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Reconstruction of the orientational pair-correlation function from neutron-diffraction data: The case of liquid hydrogen iodide

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An analysis of partial-structure-factor information on molecular liquids is described which uses the spherical harmonic expansion of the site-site structure factors to extract an estimate of the orientational pair-correlation function between molecules. Recently published neutron-diffraction data on the site-site partials in liquid hydrogen iodide at 210 K are used as the input data to this technique. The results, which are presented as a map of the orientational pair-correlation function, $g(\mathbf{r},\omega_1,\omega_2)$, show the occurrence of pronounced *relative* orientational correlations between molecules at this temperature, even though the same orientations are apparently only weakly correlated with the molecular center of mass. The same spherical harmonic expansion procedure can be applied to a number of other molecular liquids where diffraction data are available.

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I. INTRODUCTION

The hydrogen halides (HF, HCl, HBr, and HI) present an important series of liquids because, apart from their widespread use as acids, the molecules demonstrate an interesting trend in the nature of their fundamental interactions. While the repulsive hard-core interactions due to electronic overlap are expected to be nearly spherically isotropic throughout the series, the anisotropic attractions which arise from multipolar and polarization forces change monotonically down the series. Table I lists the dipole moment, quadrupole moment, and polarizability of these molecules (relative to the values for hydrogen fluoride), and it can be seen that while the dipole moment decreases, the quadrupole moment and molecular polarizability increase steadily with increasing molecular weight. It should be borne in mind [1] that dipolar forces tend to align the axes of linear molecules either parallel or antiparallel to each other, whereas quadrupolar forces prefer the axes to be perpendicular to one another, the so-called T configuration. The actual configuration found in any particular liquid will depend on the balance between these forces, which work in addition to the electronic overlap and van der Waals attractive forces found in simpler molecules, and the trend in the size of the multipole moments for hydrogen halide molecules means that they are ideally suited to study the role of multipolar forces in organizing the relative orientation of neighboring molecules in a real liquid.

Traditionally, extracting information on orientational correlations between molecules is difficult because all measurable quantities are averaged over the orientations of both molecules. Some limited information is available from spectroscopic techniques, but this is averaged over a range of intermolecular spacings as well. With neutrons it is possible to label the hydrogen atoms independently from the halogen atom and so pick out three sets of correlations: hydrogen-hydrogen (HH), hydrogen-halogen (H*X*), and halogen-halogen (*XX*). These three sets of correlations still cannot on their own provide complete information on orientational correlations, but, as will be seen below, when combined with modern image reconstruction techniques can give a remarkably detailed view of the nature of orientational correlations. A program of diffraction experiments on the hydrogen halide liquids, which exploits hydrogen isotope substitution, is underway on the SANDALS diffractometer at the ISIS pulsed neutron source, and the results from the first of these experiments, on hydrogen iodide, have recently been published [2].

The structure factors that were obtained in the SANDALS experiment are shown in Fig. 1. It will be seen

TABLE I. Values of the dipole moment, quadrupole moment, and polarizability of the hydrogen halide molecules, relative to the values for hydrogen fluoride. The quadrupole moment and polarizability values are approximate as different measurements and calculations do not always agree [1].

Molecule	Dipole moment	Quadrupole moment	Polarizability
Hydrogen fluoride	1.0	1.0	1.0
Hydrogen chloride	0.6	1.6	3.1
Hydrogen Bromide	0.5	1.8	4.4
Hydrogen Iodide	0.3	2.5	6.6

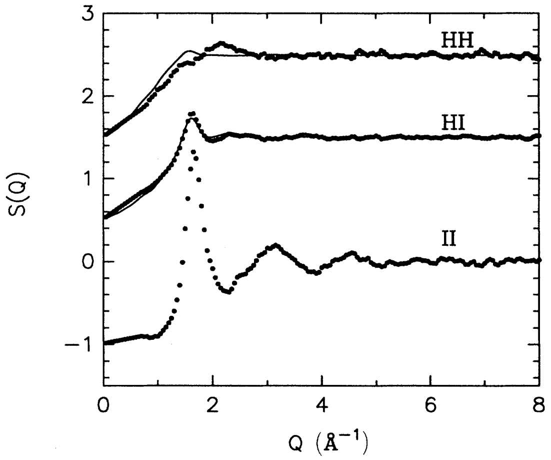

FIG. 1. Partial structure factors for liquid hydrogen iodide at 253 K. The dots show the data measured on SANDALS while the continuous line shows the fit assuming an isotropic orientational correlation function.

that the iodine-iodine structure factor has all the signatures of a simple liquid structure factor, that is a pronounced first peak at $Q=1.67$ Å^{-1} followed by a series of decaying oscillations with peaks at roughly integer multiple values of the first peak Q value. The hydrogen-iodine structure factor shows a similar series of oscillations but these are much weaker in amplitude. However, for the hydrogen-hydrogen structure factor, the main peak is at a larger Q value and there is no sign of the oscillations.

In order to gauge some idea of the implications of these results it is an excellent approximation to regard the iodine as at the center of mass of the hydrogen iodide molecule [2]. Therefore, the iodine-iodine partial structure factor and correlation function can be assumed to represent the corresponding molecular centers structure factor and correlation function, respectively. In that case the hydrogen-iodine structure factor is sensitive to correlations between the center of mass of one molecule and the *orientation* of neighboring molecules, while the hydrogen-hydrogen structure factor is sensitive primarily to *relative* orientations of neighboring molecules.

If the hydrogen atom were randomly distributed over the surface of a sphere with the iodine at the center then the hydrogen-iodine and hydrogen-hydrogen partial structure factors can be calculated directly from the iodine-iodine structure factor simply by multiplying by the spherical form factor for each hydrogen atom. Such a calculation is shown as the continuous line in Fig. 1 and it is immediately clear that while the fit to the HI structure factor is quite good, it is definitely not adequate for the HH function because it predicts the main peak position in the wrong place. Therefore even at this simple level of analysis it appears that while there is only weak correlation between the *center of mass* of one molecule and the *orientation* of a neighboring molecule, the *relative* orientational correlation between neighboring molecules cannot be spherically isotropic.

This point is reinforced by looking at the site-site pair-correlation functions for the data of Fig. 1 (see Fig. 2). It can be seen that the average nearest-neighbor hydrogen-hydrogen distance is markedly shorter than that for iodine-iodine; they would nearly coincide if the molecules were oriented isotropically with respect to one another. Given that these diffraction data and the associated correlation functions indicate relative orientational correlations between molecules it becomes an important and interesting question to determine whether any estimate of the relative molecular orientational correlations can be made; if so then the information derivable from a diffraction experiment is considerably greater compared to that obtained by simply calculating the site-site correlation functions and comparing with a theoretical or computer model.

One possible way of investigating these orientational correlations is via the reverse Monte Carlo (RMC) technique [3], i.e., a Monte Carlo simulation in which the distributions of molecules are generated whose structure factors correspond to those measured. There are no intermolecular potentials in such a simulation, only the diffraction data and some assumed information about the short-range potential to prevent atomic and molecular overlap. Starting from an arbitrary distribution, the molecules in the simulation are rotated and translated in random steps until the calculated site-site structure factors for the ensemble of molecules agree with the measured data. The nature of the orientational correlations can then be determined from the coordinates of the simulated molecules, but it would be necessary to perform a large number of moves to obtain a convergent ensemble average. The principle strength of the RMC procedure is that it ensures the positivity of both pair-correlation function $g(r)$ and structure factor $S(Q)$, something which is difficult to achieve by traditional approaches us-

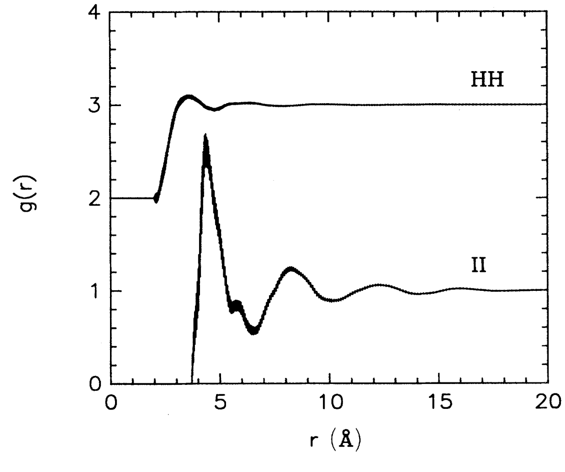

FIG. 2. Partial pair-correlation functions for hydrogen-hydrogen (HH) and iodine-iodine (II) pairs as determined from the data of Fig. 1. The HH nearest-neighbor distance is noticeably shorter than the corresponding II distance, indicating that the relative orientations of neighboring molecules are correlated.

ing direct Fourier transform of the measured data. It also allows one to apply known physical constraints on the distribution functions, such as a realistic distance of minimum approach.

The approach described here, however, takes a different tack. It is well known [1] that the site-site partial structure factors can be expanded as series in spherical harmonic coefficients $H(l_1 l_2 l;Q)$, which in turn are related by an inverse Hankel transform to the real-space expansion coefficients $h(l_1 l_2 l;r)$ of the orientational pair-correlation function. Direct inversion of the partial structure factors to the spherical harmonic coefficients is not possible because the latter are heavily underdetermined. However, by requiring a *minimum* amount of information compatible with the measured data (or in other words maximize the entropy in the coefficients), it *is* possible to obtain solutions for the radial dependence of the harmonic coefficients $h(l_1 l_2 l;r)$ and so make estimates for the orientational pair-correlation function $h(\mathbf{r},\omega_1,\omega_2)$. In this way a three-dimensional picture of the relative orientations of neighboring molecules can be estimated.

The method is generally applicable to all rigid molecular units, but gets complicated if parts of molecules are free to rotate about a particular molecular bond. There has been a previous attempt to derive a few of the spherical harmonic coefficients for liquid acetonitrile [4], but no reconstruction of $h(\mathbf{r},\omega_1,\omega_2)$ was possible. The results given here are for diatomic molecules and represent a powerful new method of obtaining fundamental information from diffraction experiments on the nature of orientational correlations in molecular fluids.

The paper is organized as follows. The underlying theoretical expressions are defined in Sec. II. The maximum entropy method (ME) used in this work follows a nonstandard prescription (called MIN; see Sec. III) which has been referred to in a previous article [5]. However, because this approach is an essential part of the present analysis, it is described in some detail here in Sec. III. The application of the MIN technique to the spherical harmonic problem is described in Sec. IV. The results of applying the analysis to the liquid hydrogen iodide data are shown in Sec. V, which is followed by a general discussion and conclusions.

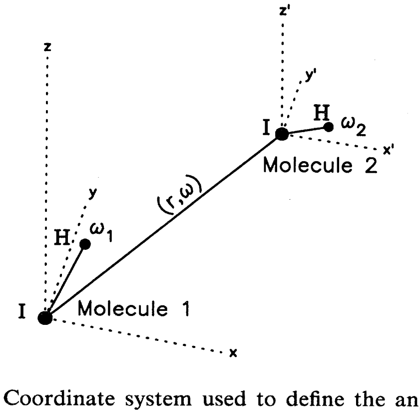

FIG. 3. Coordinate system used to define the angular pair-correlation function. Molecule 1 is at the origin and subtends an orientation ω_1 ($=\theta_1\phi_1$) with the laboratory coordinate frame. Molecule 2 subtends an orientation ω_2 with the same coordinate system, and the vector $\mathbf{r}$ which joins their center of mass subtends a third angle ω with these same axes. Although in principle the angular correlation function depends on seven variables symmetry restrictions for linear molecules reduce the number of independent variables to four (r, θ, θ_2, and ϕ_2).

II. SPHERICAL HARMONIC EXPANSION OF THE SITE-SITE PARTIAL STRUCTURE FACTORS

A comprehensive account of the expansion of the orientational pair-correlation function in terms of spherical harmonic coefficients is given by Gray and Gubbins [1]. The notation and phase conventions given there are adopted here. For linear molecules the formulas are simplified. The angular pair-correlation function is expanded as the product of three spherical harmonics, one for the orientation of molecule 1, ω_1, one for the orientation of molecule 2, ω_2, and one for the orientation of the vector going from 1 to 2, ω (see Fig. 3),

$$h(\mathbf{r},\omega_1,\omega_2)=\sum_{l_1,l_2,l}\sum_{m_1,m_2,m} h(l_1 l_2 l;r)\times C(l_1 l_2 l;m_1 m_2 m)\times Y_{l_1 m_1}(\omega_1)Y_{l_2 m_2}(\omega_2)\times Y^*_{lm}(\omega)\ , \tag{1}$$

where $C(l_1 l_2 l;m_1 m_2 m)$ is the Clebsch-Gordon coefficient. In principle $h(\mathbf{r},\omega_1,\omega_2)$ is a function of seven variables, but in practice only four of these are independent. Without loss of generality molecule 1 can be held fixed at the origin with its axis pointing along the z axis, so that $(\theta_1\phi_1)=(0,0)$ if the angular correlation function is to be mapped out. Thus when summing the series in Eq. (1) we set $m_1=0$, which means, by virtue of the selection rules on the Clebsch-Gordon coefficients, that $m_2=m$.

In reciprocal space the site-site partial structure factors have an exact definition in terms of Hankel transforms of the spherical harmonic coefficients,

$$H_{\alpha\beta}(Q)=\sum_{l_1 l_2 l} f(l_1 l_2 l)j_{l_1}(Qd_\alpha)j_{l_2}(Qd_\beta)\times H(l_1 l_2 l;Q)C(l_1 l_2 l;000)\times Y^*_{l_1 m_1}(\omega'_{1\alpha})Y^*_{l_2 m_2}(\omega'_{2\beta})\ , \tag{2}$$

where

$$H(l_1 l_2 l;Q)=4\pi\rho\int_0^\infty r^2 h(l_1 l_2 l;r)j_l(Qr)dr\ , \tag{3}$$

$j_l(x)$ is the spherical Bessel function of order l, $\omega'_{1\alpha}$ is the orientation of atom α with respect to the axes of molecule 1, d_α is its distance from the molecular center, ρ is the molecular number density, and

$$f(l_1 l_2 l)=i^{3l_1+l_2+l}\left[\frac{2l+1}{4\pi}\right]^{1/2}\ . \tag{4}$$

In practice, because of the requirement from the Clebsch-Gordon coefficients that $l_1+l_2+l=$ *even,* we see that

$$f(l_1l_2l)=(-1)^{(3l_1+l_2+l)/2}\left[\frac{2l+1}{4\pi}\right]^{1/2}, \tag{5}$$

so, because $\omega_{1\alpha}$ and $\omega_{2\beta}$ are either zero or π, all the coefficients $H(l_1l_2l;Q)$ are real.

Equation (2) shows why it is in principle possible to extract information on the orientational correlation function from the site-site structure factors: for hydrogen iodide $d_{\mathrm{I}}\approx 0$ while $d_{\mathrm{H}}\approx 1.6$ Å. Therefore for $H_{\mathrm{II}}(Q)$, the spherical Bessel functions $j_{l_1}(Q_{d_\alpha})$ and $j_{l_2}(Qd_\beta)$ are zero unless $l_1l_2=0$. Therefore the II structure factor can only yield the centers correlation $H(000;Q)$.

On the other hand, for the iodine-hydrogen structure factor, only $d_{1\alpha}\approx 0$, so the terms (000), (011), (022), etc., will appear in the summation. Finally, for the HH structure factor, since both $d_{1\alpha}$ and $d_{2\beta}$ are greater than zero, all the terms contribute. The requirement that a *single* set of coefficients $h(l_1l_2l;Q)$ must satisfy all three datasets (HH, HI, II) according to Eq. (2), already is a strong constraint on their values.

III. THE MINIMUM NOISE (MIN) RECONSTRUCTION METHOD

The aim of this approach is to restrain all possible solutions to an inverse problem to be as smooth as possible, and although it is very similar in concept it is to be distinguished from the traditional maximum entropy approach which requires the solution to be as *uniform* as possible. The degree of smoothness is measured by the square of the second derivative of the function being estimated. A preliminary account of this method and the reasons why conventional maximum entropy methods fail in this instance have been given in a previous article [5].

The object of the minimum noise reconstruction method is to find solutions that minimize the quality factor Q_f, where

$$Q_f=\chi^2+\lambda S \tag{6}$$

and

$$\chi^2=\sum_i\frac{(D_i-M_i)^2}{\sigma_i^2}\ . \tag{7}$$

M_i represents an estimate of the ith data point D_i and σ_i is the statistical measuring uncertainty of this point. The estimate M_i is derived from a trial distribution N_j via the transform matrix T_{ij},

$$M_i=\sum_j T_{ij}N_j\ . \tag{8}$$

In Eq. (6) S is a measure of the noise in the distribution and is given formally by

$$S=\sum_j S_j\ , \tag{9}$$

where

$$S_j=\begin{cases}\Delta_j^2/R_j & -\frac{1}{2}R_j<\Delta j<\frac{1}{2}R_j\\ |\Delta_j| & -\frac{1}{2}R_j>\Delta_j>\frac{1}{2}R_j,\end{cases} \tag{10}$$

and where

$$R_j=\tfrac{1}{2}|N_{j+1}-N_{j-1}|\ , \tag{11}$$

$$\Delta_j=N_j-P_j\ , \tag{12}$$

and

$$P_j=\tfrac{1}{4}[N_{j-1}+2N_j+N_{j+1}]\ . \tag{13}$$

The weight λ controls the extent to which the distribution N_j is forced to be smooth, so it chosen to be as large as possible consistent with the requirement of obtaining a satisfactory value of χ^2. The distribution P_j can be regarded as a "prior" distribution which is always smoother than the distribution from which it was derived. Thus by minimizing S the distribution N_j is the smoothest possible. Distribution R_j is a normalizing function whose role will become clearer below.

Although apparently simple in form it is not immediately obvious that the noise function defined by Eq. (9) (which differs only in detail from that proposed originally [5]) has two unique characteristics which render it rather powerful. To understand this it will be appreciated that in order to minimize the quality factor Q_f, it is necessary to calculate $(\partial Q_f/\partial N_j)$ at each stage of the refinement procedure. Now

$$\left[\frac{\partial Q_f}{\partial N_j}\right]=-\sum_i\frac{2(D_i-M_i)}{\sigma_i^2}T_{ij}+\lambda\left[\frac{\partial S_j}{\partial N_j}\right]\ . \tag{14}$$

Thus $(\partial S_j/\partial N_j)$ acts as a "restoring force" on the N_j to stop them from becoming too noisy. With the definitions given above it is easy to see that

$$\left[\frac{\partial S_j}{\partial N_j}\right]=\begin{cases}2\Delta_j/R_j, & -\frac{1}{2}R_j<\Delta_j<\frac{1}{2}R_j\\ +1, & \Delta_j>\frac{1}{2}R_j\\ -1, & -\frac{1}{2}R_j>\Delta_j.\end{cases} \tag{15}$$

Figure 4(a) shows the value of S_j/R_j as a function of Δ_j/R_j, while Fig. 4(b) shows the derivative (or restoring force), Eq. (15). Note that $(\partial S_j/\partial N_j)$ is dimensionless: it depends *only* on the relative values of N_{j-1}, N_j, and N_{j+1}, not on their absolute values. Therefore the restoring force has the same magnitude irrespective of the order of magnitude of the N_j. At the same time once a clear peak or valley has formed $(-\frac{1}{2}R_j>\Delta_j>\frac{1}{2}R_j)$, the magnitude of the restoring force saturates and becomes *independent* of the height of the peak or valley, respectively, i.e., this form of constraint makes no prejudgment of how high the peak should be. Traditional ME techniques, on the other hand, place a greater restoring force the greater the N_j deviate from the prior P_j and therefore attempt to make large peaks smaller, while leaving small peaks unaffected. The minimum noise approach treats all peaks equally, irrespective of their magnitude: the peak magnitude is controlled only by the requirement of fitting the measured data. Therefore it is equally likely that

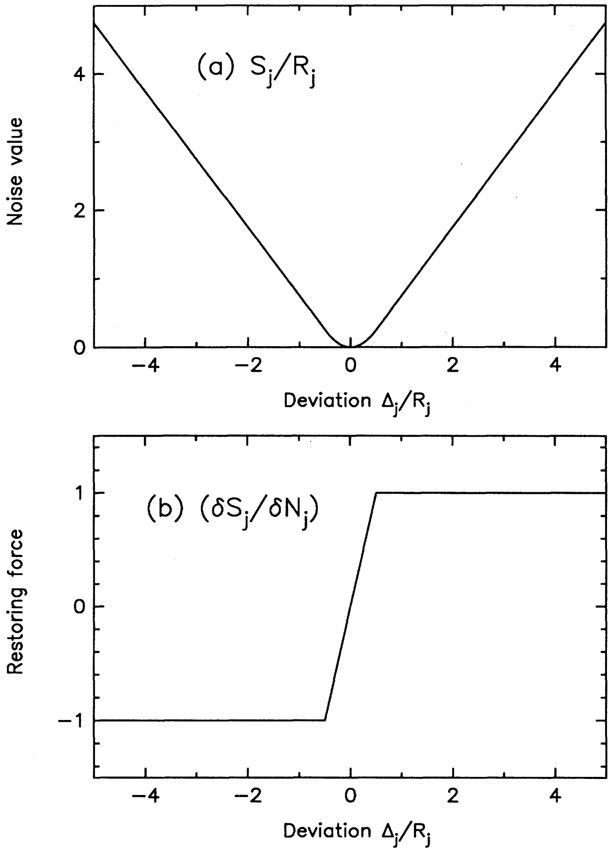

FIG. 4. Variation of (a) the noise function [Eq. (10)] and (b) its derivative [Eq. (15)] with respect to the deviation of the jth point in a distribution from its neighbors $j-1$ and $j+1$. Note that the derivative saturates if the jth point goes outside the range defined by $j-1$ and $j+1$.

small peaks or large peaks which are artifacts of the measuring uncertainties will be removed or reduced in amplitude in the estimated N_j. As a result the MIN reconstruction is extremely reliable.

The quality factor is minimized in this work by a series of iterations, which involve small steps in the values of the N_j. The direction and size of the steps is driven by $(\partial Q_j/\partial N_j)$, but a stochastic component is added to each step to avoid false minima and to ensure that the N_j sample a range of distributions consistent with the data.

IV. APPLICATION TO SPHERICAL HARMONIC ANALYSIS

The analysis of the preceding section was written for a single distribution function N_j. For the spherical harmonic analysis described in Sec. II, however, it is necessary to set up a series of such distributions in parallel, each one corresponding to a particular set of values of (l_1l_2l). Each member of this series will have its own transform matrix from r space to Q space, $T_{ij}^{(\alpha\beta)}(l_1l_2l)$. The elements of this matrix are given by the coefficients outside the $h(l_1l_2l;r)$ in Eq. (2),

$$T_{ij}^{(\alpha\beta)}(l_1l_2l)=f(l_1l_2l)C(l_1l_2l;000) \times j_{l_1}(Q_id_\alpha)j_{l_2}(Q_id_\beta)j_l(Q_ir_j) \ . \tag{16}$$

Similarly each member of the series will have its own noise value, $S(l_1l_2l)$ and the total noise in the ensemble is given by

$$S=\sum_{l_1l_2l} w_{l_1l_2l}S(l_1l_2l) \ . \tag{17}$$

with $w_{l_1l_2l}$ a weighting function to be determined.

There are at present two criteria that can be used to determine the magnitude of the weights $w_{l_1l_2l}$. In the first case the weights are chosen so that the individual noise terms $S(l_1l_2l)$ are inversely proportional to the average magnitude of the transform matrix, and to the weighting factor that comes from the spherical harmonics and Hankel transform, i.e., $\sqrt{(2l_1+1)(2l_2+1)(2l+1)}$. For a particular set of (l_1l_2l),

$$S(l_1,l_2l)\sim\frac{1}{\sqrt{(2l_1+1)(2l_2+1)(2l+1)}\sum_{i,j,\alpha,\beta}|T_{ij}^{(\alpha\beta)}(l_1l_2l)|} \ . \tag{18}$$

In this way values of $N_j(l_1l_2l)$ which affect χ^2 strongly are allowed to have more structure. Conversely values which affect it weakly on average are prevented from developing undue structure.

A further refinement in the values of $w_{l_1l_2l}$ can be achieved by the requirement that ideally the calculated orientational correlation function should be non-negative over all space. This can be difficult to achieve in practice at short distances with a finite number of terms [1], because the short-range correlations induced by hard-core potentials are very pronounced, even when they are weak at longer distances. However, the problem can be alleviated as much as possible by increasing the noise weighting on those (l_1l_2l) coefficients which cause the largest negative excursions. This additional adjustment to the weights is made at regular intervals through the refinement procedure.

The methods of assigning weights described here are to some extent arbitrary, and it is quite possible that alternative schemes could be adopted, based perhaps on a sum-rule constraint on the $N_j(l_1l_2l)$. The constraints used here are consistent with the primary purpose of allowing only sufficient structure or noise in the reconstructed correlation functions as is needed to reproduce the trends in the measured data.

V. RESULTS

The data shown in Fig. 1 were subjected to the spherical harmonic refinement described in the preceding sections, using a total of 27 distinct coefficients (up to a maximum l value of 4). The actual assignments of quantum numbers are listed in Table II. Some of the possible coefficients include pairs of coefficients which are identical or of opposite sign only due to the symmetry properties of the coefficients themselves and the associated Clebsch-Gordon coefficients [1]. Only one of such pairs is tabulated. A selection of the calculated radial dependence for some of the $(l_1 l_2 l)$ values is shown in Fig. 5. It is clear that the (000) term has by far the most structure and confirms that the predominant feature of hydrogen iodide liquid is the pronounced hard-core structure that has already been described [2]. It will also be noted that those which affect the HI correlation [(101) and (202)] have smaller amplitude than (110) and (112) which affect only the HH correlation.

Further information on these correlations can be obtained by plotting contour maps of

$$g(\mathbf{r},\omega_1,\omega_2)[=h(\mathbf{r},\omega_1,\omega_2)+1]$$

for selected values of the direction of the radius vector ω.

TABLE II. Angular momentum quantum numbers for the spherical harmonic expansion used to generate Fig. 6.

No. of coefficient	l_1 value	l_2 value	l value
1	0	0	0
2	1	0	1
3	1	1	0
4	1	1	2
5	2	0	2
6	2	1	1
7	2	1	3
8	2	2	0
9	2	2	2
10	2	2	4
11	3	0	3
12	3	1	2
13	3	1	4
14	3	2	1
15	3	2	3
16	3	3	0
17	3	3	2
18	3	3	4
19	4	0	4
20	4	1	3
21	4	2	2
22	4	2	4
23	4	3	1
24	4	3	3
25	4	4	0
26	4	4	2
27	4	4	4

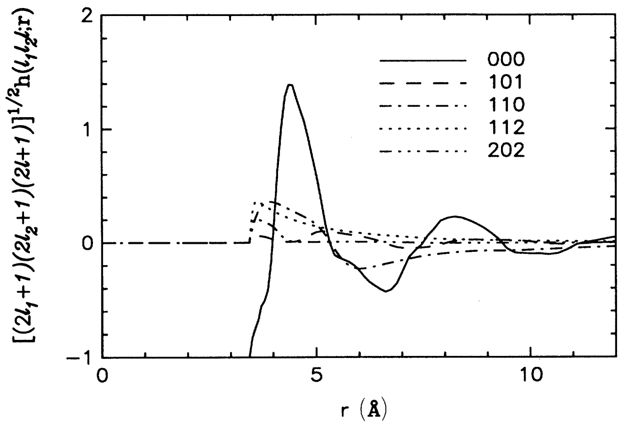

FIG. 5. The fist five coefficients (see Table II) in the spherical harmonic expansion of the partial structure factors of liquid hydrogen iodide. Note that the centers correlation 0,0,0 dominates the distribution, and that those terms which generate the HI correlation, i.e., 1,0,1 and 2,0,2, are noticeably smaller than the 1,1,0 and 1,1,2 terms which affect only the HH correlation.

For this purpose molecule 1 is held at the origin as described in Sec. II, Fig. 3, while $g(r,0,\omega_2)$ is shown as a function of r and θ_2, with $\phi_2=0$ or π. These maps are shown in Fig. 6 for a variety of angles of the radius vector between $\omega=(\theta,\phi)=(0,0)$ and $(\pi,0)$, respectively. The dark areas on these maps correspond to regions of high intensity in $g(r,0,\omega_2)$, and it will be appreciated that the reconstructed orientational correlation function reveals considerable detail about the way the liquid is organized. In particular, it can be seen that in the polar regions of a given molecule, the adjacent molecules tend to align their dipoles either parallel or antiparallel to the molecule at the origin, but there is a broad range of angles that the molecules can adopt. At other positions the darkest spot gradually moves around in a pattern which bears some resemblance to the distribution of magnetic dipoles around the poles of a permanent magnet.

In the equatorial plane the molecules are apparently quite disordered but have a preference for their dipoles to point towards the molecule at the origin. Due to the intensity level scheme it will not be apparent from Fig. 6, but a detailed examination of these correlation functions shows that some orientational correlations do occur in the second neighbor shell of molecules at $r=9$ Å, although they are clearly much weaker in that region.

The fit to the original diffraction data obtained in this spherical harmonic simulation is shown in Fig. 7: it can be seen that the simulated orientational correlation function provides a good fit to the data, and so confirms that at the very least the solution obtained is a *possible* reconstruction which agrees with the data. What remains to be done now is to discuss, to the extent possible, whether there might be other, radically different, solutions which would also agree with the data.

VI. DISCUSSION

The results of the spherical harmonic reconstruction technique described here represent a major alternative approach to extracting information on orientational correlations from diffraction data which apparently has not been attempted before. It has been frequently pointed out [1] that the site-site pair-correlation functions determined by neutron and x-ray diffraction contain less information than the complete orientational pair-correlation functions. With no additional constraints other than the measured data this is formally correct: there are probably a very wide range of solutions for $g(\mathbf{r},\omega_1,\omega_2)$ which can be made consistent with the data. However, it is not unreasonable to ask what is the least amount of structure in this function that is compatible with the measured data? After all the basis for much of our understanding of the statistics of physical processes is that at equilibrium the information content is held to a minimum. The use of the minimum noise procedure gives a viable solution to this problem by obtaining a set of spherical harmonic coefficients which have the least amount of structure while obtaining agreement with the data.

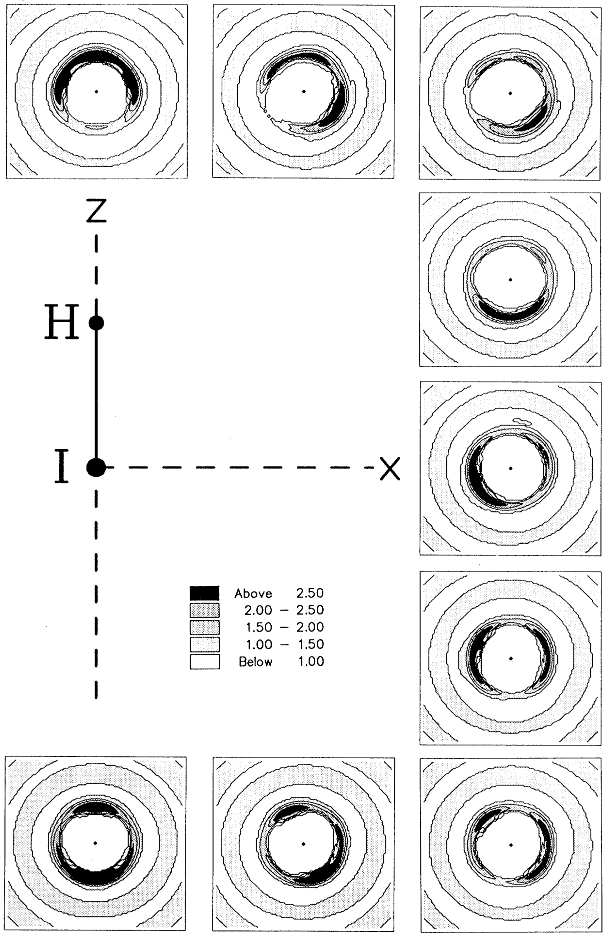

FIG. 6 Density maps of the angular pair-correlation function for a range of θ values. Each map is plotted in a 20×20 Å square. The value of θ corresponds approximately to the angle each map makes with the z-axis of the coordinate system shown, and the molecule at the origin is held fixed with its hydrogen pointing along the z axis. Dark regions correspond to areas of enhanced density. For clarity only values of the correlation function greater than unity are shown. In each map the pair-correlation function is shown as a function of the distance of molecule 2 from molecule 1 (represented as the central black dot): angular variation of the intensity in these maps corresponds to molecule 2 pointing in different directions relative to molecule 1.

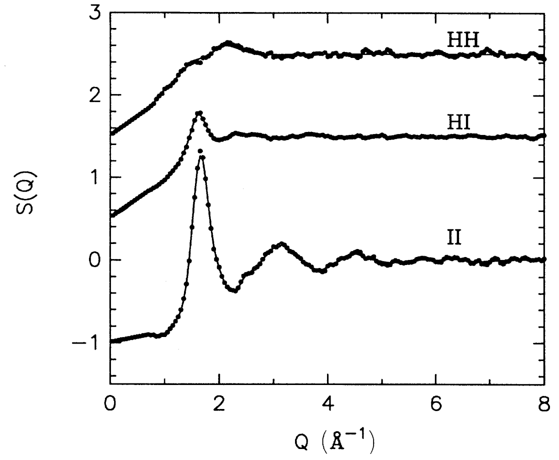

FIG. 7. Fit (line) to the original diffraction data (dots), using the spherical harmonic coefficients. It can be seen that an excellent fit is obtained for all three partial structure factors.

As a further check that the solution given in Fig. 6 does indeed give the correct structure factors, we have used the reconstructed orientational correlation function to estimate $g_{\mathrm{HH}}(r)$ directly, by numerical integration (instead of via the spherical harmonic expansion of the partial structure factor). The results are shown in Fig. 8 and show generally good agreement with direct Fourier analysis. The first peak is seen to shift substantially to lower r values as was seen in the direct transform of the partials, although the shift is not quite as marked as in the direct transform. This disagreement is believed to be due to there being insufficient coefficients in the expansion in the low r, hard-core region, where as we have already described it is difficult to ensure the simulated orientational correlation function is precisely nonnegative. Memory limitations on the transform matrix equation (16) prevented us from using more than 27 coefficients in this work, but it would be perfectly feasible to increase this number significantly in the short-range region by using higher-order coefficients over only a limited range of radius values. The higher-order coefficients are only needed at short distances, but it will be necessary first to determine how the range of a coefficient depends on the values of $(l_1 l_2 l)$.

In the present work the use of the noise constraint, Eq. (10), plus the associated weighting factors, is highly restrictive and does not allow a very wide range of solutions. In the initial development of the method the weights were set to uniform, which resulted in some differences in the reconstructed distributions, although the basic features of Fig. 6 were still observed. However, those distributions also had larger regions where $g(\mathbf{r},\omega_1,\omega_2)$ went

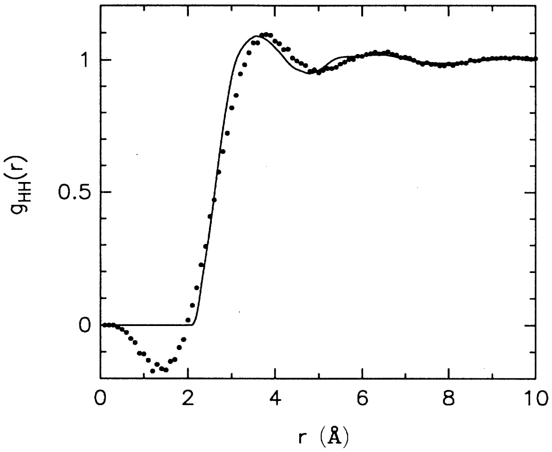

FIG. 8. The reconstructed HH pair-correlation function obtained by integrating the reconstructed pair-correlation function directly (dots) compared to the pair correlation obtained by direct Fourier transform of the diffraction data. Some mismatch is seen in the low r region, probably due to an insufficient number of coefficients being used in that region, but the general trend is correct: the first peak is shifted to significantly smaller r values compared to the main peak in the center pair-correlation function. This small r discrepancy is not nearly so apparent in the fit to the structure data, Fig. 7.

negative, so on that basis cannot be regarded as reliable.

It is also possible that use of a constraining function different to the noise function used here (such as the traditional entropy constraint) would result in a different reconstruction. However, it is our experience that the noise function equation (6) is extremely robust in problems of linear inversion, whereas the traditional ME technique can give spurious structure in those situations [5].

It is worth mentioning two other aspects of the present work, which justifies further development of the method. First, the spherical harmonic approach is ideally suited to incorporating molecular symmetry into the problem: most molecules have several symmetries which act as a further constraint on possible solutions. The effect of symmetry is to limit the choice of (l,m) values that can be accessed. Therefore limiting the choice of solutions to only those that are allowed from symmetry arguments is likely to improve confidence in the reconstruction.

Second, it also should be borne in mind that the spherical harmonic expansion is a relatively compact way of describing a function with a large number of degrees of freedom; to actually digitize the orientational correlation function in the detail shown in Fig. 6 would require an enormous amount of computer memory: the present 27 coefficients occupy about 27×400 words of memory.

To summarize we feel that a full discussion of the uniqueness of the solution will require more detailed analysis than is possible in this preliminary account of the method. However, we have tried different weighting schemes and although this does cause some differences in the detail of the maps of the orientational correlations, the general picture is unchanged. The indications to date are that it is quite robust, given the requirement of the least amount of structure combined with positivity of the reconstructed correlation function.

The present approach is equally applicable to many equivalent problems in the fluid or solid state which involve determination of the relative orientations between nearly rigid molecular units. The underlying equations of the spherical harmonic expansion are formally exact, but it would clearly be useful to test our predictions against a known result from a computer simulation. We hope to report on such a test in the future.

VII. CONCLUSION

The spherical harmonic expansion of the site-site partial structure factors for a molecular fluid have been used to derive an estimate of the orientational pair-correlation function for liquid hydrogen iodide. The input data to this calculation are the HH, HI, and II structure factors measured by neutron diffraction. The results indicate preferred *relative* orientations of the nearest-neighbor molecules with respect to a molecule at the origin. Orientational correlations are also weakly present in the second-neighbor shell. The power of the method is that once the spherical harmonic coefficients are refined the orientational correlation function can be calculated for an arbitrary choice of angles and distances between molecules and is not limited to a specific set of coordinates. It also has the advantage that molecular symmetry can be built naturally into the correlations, by appropriate choice of (l,m) values.

A number of questions remain to be addressed, particularly that of uniqueness, and the highest order of (l_1l_2l) that is needed to ensure positivity of the correlation function at all radius values. The present preliminary results already demonstrate the remarkably detailed information on orientational correlations that it is possible to obtain from diffraction data by application of a rather simple constraint on possible solutions. We hope to report on further applications of this method to other hydrogen halide liquids and to other liquids such as water, and to address the question of uniqueness in the future.

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