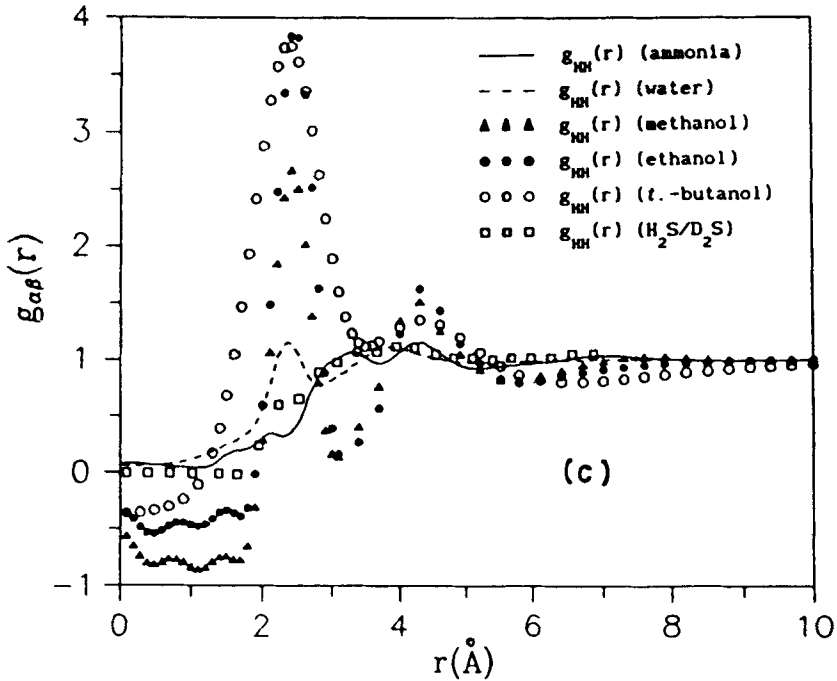


Figure 4. (a) $g_{OO}(r)/g_{NN}(r)$ for different H-bonded liquids; (b) $g_{OH}(r)/g_{NH}(r)$ for different H-bonded liquids; (c) $g_{HH}(r)$ for different H-bonded liquids.

Thus expressions are

$$\text{HNC} : \phi_{\text{eff}}(r) = k_B T [g(r) - \ln g(r) - C(r) - 1], \quad (15)$$

$$\text{PY} : \phi_{\text{eff}}(r) = k_B T \ln \left[1 - \frac{C(r)}{g(r)} \right]. \quad (16)$$

The mean spherical approximation (MSA) for the pair distribution function of the system of particles with impenetrable hard cores was proposed by Lebowitz and Percus [16]. For large r , $\phi_{\text{eff}}(r)$ through MSA is known to be very accurate [17] and gives better results than HNC and PY theories. In MSA,

$$\phi_{\text{eff}}(r) = -k_B T C(r) \quad \text{for large } r. \quad (17)$$

3. Results and discussions

Water is a prototype of H-bonded liquid and its partial structures and distribution functions have been obtained in details through the cluster model in [1]. In this communication we discuss the cases of three alcohols and ammonia which are also H-bonded liquids. The results for water at room temperature are also shown for comparison. Using hexamer closed chain cluster models as predicted in [1] for liquid methanol, ethanol, *tert*-butanol and heptamer symmetrical cluster model as proposed in [2] for liquid ammonia, we have calculated the cluster structure functions $H_c(k)$ and

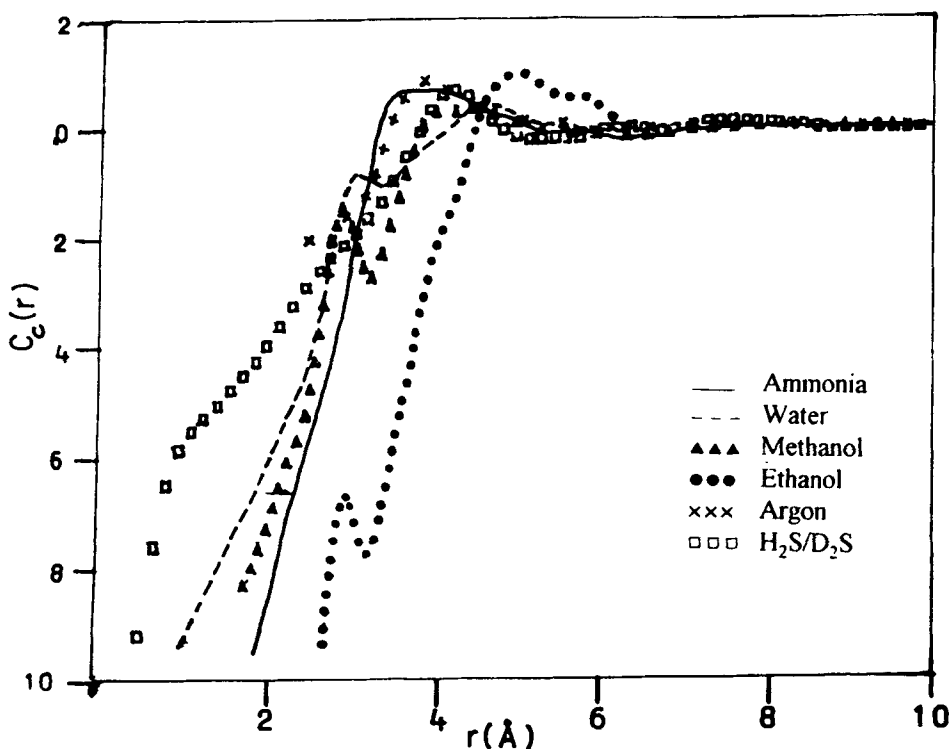


Figure 5. $C_c(r)$ for different H-bonded liquids.

uncorrelated form factor $F_{20}(k)$ involving interaction of α and β atoms. Using (6) we have then evaluated the partial structure functions using previously evaluated $S_c(k)$ and $f_3(k)$ values.

Methanol has three non-equivalent sites $R(\equiv \text{CH}_3)$, O and H. So there are six partial structure functions such as $H_{\text{OO}}(k)$, $H_{\text{HH}}(k)$, $H_{\text{RR}}(k)$, $H_{\text{OH}}(k)$, $H_{\text{OR}}(k)$ and $H_{\text{HR}}(k)$. In evaluating these for convenience we choose oxygen as the geometric center of bonded methanol monomers. The corresponding partial pair distribution functions have been calculated through (7) taking care of truncation corrections for Fourier transforms. All $g_{\alpha\beta}(r)$'s for liquid methanol are plotted in figure 1. Corresponding results of computer simulation based on potential models, transferable intermolecular potential structure (TIPS) and results from reference interaction site model (RISM) [18] using a slightly modified TIPS model are also shown in these figures. There are some discrepancies between our calculated results and simulation/RISM results. The discrepancies are attributed mainly to the choice of oxygen as geometric center in our calculation.

Ethanol molecule contains four non-equivalent scattering units and hence there are ten partial structure and pair distribution functions. We chose ethylene group (i.e., $\text{CH}_2 \equiv R'$) as the center of ethanol monomer. Out of ten, we have evaluated four partial structure functions $H_{\text{OO}}(k)$, $H_{\text{HH}}(k)$, $H_{\text{OH}}(k)$, and $H_{\text{R}'\text{R}'(k)}$. The corresponding $g_{\alpha\beta}(r)$'s for liquid ethanol are plotted in figure 2(a). Computer simulation and RISM results on partial pair distribution functions for liquid ethanol are not available for comparison. Comparison of the functions with those of methanol shows that these are reasonable.

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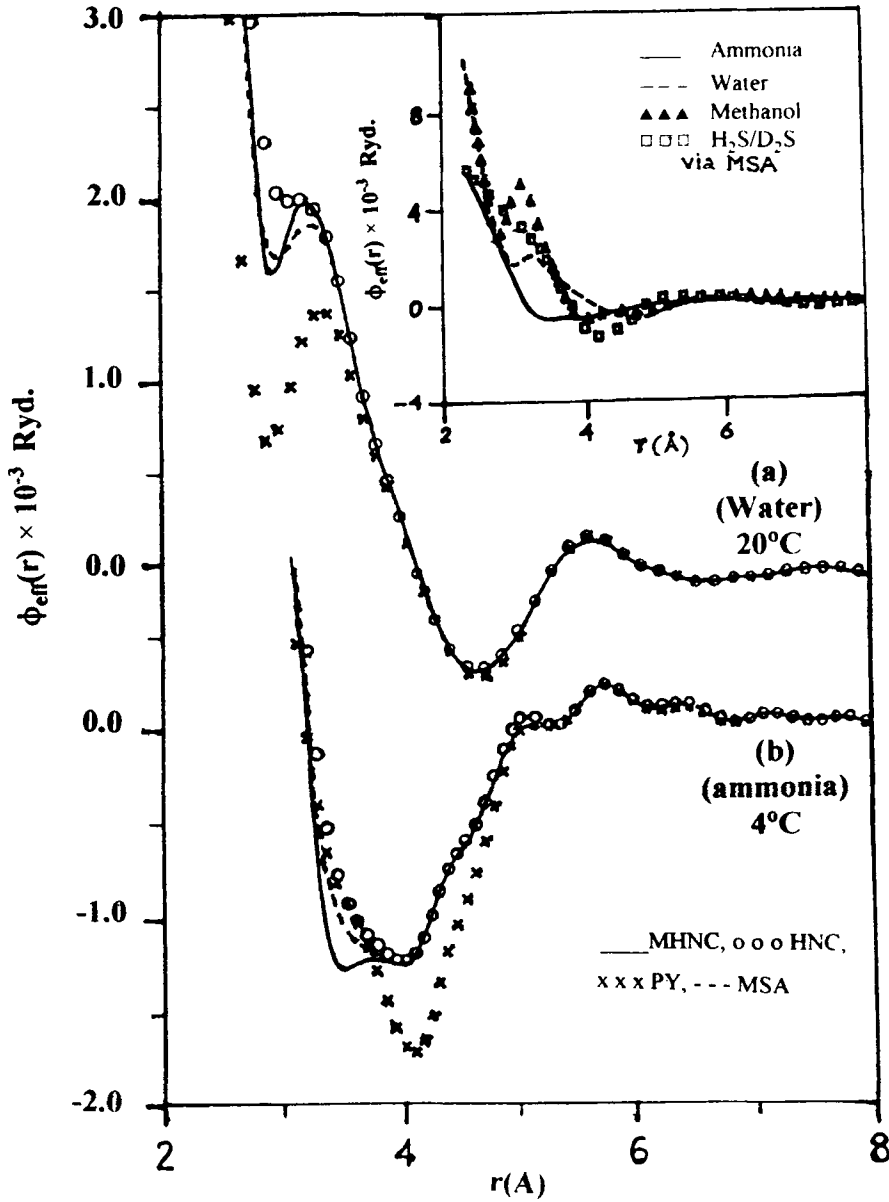


Figure 6. Effective pair potential $\phi_{\text{eff}}(r)$ of H-bonded liquids: (a) water at 20°C, (b) ammonia at 4°C. Subset: $\phi_{\text{eff}}(r)$ for large r via MSA of several liquids compared.

Tert-butanol molecule also contains four non-equivalent scattering units and hence it has ten partial structures and pair distribution functions. We have taken conveniently carbon as the center of bonded *tert*-butanol molecule. We have considered the center structure factor $S_c(k)$ as the one center hard sphere structure factor given by PY theory [9]

with appropriate core diameter 4.95 \AA [2]. We have calculated four partial structure functions $H_{OO}(k)$, $H_{HH}(k)$, $H_{OH}(k)$ and $H_{CC}(k)$ and four partial pair distribution functions $g_{OO}(r)$, $g_{HH}(r)$, $g_{OH}(r)$ and $g_{CC}(r)$ which are shown in figure 2(b). The results of computer simulations are again not available for comparison. The RISM calculations [19] with van der Waals model fail to reproduce the experimental data and hence not shown here for comparison.

Liquid ammonia is a weakly H-bonded liquid. There are three partial structure and pair distribution functions. Our calculation has been based on the assumption that nitrogen is at the center of ammonia molecule. The evaluated $g_{NN}(r)$, $g_{NH}(r)$ and $g_{HH}(r)$ functions are illustrated in figure 3. We have compared our results with simulated $g_{\alpha\beta}(r)$'s based on SCF-MO calculations (model-A) potential [20] in figure 3. There is a remarkable agreement between the simulated results and our calculated results based on cluster model. Narten's [21] center-center distribution function $g_{NN}(r)$ has a splitted peak in the region from $r = 3.5 \text{ \AA}$ to $r = 4 \text{ \AA}$, which is absent in the calculated and simulated results. Very recently, experiment on isotopic mixtures of hydrogenated and deuterated ammonia has been performed and partial distribution functions could be evaluated [22]. These results are also shown for comparison. It is to be noted that these authors did not separate the intra and inter parts. In $g_{NH}(r)$ and $g_{HH}(r)$ curves the inner prominent peaks are intra peaks. It is however seen that the inter distribution functions agree reasonably well with our cluster model results.

We now compare the partial distribution functions $g_{OO}(r)/g_{NN}(r)$, $g_{OH}(r)/g_{NH}(r)$ and $g_{HH}(r)$ of these liquids (figure 4). We also show the functions for water at room temperature from ref. [1]. The comparison is expected to bring out the relative strength of H-bonding in these liquids. In figure 4(a) we compare the nature of $g_{OO}(r)$ for liquid alcohols and $g_{NN}(r)$ for liquid ammonia studied here together with $g_{OO}(r)$ for liquid water from ref. [1]. For water and methanol $g_{OO}(r)$ and for ammonia $g_{NN}(r)$ give the distribution of molecular centers. The first major peak of $g_{OO}(r)$ for water and alcohols lies at about $r \sim 2.8 \text{ \AA}$ whereas the first major peak of $g_{NN}(r)$ for ammonia occurs at about 3.5 \AA indicating intermolecular H-bonding. In the calculated curve the first minimum of $g_{OO}(r)$ for methanol has the value slightly below the zero line and this is probably due to the fact that our choice of center for methanol at oxygen site is only approximate. The functions $g_{HH}(r)$ and $g_{OH}(r)/g_{NH}(r)$ give the orientational distribution functions between adjacent molecules. Comparative studies of the nature of these distribution functions for three alcohols, water and ammonia are shown in figures (4b) and (c). For comparison we also show $g_{HH}(r)$ and $g_{SH}(r)$ for liquid $\text{H}_2\text{S}/\text{D}_2\text{S}$ at or near the room temperature [23] where H-bonding is known to be absent. Both the distribution functions $g_{HH}(r)$ and $g_{OH}(r)$ for water and alcohols show two well-defined peaks which are related to the presence of H-bonds and to the short-range order [6] in the liquid. These characteristics are weakly present in $g_{NH}(r)$ and $g_{HH}(r)$ for liquid ammonia. In liquid $\text{H}_2\text{S}/\text{D}_2\text{S}$ these characteristics are practically absent showing the absence of H-bonds. The major peak of $g_{HH}(r)$ occur at about $r \sim 2.4 \text{ \AA}$ for all the H-bonded liquids studied except ammonia for which a small peak or hump occurs and that too shifted considerably to a larger r . For $\text{H}_2\text{S}/\text{D}_2\text{S}$ there exists no peak at all and distribution function has no substantial oscillations. The first peak of $g_{OH}(r)$ occurs at $r \sim 1.65 \text{ \AA}$ – 1.80 \AA for alcohols and water. For ammonia, corresponding $g_{NH}(r)$ occurs at about $r \sim 2.2 \text{ \AA}$. For $\text{H}_2\text{S}/\text{D}_2\text{S}$ system such a peak is practically absent and small

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oscillations occur at larger r . The distances at which the first peaks of $g_{HH}(r)$ and $g_{NH}(r)$ for liquid ammonia occur are larger than that for the other H-bonded liquids discussed. The heights of first peak in these two distribution functions are gradually increasing in the order ammonia < water < methanol < ethanol < *tert*-butanol. As far as the peak heights are concerned it can be concluded that H-bonding is stronger in alcohols than in water and ammonia seems to be weakest. The liquid H₂S/D₂S is however seen to be almost without any orientational correlations indicating absence of short-range correlations.

The center-center correlations though represent some average intermolecular correlations which yield very useful information about the characteristics of H-bonded liquids. In figure 5 we show the CDCFs for liquid methanol, ethanol, ammonia and water systems [1–3]. This function for a simple liquid e.g., argon is also shown. $C_c(r)$'s show special feature of a negative peak at about 2.8 Å, the H-bonded O–O distance followed by a positive peak and the function is short-range with no substantial oscillations at large r . The double peak is only slightly present in ammonia and no such peak exists in a simple liquid like argon. We have also computed this function from the x-ray data of liquid H₂S [23]. The function is more similar to that for argon.

In figure 6 we have shown the average effective pair potential $\phi_{\text{eff}}(r)$ for ammonia evaluated from the center-center correlations through the accurate MHNC theory [9]. The results via HNC, PY and MSA theories yield similar characteristic features. The results for room temperature water from ref. [13] are also shown for comparison. For water too the basic features of the potentials are more or less same in all the methods. For water, the potential is characterized by two minima, first minimum being a positive one occurring at $r \sim 2.8$ Å. This is the position of the RDF first peak. The potential is very different from that for simple liquids. The first minimum in the potential is possibly due to short range hydrogen bonding interaction between neighboring molecules. In ref. [13] it is shown that at about 200°C where most of the H-bonds are broken the potential shows a single minimum at $r \sim 2.8$ Å (at the position of RDF first peak) somewhat similar to that in simple liquids. The justification of the double minima potential of room temperature water was presented in ref. [13]. It is noteworthy that $\phi_{\text{eff}}(r)$ for ammonia (4°C) also shows feature like that of water but it is only weakly present evidently showing the weak H-bonding of liquid ammonia.

The MHNC method is not straightforward enough to be easily applicable to liquid methanol and ethanol. We have therefore shown through simple MSA to compare $\phi_{\text{eff}}(r)$'s for large r of several H-bonded liquids and also of non H-bonded liquid H₂S. MSA is also known to yield accurate potential for large r [17]. The $\phi_{\text{eff}}(r)$ values for large r via MSA are shown in the subset of figure 6. What we find here is that the basic features of the potentials for water and methanol are the same having two minima, the first positive minimum being at $r \sim 2.8$ Å. For ethanol also the basic feature is the same (not shown). Ammonia has somewhat similar feature at $r \sim 3.5$ Å. In literature such potential forms are not uncommon. The liquid semimetals with covalent bonds which exhibit shouldered first peak in their structure factors show characteristic humps in their potentials just outside the core at the position of first RDF peak. The feature is however absent in liquid H₂S for which the potential appears similar to that for simple liquids (e.g. argon). With small oscillations at large r it is more similar to water potential at high temperature [13].

4. Summary

The basic information on the equilibrium structure of H-bonded molecular liquid is represented by the partial pair distribution functions, one of them gives the distribution of molecular centers and the others give the orientational correlations between neighboring molecules. In the present work we compute the partial radial distribution functions of a few H-bonded liquids through geometric cluster models and the comparison gives information about the relative strengths of H-bonding features. From the point of view of chemical physics, informations on the variation of these partials as a function of temperature are more important than the values of these partials at a specific temperature state, say room temperature. Integration of the partial pair distribution functions up to their first minima give the average number of associated neighbors.

For simple molecules, the $g(r)$ formalism is clearly advantageous but as the molecular size and complexity increases, the set of individual partial terms become less informative and it is the behavior of the total molecular units that essentially characterizes the properties of the liquid. The center-center correlations yield characteristic informations. Little work has yet been done on organic liquids of this type but it seems clear that simulation work will be required to provide a physical interpretation of the experimental data in the form which is most appropriate.

We also discuss here a method for finding the average effective intermolecular potential for H-bonded liquids. The curves show that there is some characteristic peculiarity in the average effective intermolecular potential just beyond the core and this feature is totally absent in simple liquids. At high temperature when all H-bonds are broken this feature vanishes [1, 13].

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