Molecular Clusters and Correlations in Liquid Ammonia

S. Sarkar, A. K. Karmakar, and R. N. Joarder*

Department of Physics, Jadavpur University, Calcutta−700032, India

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The available X-ray diffraction data of liquid ammonia at 4 °C exhibit considerable symmetry in the intermolecular structure in spite of hydrogen bonding. The intermolecular structure is modeled well by a heptamer cluster close to that of the solid state. The model reproduces reasonably well the available neutron diffraction and computer simulation data for liquid ammonia.

I. Introduction

Liquid ammonia differs from other hydrogen-bonded liquids in possessing one of the weakest hydrogen bonds found in nature.[1] Apparently therefore, one might expect that this fact makes ammonia a simple problem, but in reality it is not always true. A large number of papers that appeared during the last two decades amply corroborate this observation. For example, a model that was parametrized[2] by fitting the second-virial coefficient of ammonia gas and that successfully explained the experimental results on the differential collision cross section of $NH_3 + NH_3$ gave rise to a liquid structure[3] that is free from a significant degree of molecular association. This structure conflicts with the structure obtained from X-ray scattering experiments on the liquid.[4] Again the X-ray data on liquid ammonia[4] yielded an intermolecular nitrogen−nitrogen pair distribution function that showed several characteristic features, but the details of these features are never produced by computer simulations.[3]

In the solid state, ammonia has a well-defined cubic ($P2_13$) intermolecular structure. The X-ray diffraction analysis on solid NH_3 and solid ND_3[5] suggested a slightly deviated face centered cubic (fcc) intermolecular structure in which each monomer is hydrogen bonded to six nearest neighbors at 3.4 Å and there occur six nonbonded neighbors at 3.9 Å. The neutron diffraction data on solid ND_3 suggested a more or less similar structure.[6] For liquid ammonia Kruh and Petz[7] interpreted their X-ray results (at three temperatures, in the range 199−277 K) in relation to the crystal structure of solid ammonia and concluded that the hydrogen bonding occurs at a mean distance of 3.56 Å. Narten however suggested that his results on liquid ammonia and a water−ammonia mixture (at 277 K)[8] fit with the ice-I model for water better than they fit with the crystal structure of solid NH_3. Later, Narten[4] assumed ammonia molecules, seen by X-rays, to be spherically symmetric and used his data on liquid ammonia to evaluate the intermolecular nitrogen−nitrogen pair distribution function $g_{NN}(r)$.[4] The first coordination shell around any ammonia monomer evaluated was quite complex, with one subsidiary hump and a peak at 3.7 and 4.6 Å, respectively, in addition to the general hydrogen-bonded N−N peak at 3.4 Å. The general distribution of the nearest neighbors was somewhat similar to that in the solid state. It is, however, to be noted that the hump at 3.7 Å was absent in the earlier X-ray data of Kruh and Petz.[7] Despite deviations in the detailed features, both X-ray[4] and neutron diffraction[9] data suggest that the general structure of liquid ammonia is similar to a slightly deviated solid state molecular association.

A number of theoretical potential models have been developed in the literature for the simulation works;[3,10−14] all were basically aimed at generating the experimental X-ray split peak in the $g_{NN}(r)$ curve of Narten[4] but none with any success. The simulation results of Jorgensen and Ibrahim[10] even showed that the monomers were only in one or two hydrogen bonds with the neighbors, a picture similar to that in methanol and other alcohols. The models that lead unambiguously to a strong associated liquid are those derived from solid state structure. The simple intermolecular potential in some cases was unable to stabilize the orientationally disordered fcc phase, and so an explicit inclusion of many-body polarization effects was felt necessary. David[15] extended the polarization model of water to ammonia and showed that the heptamer cluster of ammonia adopts a stable structure suggestive of the solid. For seven ammonia molecules, the most "solid-like" structure consists of one central ammonia surrounded approximately at equal distances by six neighbors at the corners of the adjacent cubes. This structure was equilibrated at low temperature using standard Monte Carlo (MC) techniques, achieving a completely satisfactory minimum energy, and the structure was stable over a wide range of temperature.

Under these circumstances we decided to repeat a careful analysis of Narten's X-ray data.[8,16] We have considered the plausible hydrogen-bonded clustering of ammonia monomers in the liquid state through our earlier method of analysis, which was successfully applied to hydrogen-bonded liquids such as water[17,18] and alcohols.[19,20] We assume David's heptamer model[15] and also the solid state hydrogen-bonded cluster as the general guide for plausible H-bonded clusterings of ammonia monomers in the liquid state. This is done on the belief that there is not much hydrogen bond breaking during melting, and therefore to a large extent the solid state structure is retained in the liquid state. We consider a model of seven molecules that differs from the David's model. In David's model six NH_3 molecules are at the nearest corners of the eight adjacent cubes common to the central ammonia molecule. In our model, six NH_3 molecules lie symmetrically on the base circles of the oppositely directed cones of different semivertical angles with the central ammonia molecule at the common vertex. It is closer to the solid state H-bonded cluster than David's model. In the procedure, we have used the molecular parameters from the recent neutron experiment[21] and evaluated the intermolecular cluster information of liquid ammonia from Narten's X-ray diffraction data.[8,16] We have verified the model cluster subsequently through neutron data.[21]

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* Corresponding author.

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II. Structural Analysis

Theoretical Background. The general expression for the total structure function $H(k)$ devoid of "self-scattering term" is given by[19]

$$H(k) = M(k)N_{\mathrm{m}}^{-1}\sum_{i=1}^{N_{\mathrm{m}}}\sum_{j=1}^{N_{\mathrm{m}}}\sum_{n_i=1}^{n_{\mathrm{m}}}\sum_{n_j=1}^{n_{\mathrm{m}}} f_{n_i}(k)\, f_{n_j}(k)\, j_0(kr_{n_in_j}) \exp(-\lambda_{n_in_j}^2 k^2/2) \tag{1}$$

where k, the magnitude of the momentum transfer vector $\mathbf{k}$, is defined as $k = (4\pi/\lambda)\sin\theta$, with θ half the scattering angle and λ the wavelength of the incident radiation. N_{m} and n_{m} are respectively the total number of molecules in the system and the number of atoms in a molecule. i and j label molecules in the liquid; n_i denotes the nth atom in the ith molecule; $r_{n_in_j}$ is the distance between atoms n_i and n_j; $f_{n_i}(k)$ is the X-ray atomic scattering factor of the atom n_i; $\lambda_{n_in_j}$ is the root-mean-square deviation of the local instantaneous atom−atom separation distance $r_{n_in_j}$, and $j_0(x) = x^{-1}\sin x$. The factor $M(k)$ is given by

$$M(k) = [\sum_{n_i=1}^{n_{\mathrm{m}}} f_{n_i}(k)]^{-2}$$

The "self-scattering term" due to the scattering of radiation by individual uncorrelated atoms is defined as

$$S_{\mathrm{s}}(k) = M(k)\sum_{n_i=1}^{n_{\mathrm{m}}} f_{n_i}^{\,2}(k)$$

Assuming that the liquid on average contains distinct molecular clusters due to H-bonding, the right-hand side of eq 1 can be split into physically distinct terms,[19] namely, the contributions of atom-pair terms within a cluster, $H_{\mathrm{c}}^{\mathrm{m}}(k)$, and the intercluster term, $H_{\mathrm{c}}^{\mathrm{int}}(k)$. Thus

$$H(k) = H_{\mathrm{c}}^{\mathrm{m}}(k) + H_{\mathrm{c}}^{\mathrm{int}}(k) \tag{2a}$$

where

$$H_{\mathrm{c}}^{\mathrm{m}}(k) = M(k)N_{\mathrm{m}}^{-1}\sum_{\alpha=1}^{N_{\mathrm{cl}}}\sum_{\beta=1}^{N_{\mathrm{cl}}}\sum_{l_\alpha=1}^{N_{\mathrm{c}}}\sum_{l'_\beta=1}^{N_{\mathrm{c}}}\sum_{n_{l_\alpha}=1}^{n_{\mathrm{m}}}\sum_{n_{l'_\beta}=1}^{n_{\mathrm{m}}} f_{n_{l_\alpha}}(k)\, f_{n_{l'_\beta}}(k) \times j_0(kr_{n_{l_\alpha}n_{l'_\beta}}) \exp(-\lambda_{n_{l_\alpha}n_{l'_\beta}}^2 k^2/2)$$

$$H_{\mathrm{c}}^{\mathrm{int}}(k) = M(k)N_{\mathrm{m}}^{-1}\sum_{\substack{\alpha=1\\ \alpha\neq\beta}}^{N_{\mathrm{cl}}}\sum_{\beta=1}^{N_{\mathrm{cl}}}\sum_{l_\alpha=1}^{N_{\mathrm{c}}}\sum_{l'_\beta=1}^{N_{\mathrm{c}}}\sum_{n_{l_\alpha}=1}^{n_{\mathrm{m}}}\sum_{n_{l'_\beta}=1}^{n_{\mathrm{m}}} f_{n_{l_\alpha}}(k)\, f_{n_{l'_\beta}}(k) \times j_0(kr_{n_{l_\alpha}n_{l'_\beta}}) \exp(-\lambda_{n_{l_\alpha}n_{l'_\beta}}^2 k^2/2)$$

l and l' label the molecules, l_α and l'_β denote the molecules in the clusters α and β, and N_{cl} and N_{c} are respectively the total number of clusters in the system and number of molecules in a cluster.

Now, by assuming that the molecules belonging to different clusters are orientationally uncorrelated, $H_{\mathrm{c}}^{\mathrm{int}}(k)$ can be simplified and eq 2a can be put into the form[19]

$$H(k) = H_{\mathrm{c}}^{\mathrm{m}}(k) + F_{2\mathrm{u}}(k)[S_{\mathrm{c}}(k) - F_3(k) - 1] \tag{2b}$$

where $F_{2\mathrm{u}}(k)$, the form factor representing completely uncorrelated orientational configuration between molecules, is given by

TABLE 1: Intramolecular Parameters of Liquid Ammonia[21]

NH distance (Å)	H−N−H angle (deg)	λ_{NH}^2 (Å^2)	λ_{HH}^2 (Å^2)
1.0255	104.5	0.002 75	0.005 16

$$F_{2\mathrm{u}}(k) = M(k)\,[\sum_{n=1}^{n_{\mathrm{m}}} f_n(k)\, j_0(kr_{\mathrm{c}n}) \exp(-\lambda_{\mathrm{c}n}^{\,2}k^2/2)]^2$$

where the subscript c refers to the center of a molecule. $S_{\mathrm{c}}(k)$ and $F_3(k)$ are respectively the intermolecular center structure factor of the liquid and the structure factor resulting from molecular center pairs within a cluster and are defined as

$$S_{\mathrm{c}}(k) = 1 + N_{\mathrm{m}}^{-1}\sum_{\substack{i=1\\ i\neq j}}^{N_{\mathrm{m}}}\sum_{j=1}^{N_{\mathrm{m}}} j_0(kr_{\mathrm{c}_{ij}}) \exp(-\lambda_{\mathrm{c}_{ij}}^{\,2}k^2/2)$$

$$F_3(k) = N_{\mathrm{c}}^{-1}\sum_{\substack{l=1\\ l\neq l'}}^{N_{\mathrm{c}}}\sum_{l'=1}^{N_{\mathrm{c}}} j_0(kr_{\mathrm{c}_{ll'}}) \exp(-\lambda_{\mathrm{c}_{ll'}}^{\,2}k^2/2)$$

Again $H_{\mathrm{c}}^{\mathrm{m}}(k)$ can be separated into the intramolecular structure function $H_{\mathrm{m}}(k)$ and the intermolecular structure function $H_{\mathrm{c}}(k)$ within a cluster. Thus we have

$$H(k) = H_{\mathrm{m}}(k) + H_{\mathrm{c}}(k) + F_{2\mathrm{u}}(k)\,[S_{\mathrm{c}}(k) - F_3(k) - 1] \tag{2c}$$

where $H_{\mathrm{m}}(k)$, the intramolecular structure function (contribution from various atoms in a molecule), is given by

$$H_{\mathrm{m}}(k) = M(k)\sum_{\substack{n=1\\ n\neq n'}}^{n_{\mathrm{m}}}\sum_{n'=1}^{n_{\mathrm{m}}} f_n(k)\, f_{n'}(k)\, j_0(kr_{nn'}) \exp(-\lambda_{nn'}^{\,2}k^2/2)$$

and $H_{\mathrm{c}}(k)$, the intermolecular structure function within a cluster, is defined by

$$H_{\mathrm{c}}(k) = M(k)N_{\mathrm{c}}^{-1}\sum_{\substack{l=1\\ l\neq l'}}^{N_{\mathrm{c}}}\sum_{l'=1}^{N_{\mathrm{c}}}\sum_{n=1}^{n_{\mathrm{m}}}\sum_{n'=1}^{n_{\mathrm{m}}} f_{n_l}(k)\, f_{n_{l'}}(k)\, j_0(kr_{n_ln_{l'}}) \times \exp(-\lambda_{n_ln_{l'}}^{\,2}k^2/2)$$

The second and third terms in eq 2c combine to form the conventional intermolecular "distinct" structure function, $H_{\mathrm{d}}(k)$, and eq 2c can be written as

$$H(k) = H_{\mathrm{m}}(k) + H_{\mathrm{d}}(k) \tag{3a}$$

$$H_{\mathrm{d}}(k) = H_{\mathrm{c}}(k) + F_{2\mathrm{u}}(k)\,[S_{\mathrm{c}}(k) - F_3(k) - 1] \tag{3b}$$

The intercluster contribution goes to zero for large k, and hence $H_{\mathrm{d}}(k)$ tends to $H_{\mathrm{c}}(k)$ for large k, as seen from eq 3b, which thus is very useful in identifying any intermolecular association present in the liquid, while eq 3a is useful in defining the molecular structure within a molecule.

We examine the intermolecular structural model of liquid ammonia according to the theoretical analysis given above. The X-ray data for $H(k)$ are obtained from Narten's experimental data[16] on liquid ammonia at 4 °C. Subtracting the calculated $H_{\mathrm{m}}(k)$ based on molecular parameters from the recent neutron

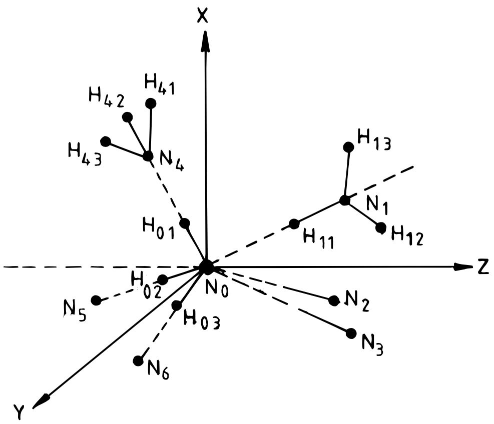

Figure 1. Heptamer cluster structure of ammonia monomers (4 °C).

work[21] (listed in Table 1) from $H(k)$, we have obtained the experimental X-ray $H_d(k)$ data (see eq 3a).

Intermolecular Cluster Structure. We have observed from Narten's X-ray diffraction data that the k-weighted distinct structure function, $kH_d(k)$, is quite symmetrical except the region $k = 8.0-9.5$ Å^{-1}, where the structural curve shows a peculiar feature (with sudden up and down). To construct the intermolecular cluster structure function $H_c(k)$, we have considered as a plausible intermolecular hydrogen bonded cluster for liquid ammonia a heptamer cluster model close to the solid state H-bonded cluster.[5]

The model (Figure 1) contains one central ammonia molecule N_0 at the common vertex of two opposite cones containing molecules N_1, N_2, N_3 and N_4, N_5, N_6. The molecules N_1, N_2, N_3 and N_4, N_5, N_6 are connected with N_0 through straight hydrogen bonding. In the $N_1N_2N_3N_0$ cone one H atom is fixed on the bonded axis and two H atoms are free to rotate about this axis, while all the H atoms in the $N_4N_5N_6N_0$ cone are free to rotate about the corresponding hydrogen-bonded axes. The axes of the two cones are at a phase difference of 180°. For each of N_1, N_2, and N_3 one H atom is fixed on the hydrogen-bonded axis and the remaining two H atoms are free to rotate about this bonded axis. For each of N_4, N_5, and N_6, all three H atoms are free to rotate about the corresponding hydrogen-bonded axes according to Figure 1. The following conditions are satisfied.

$$\begin{gathered} N_0N_1 = N_0N_2 = \cdots = N_0N_6 = r_{NN} \\ \angle N_2N_0N_1 = \angle N_3N_0N_1 = \angle N_3N_0N_2 \\ \angle N_5N_0N_4 = \angle N_6N_0N_4 = \angle N_6N_0N_5 \end{gathered} \tag{4}$$

The positions of all the H and N atoms can be expressed in terms of the molecular parameters, the intermolecular N−N distances, the rotation angles of the N's, and the twist angles of all the H's about the corresponding bonded axes. The molecular parameters listed in Table 1 are used. As seen from eq 3b, for large k, $H_d(k) \rightarrow H_c(k)$; so, the intermolecular cluster parameters for the model cluster are determined by χ^2-fitting of the X-ray $kH_c(k)$ function to the experimental X-ray $kH_d(k)$ function of liquid ammonia at 4 °C (Narten's) for the region from $k = 5$ Å^{-1} to $k = 16$ Å^{-1}. The values of λ_{ij}^2 are assumed to be proportional to the mean square amplitude of displacement such that $\lambda_{ij}^2 = \lambda_0 r_{ij}^2$. The constant of proportionality λ_0 is also determined by χ^2-fitting. The intermolecular cluster parameters are listed in Table 2.

The X-ray $kH_c(k)$ functions are shown in Figure 2a together with Narten's X-ray $kH_d(k)$ function. The agreement of the $kH_c(k)$ function for the heptamer cluster model with the experimental $kH_d(k)$ function is very good, as indicated by the low value of χ^2 (Table 2). As far as the region $k = 8.0-9.5$ Å^{-1} of the experimental X-ray $kH_d(k)$ curve is concerned, the model cannot fit the region to a very satisfactory extent, although the general shape is produced well. We have considered several asymmetrical distortions in the model, but these do not in any way improve the fitting in this region. We therefore believe that this unusual feature of the experimental curve has no physical significance, and it is probably the outcome of an earlier inaccurate data reduction procedure of the X-ray diffraction analysis. Barring this anomaly, we consider that the overall fit of the heptamer cluster model is satisfactory. The picture of this model is consistent with the published data and with the idea that the seven-molecular-H-bonded cluster present in the solid seems to be preserved in the liquid state.

TABLE 2: Intermolecular Cluster Parameters for Liquid Ammonia[a]

parameters	heptamer model
r_{NN} (Å)	3.319 (3.380, 3.349)
$\angle N_1N_0N_2$ (deg)	72.52 (71.66)
$\angle N_4N_0N_5$ (deg)	111.88 (118.05)
twist angles of H_{12}, H_{22}, H_{32} (deg)	96.26, 96.39, 96.33
twist angles of H_{41}, H_{51}, H_{61} (deg)	10.74, 250.72, 10.56
twist angle of H_{01} (deg)	22.00
value of λ_0	0.003 545
value of χ^2	0.002 794 05

[a] The values in parentheses are for the x-ray results of crystalline NH_3/ND_3.[5]

We then use Narten's[16] data to evaluate the center structure factor based on the heptamer model using eq 2 or eq 3. The X-ray scattering center is very close to the center of mass of the ammonia molecule, and both in turn are very close to the nitrogen atom of the molecule. The scattering center of the molecule is defined as[22]

$$\mathbf{r}_c = \frac{\sum_{n=1}^{n_m} f_n(k)\mathbf{r}_n}{\sum_{n=1}^{n_m} f_n(k)}$$

where n runs over the atoms in the molecule. Considering the center of mass to be the geometric center, the computed center structure factor $S_c(k)$ of liquid ammonia at 4 °C is shown in Figure 2b. In the same graph we have shown the center structure factor of liquid ammonia at 4 °C obtained by Narten[4] assuming the distribution of scattering density within the ammonia molecule to be nearly spherically symmetric. Although the two approaches are quite different, the computed center structure factors agree with Narten's $S_c(k)$ data quite well. The center structure factor could approximately be represented by the Percus−Yevick (PY) model with an appropriate hard core diameter, $\sigma = 3.15$ Å (Figure 2b).[23]

Further Testing of the Model. It is interesting to note that the general feature of Narten's X-ray molecular structure function $H(k)$ data of liquid ammonia at 4 °C[16] could be reproduced quite well by using the hard sphere center structure factor (PY model)[23] of appropriate core diameter (3.15 Å) and the heptamer cluster model, through eq 2 or eq 3 (Figure 2c). This generation of structure by the PY hard sphere model seems to be quite significant. The good fit we have obtained with symmetric heptamer clusters in the liquid and PY theory (for the center structure factor) is attributed to the fact that the PY

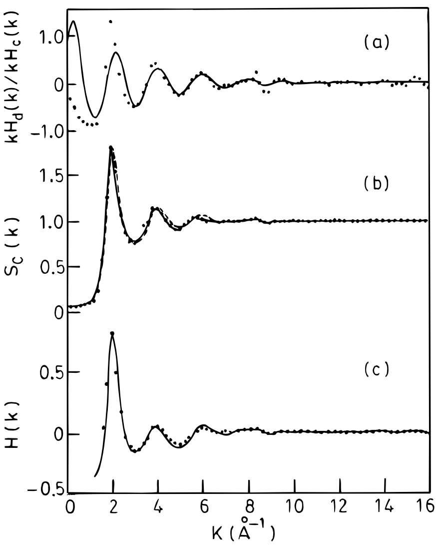

Figure 2. (a) k-weighted model $H_c(k)$ fit to k-weighted $H_d(k)$ function of liquid ammonia at 4 °C: (—) $kH_c(k)$, (···) $kH_d(k)$; (b) (—) Computed center structure $S_c(k)$ for model, (- - -) PY hard sphere center structure with appropriate diameter ($\sigma = 3.15$ Å), (···) $S_c(k)$ data of Narten (ref 4); (c) (···) Experimental X-ray $H(k)$ (refs 8, 16), (—) $H(k)$ obtained by using approximate PY hard sphere center structure ($\sigma = 3.15$ Å) and cluster model.

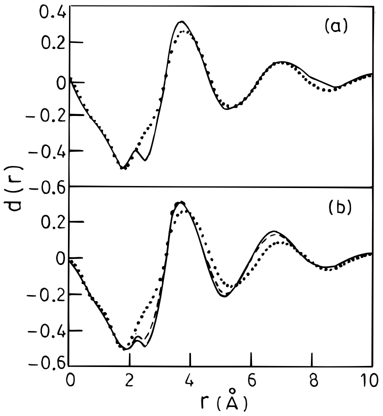

Figure 3. Neutron $d(r)$ functions of liquid ammonia: (a) (···) Experimental $d(r)$ for $T = 22$ °C (ref 9), (—) $d(r)$ for model (4 °C) with $S_c(k)$ from X-ray data (center at C.M.); (b) (···) Experimental $d(r)$ for $T = 22$ °C (ref 9), (—) $d(r)$ for model (4 °C) with PY $S_c(k)$ (center at C.M.), (- - -) $d(r)$ for model (4 °C) with PY $S_c(k)$ (center at neutron scattering center).

theory was originally developed for spherically symmetric molecules, and ammonia monomers more or less behave like spherical molecules apart from their H-bonding features.

Again the evaluation of the intermolecular pair correlation function in real space provides a good test for any model.[19] Therefore to test the model further, we use the computed $S_c(k)$ of the heptamer model to derive the neutron distinct structure function, $H_d(k)$, for neutron scattering of deuterated liquid ammonia at 4 °C with the help of eq 3b. In doing so, we have replaced the X-ray atomic scattering factors by neutron scattering lengths of the nuclei. Following the procedure discussed in ref 19, the computed neutron $H_d(k)$ function is Fourier transformed to $d(r)$, which is the r-weighted neutron pair correlation function. The computed neutron $d(r)$ curve based on the model is at 4 °C, and it is compared with that of Chieux and Bertagnolli[9] for liquid ND_3 at somewhat higher temperature (22 °C) and shown in Figure 3a. The agreement is reasonably good. The $d(r)$ data of Cheiux and Bertagnolli give a clear indication of an H-bonding hump at 2.5 Å. In the $d(r)$ curve of our model the peak at ∼2.3 Å is due to H-bonded ND terms. The model $d(r)$ curve at 4 °C however shows a stronger hydrogen-bonded feature than that shown by the data of Cheiux and Bertagnolli at 22 °C. The general peak at ∼3.6 Å is due to the intermolecular N−N distance. The humps at ∼4.65 and 5.45 Å show features that are observed in the experimental curve also. The general agreement of the model neutron $d(r)$ curve at 4 °C with the neutron experimental $d(r)$ curve at 22 °C is remarkable. The results with the PY center structure factor too agree reasonably with experimental data (Figure 3b). The results with the neutron scattering center is only slightly different. The features of the neutron $d(r)$ curve for the model also agree well with the X-ray results of liquid ammonia.[8,16]

III. Partial Structures and Correlations

It is possible to obtain the partial total structure functions, $H_{\alpha\beta}(k)$, and atom−atom distribution functions, $g_{\alpha\beta}(r)$, through the intermolecular cluster model.[17] Assuming that $H_{\alpha\beta}(k)$ is given by the terms involving α−β interactions from $H_m(k)$, $H_c(k)$, and $F_{2u}(k)$ of eq 2c, we have[17]

$$H_{\alpha\beta}(k) = H_m^{(\alpha\beta)}(k) + H_c^{(\alpha\beta)}(k) + F_{2u}^{(\alpha\beta)}(k)[S_c(k) - F_3(k) - 1] \tag{5}$$

$g_{\alpha\beta}(r)$ can be obtained from $H_{\alpha\beta}(k)$ as follows:

$$g_{\alpha\beta}(r) = 1 + \frac{1}{(2\pi)^3\rho}\int_0^\infty H_{\alpha\beta}(k)\, j_0(kr)\, d\mathbf{k} \tag{6}$$

where ρ is the density of liquid ammonia and $j_0(kr) = \sin(kr)/kr$.

In the computation of the partials we assume PY model $S_c(k)$. The computed $H_{\alpha\beta}(k)$ and $g_{\alpha\beta}(r)$ based on the heptamer model are shown in Figure 4a,b. The recent isotopic substitution neutron experimental data on NN, NH, and HH partial structure functions[24] are compared with the model results. The results for NN and NH partial structure functions agree very well. The HH partial structure functions based on the model differ considerably from experimental data. With the available X-ray data more accurate information about this partial is not possible. The NN partial structure function is also available from Narten's X-ray data analysis,[4] and this is also shown for comparison. The model results for $g_{\alpha\beta}(r)$ are in reasonable agreement with experimental data, the main features being produced very well by the present model. The positions and magnitudes of the major peaks (intrapeaks in particular) however differ considerably. The X-ray $g_{NN}(r)$ of Narten shows a split peak and hump which are not shown by neutron result.[24] The present model also does not show these features of Narten's result. In neutron work[24] the authors argue that Narten's X-ray split peak and hump were artifacts of data analysis. The present analysis too indicates similar discrepancies about Narten's X-ray data.

A number of simulation works on liquid ammonia are now available based on various simplified potential models.[3,10−14] Neither the split peak nor the hump of the $g_{NN}(r)$ curve of Narten is reproduced by the computer-simulated $g_{NN}(r)$ curves based on several potential models.[11−13] The $g_{NN}(r)$ and the intermolecular contributions of $g_{NH}(r)$ and $g_{HH}(r)$ curves based on the cluster model agree very well with the simulation results (intermolecular $g_{\alpha\beta}(r)$'s) of Klein et al. for their model-A potential.[12] Integration of the intermolecular part of $g_{NH}(r)$ up to 2.6 Å suggests that there are on average 1.16 hydrogens bonded to each nitrogen atom according to our model, whereas in simulation work, 1.2 hydrogens are bonded to each nitrogen atom. This is a remarkable agreement. The intermolecular contribution of $g_{HH}(r)$ curve based on our model does not show

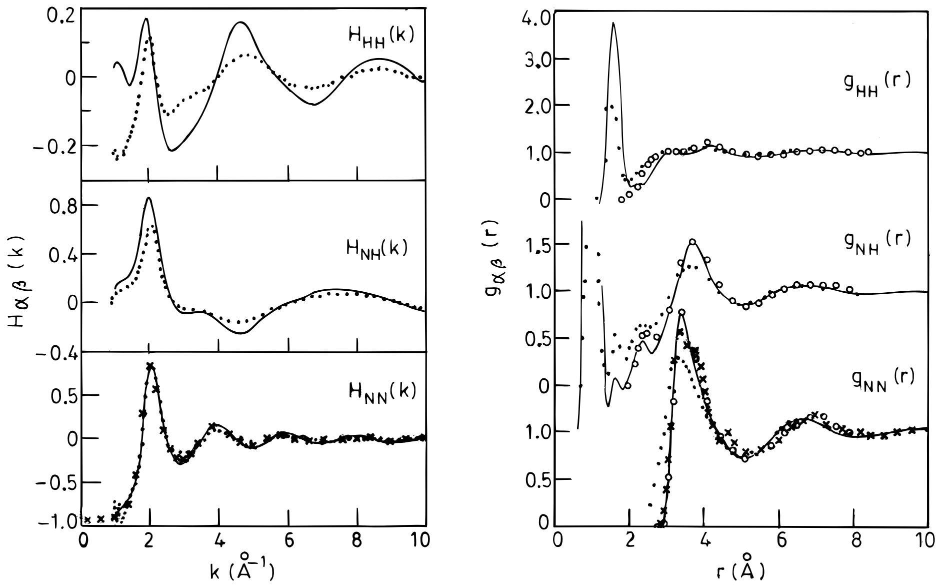

Figure 4. (a, left) Total partial structure functions, $H_{\alpha\beta}(k)$, of liquid ammonia: (—) $H_{\alpha\beta}(k)$ based on PY $S_c(k)$ (center at C.M.) at 4 °C, (···) experimental $H_{\alpha\beta}(k)$ (from ref 24) at 0 °C, (× × ×) $S_c(k)$ data of Narten at 4 °C (ref 4). (b, right) Pair distribution functions $g_{\alpha\beta}(r)$: (—) $g_{\alpha\beta}(r)$ from the model with PY center structure (center at C.M.) at 4 °C, (···) experimental $g_{\alpha\beta}(r)$ (from ref 24) at 0 °C, (× × ×) $g_{NN}(r)$ data of Narten at 4 °C (ref 4), (∘∘∘) intermolecular contribution of $g_{\alpha\beta}(r)$, simulation results (model-A) (ref 11).

any sharp peak, though the structural features are more prominent than those in neutron and simulation results. It is to be noted that in water the first peak in the intermolecular $g_{HH}(r)$ curve occurs at ~2.35 Å, and it is very sharp.[18] This indicates that hydrogen bonding exhibited by ammonia is weaker than that exhibited by water.

IV. General Remarks and Conclusion

In this communication, we have presented a combined analysis of available X-ray and neutron diffraction data on liquid ammonia to see the possible average intermolecular cluster formation due to hydrogen bonding. The method of analysis is the same as in our earlier works on methanol[19] and ethanol.[20] We have considered here a plausible intermolecular association for ammonia monomers in the liquid state at 4 °C. We have however observed that no asymmetrical distortions in the H-bonded cluster models from one close to that in the solid can help to produce the unusual nature of the experimental X-ray $kH_d(k)$ function from $k = 8.0$ Å^{-1} to 9.5 Å^{-1}, and we believe that this is linked to Narten's split peak $g_{NN}(r)$. It appears that this feature in the experimental curve might be due to inaccurate data reduction of the X-ray diffraction analysis. The inclusions of asymmetrical distortions in the model rather worsen to some extent the fitting of the basic functions for cluster information. So it appears that the intermolecular structure based on the present symmetrical heptamer H-bonded cluster model close to that of the solid state fits approximately well with the existing data. This result is consistent with the hypothesis that the seven-molecule H-bonded cluster present in the solid state tends to be approximately present in the liquid near room temperature. This study yields several other interesting points: (a) The heptamer cluster model together with the PY theory for hard sphere center structure[23] produces the overall total structure function quite well. This indicates that, except the hydrogen-bonded effects, the monomers are almost spherically symmetric and they are represented well by PY hard sphere theory. (b) The model yields intermolecular atom−atom distribution functions in remarkable agreement with simulation results.[11] The agreement with recent neutron work data[24] is also reasonable. (c) Some discrepancies remain between the model results and the diffraction data. One source of discrepancy might be in the less accurate earlier experimental data,[8,9,16] and this inaccuracy has been stressed recently by Dr. Chieux in a private communication. So the refinement of the model and conclusive evidence about the average intermolecular association of ammonia monomers in the liquid state are possible only when more accurate experimental data are available.

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