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Abstract

We have interpreted the structure factor of liquid PBr$_3$, as measured by Misawa *et al* (1990 *J. Chem. Phys.* **92** 5486) on a pulsed neutron source, by means of reverse Monte Carlo (RMC) modelling. We have used the method of fixed neighbour constraints, which accounts for the flexibility of the molecules. From the RMC models, partial pair correlation functions and cosine distributions of intra- and inter-molecular angles were calculated. Comparisons with reference systems, which were generated by hard sphere Monte Carlo simulation, were also carried out. We were able to find unique orientational correlations in liquid PBr$_3$ in terms of the cosine distribution of P–Br$\cdots$P angles (the Br atom being in the centre), involving one intra-molecular P–Br and one inter-molecular Br$\cdots$P nearest-neighbour distance.

1. Introduction

There is continuing interest in the structure of molecular liquids, especially those loosely defined as 'simple'. To some extent, what is considered simple is a matter of taste: here a liquid is simple if its constituent molecules are highly symmetric, with a well-defined shape. In addition, there should be no prominent directional forces between the molecules. Molecular liquid CCl$_4$ is a classical example of such a liquid whose structure is now well understood [1] (see also references therein).

A possible move towards complex molecular systems is to study liquids in which molecules are of the shape of slightly distorted perfect bodies. Another step towards complexity is to consider liquids whose molecules interact via somewhat more elaborate forces than those resulting from van der Waals type potentials. The present contribution is an attempt to realise both kinds of modifications, by considering (collections of) molecules that possess *both* a distorted (tetrahedral) shape *and* a molecular dipole moment.
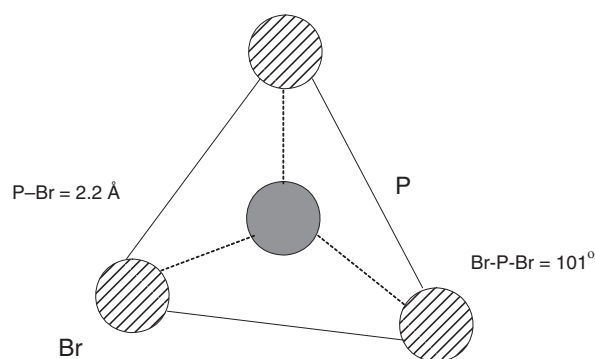
Figure 1. The trigonal pyramidal shape of a PBr_3 molecule (top view). P–Br distance and the angle Br–P–Br quoted from Enjalbert and Galy [3]. The equilibrium Br–Br distance is 3.45 Å.

Phosphorous tribromide (PBr_3, phosphorous bromide, phosphorous(III) bromide) is a colourless liquid at room temperature. Its principal application is for the conversion of alcohols into alkyl bromides in the laboratory, whereas the main commercial use is for the production of pharmaceutical products such as fenoprofen; it is also used for extinguishing fires [2]. The shape of the molecule is low-symmetry trigonal pyramidal in the crystalline state (figure 1), and was determined by Enjalbert and Galy using x-ray diffraction at low temperatures [3].

Liquid phosphorous tribromide has been studied by neutron diffraction on a pulsed neutron source at ambient temperature by Misawa *et al* [4]. They measured a single total-scattering structure factor, $F(Q)$, from which, nevertheless, they determined the three partial radial distribution functions (prdf), $g_{ij}(r)$, by applying analytical models and, further, they proposed a simple, two-molecule picture for the orientational correlations in this liquid. (Exact definitions of $F(Q)$ and $g_{ij}(r)$ functions can be found in [5].)

Here, we wish to go beyond the analyses of Misawa *et al* by constructing large models of the liquid structure by using the reverse Monte Carlo (RMC) method of structural modelling [6, 7]. From the models, partial radial distribution functions and angular distributions can be calculated without the use of any approximations.

2. Reverse Monte Carlo modelling

2.1. Method in a capsule

While the principles of RMC modelling have been described in detail elsewhere (e.g. by Evrard [7] or McGreevy [8]), it is worthwhile mentioning the basics of the approach used in this work, which is applicable to XY_3 molecules.

For the present calculations, the RMC++ software [7] has been applied. The RMC method uses an algorithm similar to that of Metropolis [9]. The procedure starts with a collection of randomly oriented flexible (see section 2.2) molecules in a cubic box, at the appropriate density. Movements are made by displacing one (randomly chosen) atom at a time. Partial radial distribution functions $g_{ij}(r)$, together with the simulated $F(Q)$, are calculated directly from the particle configuration. Moves are accepted (rejected) on the basis of decreasing (increasing) difference between simulated and experimental $F(Q)$; for avoiding bottlenecks in the course of the simulation, some moves that increase this difference are also accepted. As a result of the calculation, particle configurations (collections of atomic coordinates) are obtained that are consistent (within the level of experimental errors) with diffraction data.

Subsequently, by applying separate software for data analysis, information about angular distributions, as well as other quantities of interest, can be retrieved.

2.2. Dealing with molecules

Effectively, distances between atoms in RMC are described by a rigid hard-sphere potential, and there is no conclusive information from diffraction studies whether there are molecules in the liquid sample under study. *A priori* knowledge of the molecular structure allows for 'softening' of the potential via the incorporation of flexible molecules in the programme.

Flexible molecules are represented by collections of atoms held together by geometrical constraints, the so-called 'fixed neighbour constraints' (fnc) [10]. Something of a misnomer, fnc entails fixing numbers and types of atoms around each particle, thus taking into account the chemical structure. A neighbour list is set up for the initial configuration and it is kept unchanged throughout the entire calculation. This is the 'fixed' part. The bond lengths are allowed to vary slightly, within pre-defined tolerance, bringing in the flexibility of the molecules. This way, atoms belonging to different molecules can approach each other as closely as those within the same molecule, if required, while the integrity of molecules is preserved.

The rationale for this is to avoid difficulties inherent in the analysis of the total structure factor in terms of the intra- and inter-molecular contributions to the scattering. The fnc approach is particularly useful when inter- and intra-molecular distances between the same atom types overlap, and has been used successfully for studies of water [11], XCl_4 liquids [1] and liquid antimony pentachloride and tungsten hexachloride [12].

2.3. Comparison to a reference system

In the analysis of orientational correlations it is not possible to tell *a priori* whether they arose from random packing of molecules with a specific shape or they are due to specific inter-molecular interactions. This issue can be clarified by comparison to reference systems generated by hard-sphere Monte Carlo (HSMC) simulations. These calculations are exactly the same as the corresponding RMC runs—but without experimental data to model. Differences between structural characteristics resulting from HSMC and RMC calculations can then be unequivocally assigned to the influence of diffraction data. As a further benefit, equilibrated HSMC models can also be used as initial configurations for the RMC runs.

Comparison to such reference systems was initiated by an RMC study of liquid carbon tetrachloride [13] and is now a step performed routinely for analysing orientational correlations in simple molecular liquids [12–14].

2.4. Calculation details for PBr3

Determination of the structure of liquid phosphorus tribromide presents an interesting study case, since we have only one set of data available: one single total-scattering structure factor, $F(Q)$, from a neutron diffraction experiment. However, knowledge of the molecular structure, together with the most basic constraints such as the density, increases the available information substantially (but, unfortunately, to an extent that cannot be quantified), particularly when structural models are being generated.

Figure 1 shows the trigonal pyramidal shape of the PBr_3 molecule with P–Br distances and a Br–P–Br bond angle as determined by Enjalbert and Galy [3] using x-ray diffraction at low temperature. This geometry was used to set the starting values of fncs (see table 1). It is expected that in a liquid state the geometry of the molecule would be very close to that observed

Table 1. Details of the RMC (and HSMC) model(s). Here fnc denotes the tolarance for the given bond when fixed neighbour constraints are used; r_c is the inter-molecular cutoff distance; max_d is the maximum displacement per move for the given atom type.

N_{atoms}	fnc (P–Br) (Å)	fnc (Br–Br) (Å)	r_c (P–P) (Å)	r_c (P–Br) (Å)	r_c (Br–Br) (Å)	max_d (P) (Å)	max_d (Br) (Å)
6000	2.1–2.3	3.3–3.6	4.0	2.2	3.3	0.1	0.1

in the solid state. This choice of fncs is physically meaningful, while not implying anything about local ordering of the molecules in the liquid.

Two thousand molecules (8000 atoms) were put in a cubic box, at the atomic number density of $0.025\,56$ Å^{-3}. Weighting factors for the P–P, P–Br and Br–Br partial radial distribution functions (and partial structure factors) are 0.0163, 0.1299 and 0.2593, respectively, for the neutron diffraction data to be modelled. Table 1 provides further details of the RMC models. All models/simulations were terminated after several million moves were accepted, when the quality of the fit was already stable.

As will be seen later, the choice of the cutoff values (particle sizes) is crucial, as some might fear that the actual choice of these distances may influence even some of the conclusions. The Br$\cdots$Br cutoff was set just below the intra-molecular Br$\cdots$Br distance. Also, in liquid bromine, the non-bonded Br$\cdots$Br distance is around 4 Å [15]. The P$\cdots$P distance was chosen in relation to the inter-molecular P$\cdots$P distance found in liquid P [16]. We would like to note here that the final choices were made on the basis of extensive RMC calculations; it was via these (trial) calculations when it became apparent that the P$\cdots$Br distance had to be lowered to a value close to the lower limit of the P–Br fnc (see below).

3. Results and discussion

In figure 2, total structure factors, as calculated by RMC with fnc and as measured by Misawa *et al* [4], are presented. The agreement between the two curves is very good indeed; there are only barely visible discrepancies below 5 Å^{-1} and above 16 Å^{-1}. Figure 2 also shows the $F(Q)$ calculated from the reference HSMC model. There are two features that deserve attention: the nearly perfect agreement with the RMC model (and with experiment) above about 11 Å^{-1} and, as quite a sharp contrast, the large differences below 2 Å^{-1}, particularly in terms of the intensity of the first—'sharp diffraction'—peak ('FSDP' [17]) at about 1.4 Å^{-1}.

The former signifies that—not unexpectedly and within the limits set by the fncs—the molecular geometry is identical in the RMC and HSMC models. The quantitative agreement also means that above 11 Å^{-1} the scattered intensity originates from the intra-molecular structure factor *exclusively*; such a clear-cut separation is very rarely possible since—as the present case exemplifies—it must be based on extensive structural modelling. (We note here that Misawa *et al* [4] have also pointed out that the 'high Q' part of the structure factor is dominated by the molecular structure.)

Concerning deviations between RMC and HSMC models at low Q values, the first thing to notice is that the HSMC model, the one that is supposed to reflect a random packing of molecules, exhibits a much higher first peak than that found experimentally. As a rule of thumb, it is generally accepted that a sharp maximum at low Q corresponds to 'medium range ordering' (MRO) [18]. Qualitatively, if the intensity of such a maximum decreases drastically, then the extent of MRO should also decrease. Concerning the present case, it seems as if the necessarily randomly oriented molecules in the HSMC model could be represented by large
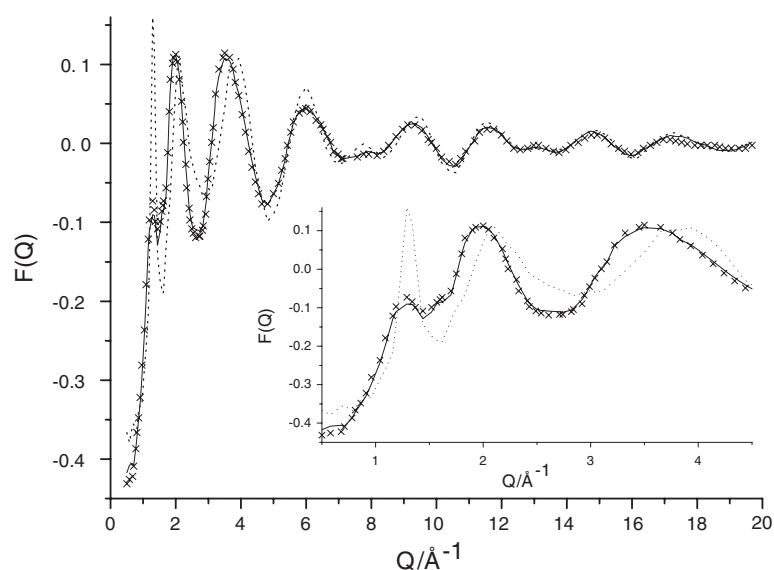
Figure 2. Total structure factors for liquid PBr$_3$. Symbols: experimental data (Misawa); solid line: RMC with fnc; dots: hard-sphere reference system. Inset: a close-up of the region up to 4.5 Å^{-1} emphasizing the dramatic decrease in terms of the intensity of the first (sharp diffraction) peak (FSDP).

spheres (cf [4]), which spheres, in turn, exhibit a kind of ordering (MRO) characteristic to closely packed spheres. On the other hand, when diffraction data are considered in the RMC model, the molecules can no longer be represented by simple big spheres: they now exhibit preferential short-range ordering and thus breaking the rhythm of the MRO that was a feature of the HSMC structure. This is nicely demonstrated by comparing partial structure factors for the HSMC and RMC models (figure 3); the intensity of the sharp peak at about 1.4 Å^{-1} is, indeed, systematically *lower* for the RMC models. In what follows, the validity of this conjecture will be checked, and the nature of the preferential short-range (orientational) ordering will be sought.

In figure 4, partial radial distribution functions calculated directly from particle coordinates are shown, for both the RMC and HSMC structural models. The first thing to notice is that P–P $g_{ij}(r)$ (which may be considered to be the molecular centre–centre $g(r)$) is, indeed, less structured for the RMC model, in agreement with what was speculated on the basis of the total and partial structure factors. A smaller but equally important difference is that the first non-zero value of the $g_{PP}(r)$ function occurs at a significantly lower (by about 0.5 Å) r value for the RMC model, which is consistent with diffraction data and also that the position of the first peak is shifted slightly towards larger (by nearly 1 Å!) r values. Since the parameters of the RMC and HSMC calculations are identical, including the distances of closest approach ('cutoffs'), one has to accept that these, quite unique, changes are direct consequences of the experimental data. It appears that some of the molecules must approach each other more closely than pure steric effects would require; for this, specific mutual orientation of neighbouring molecules is necessary (which, at this point, cannot yet be identified).

Let us consider next the P–Br $g_{ij}(r)$ function (figure 4). In the HSMC model, there is a clear gap between the intra-molecular maxium (at 2.2 Å) and the inter-molecular parts of the curve. On the other hand, in the data-based RMC model, the intra-molecular P–Br peak
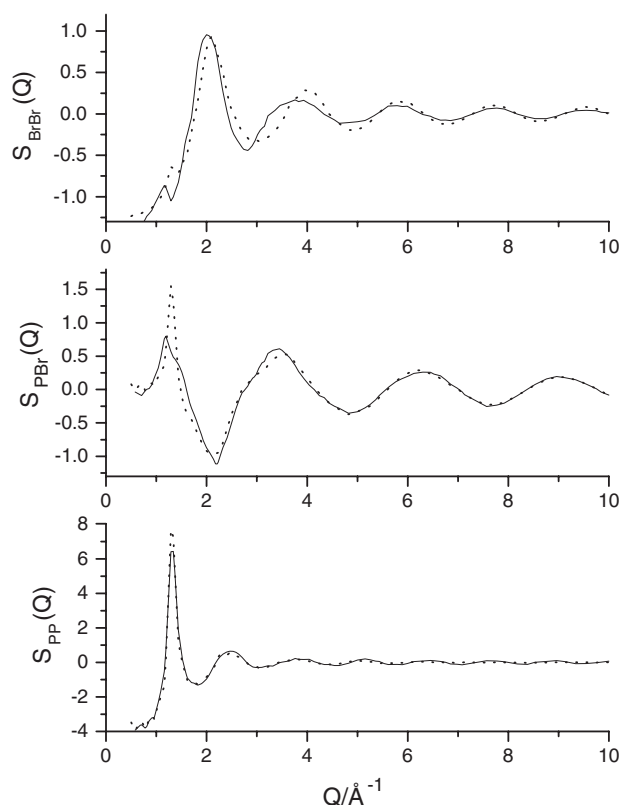
Figure 3. Partial structure factors for liquid PBr$_3$. Solid line: RMC; dots: hard-sphere reference system.

has a well-observable shoulder and the $g_{PBr}(r)$ function remains above zero for all r values. This finding is consistent with the above observation concerning $g_{PP}(r)$; we note here that the behaviour of both $g_{PP}(r)$ and $g_{PBr}(r)$ is highly unusual among simple molecular liquids (cf [1, 12–14]).

Perhaps the most apparent (most visible) difference between HSMC and RMC models at the partial radial distribution function level can be spotted in the Br–Br $g_{ij}(r)$ (figure 4); a definite maximum appears at about 4 Å as the result of requiring consistency with diffraction data. This maximum corresponds to the first inter-molecular Br–Br neighbours and, as such, it is also consistent with the notion that some molecules approach each other much more closely than would be necessary by excluded volume effects (density, closest approaches, molecular shape). The reason why this feature appears to be less exciting is that in other liquids containing tetrahedral molecules, such as in carbon tetrachloride [13], the emergence of a very similar pattern is observed.

Concerning the partial radial distribution functions in general, we would like to point out that the prdfs derived here as a result of extensive computer modelling are in at least semi-quantitative agreement with those obtained earlier by Misawa *et al* [4]—which, taking into account that they derived prdfs from a single $F(Q)$ without modelling, should be considered as a remarkable achievement of the authors of [4]. The only important (although, admittedly, small) feature that they seem to have missed is the extra intensity in between the intra- and inter-molecular regions of the P–Br $g_{ij}(r)$.
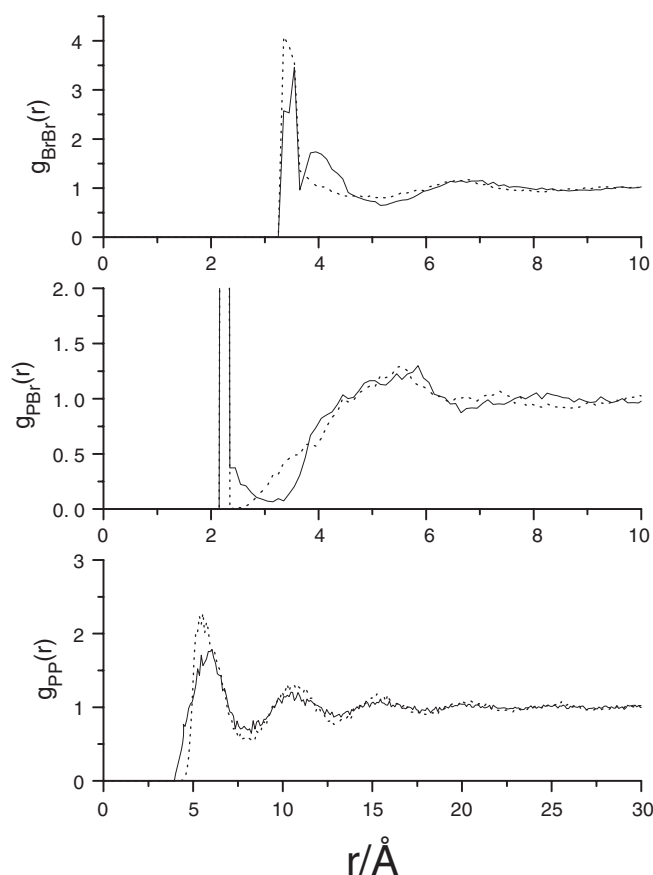
Figure 4. Partial radial distribution functions for liquid PBr$_3$. Solid line: RMC; dots: hard-sphere reference system. The *r*-scale for $g_{PP}(r)$ is different, so that longer-range ordering between molecular positions is visible.

In the pursuit of the specific mutual orientation(s) of neighbouring molecules mentioned previously, now we wish to consider not only two-, but also three-particle correlations. The simplest way of doing this is to join particle pairs within the first minimum of the corresponding prdf (in other words, within the first coordination sphere; appropriate distances for P–P, P–Br and Br–Br pairs are 8, 2.5 and 3.6 Å, respectively) with lines and form angles of these lines that originate from the same particle as centre. The distribution of these angles (or, more frequently, of their cosines) is only a simple projection of the full three-particle correlation function—still, for its usefulness, it has become a standard tool for analysing particle configurations [1, 8, 11–13]. Cosine distributions of some of the X–Y–Z (X,Y,Z:P, Br; Y is the centre) angles are provided in figure 5 ('–' denotes a line joining two atoms in the same molecule whereas '···' are used for describing a line that connects atoms of different—but neighbouring—molecules).

The easiest curve to understand is probably the distribution of Br–P–Br angles (figure 5): the centre of the only peak is at the cosine value corresponding to the intramolecular Br–P–Br bond angle (about 101°). The low-intensity tail towards larger angles (more negative cosine values; appearing only on the curve calculated from the RMC model) comes from the few
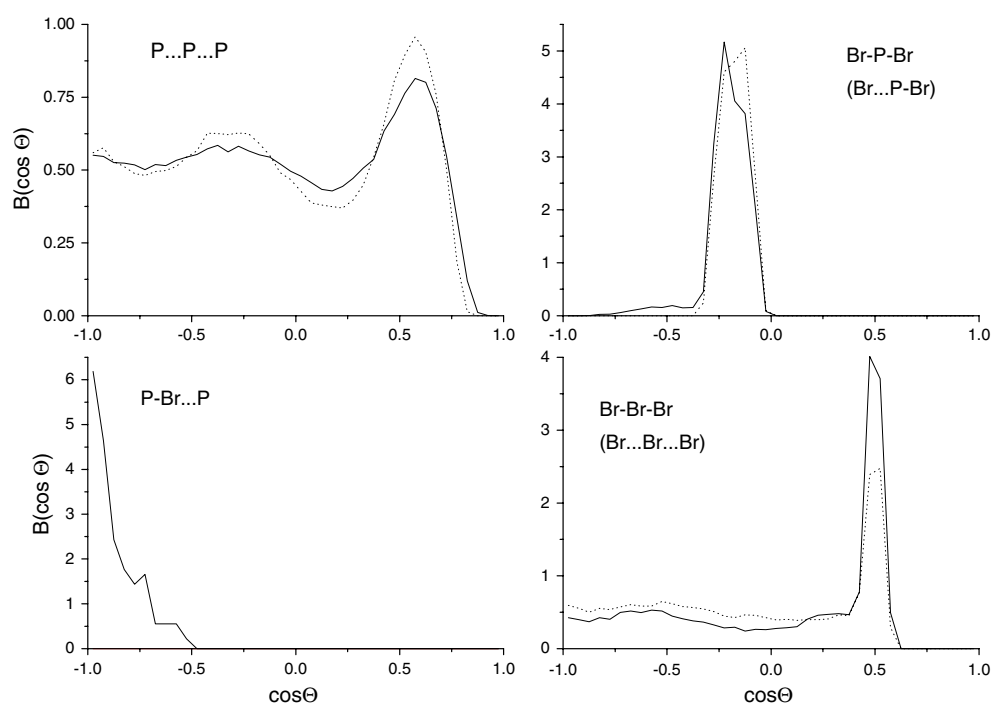
Figure 5. Cosine distributions calculated up to the first minima of the partial radial distribution functions. Solid lines: RMC; dots: hard-sphere reference system. (Note that, for the P–Br $\cdots$ P distribution, there were no angles within these distance ranges for the reference system.)

molecules whose Br atoms reach within the distance range of the intra-molecular P–Br bond. The shape of the top part of the peak is somewhat strange (similarly to the shape of the first maximum of the Br–Br prdf); we assign this aesthetic shortcoming to small uncertainties in the data at higher Q values (which, in turn, may well originate from the fact that the data had to be digitized from a paper copy). Still considering the molecular structure, the large peak in the distribution (of the cosines) of Br–Br–Br angles at $\cos \Theta = 0.5$ (60°) can easily be identified as characterizing the equilateral base triangle of the molecule. The rest of the intensity stems from inter-molecular correlations.

The distribution of the P $\cdots$ P $\cdots$ P angles follows the typical pattern that is characteristic of densely packed spheres, where touching spheres form equilateral triangles (see also [12]). Note, again, that the curve corresponding to the HSMC model exhibits sharper features.

Unexpectedly, it is the distribution of the P–Br $\cdots$ P angles that finally is able to reveal the nature of orientational correlations in liquid phosphorous tribromide (figure 5). No such angles could be found in the HSMC reference system, since—as may be obvious from figure 4—Br atoms of neighbouring molecules did not approach the P atom of the central molecule to within the range of the P–Br bonding distance. For the data-based RMC model, on the other hand, a striking feature, a sharp peak at $\cos \Theta = -1$ (180°), emerged that is an unequivocal sign that a Br atom of one of the molecules can be found on a (nearly) straight line connecting the P atoms of two neighbouring molecules. (The width of the $\cos \Theta$ bin is 0.05, that is, the first bin allows for angles between 180° and 162°; about 37% of the angles found are in this first bin.) It is important to stress that not every molecular pair possesses this feature, only those that are closest to each other; about 10% of the P atoms have a fourth (inter-molecular) Br

neighbour within the strictly defined first coordination shell (up to 2.4 Å). We note that such a clear indication of molecular orientations (which can be identified in a particle configuration) is extremely rare: perhaps the only similar example is the hydrogen bonding angle in liquid water (see, e.g., [11] and references therein).

It is now possible to compare the preferred mutual orientations of neighbouring molecules emerging from RMC modelling and from analytical (but approximate) considerations [4]. Misawa *et al* proposed that, the phosphorus atom being top, two neighbouring molecules are aligned in almost the same direction, with the basal planes of the pyramid (defined by bromide atoms) rotated by about 30° with respect to each other. The present analyses do not tell anything about the relative positions of the basal planes (i.e. we can neither confirm nor exclude the possibility just mentioned); indeed, this feature seems to be too fine to be identified unequivocally on the basis of available diffraction data.

4. Conclusion

It has been revealed that PBr_3 at room temperature is a liquid with intriguing properties at the level of the atomic structure. Some of the molecules in the liquid approach each other significantly more closely than in the hard-sphere-like reference system. For these neighbouring molecules, a well-defined orientational order was detected, according to which the line connecting two P atoms goes through a Br atom of one of the molecules. As a result, the long-range ordering of P atoms (acting as molecular 'centres') weakens, which shows up both in the P–P partial radial distribution function and in the total structure factor upon comparison of data-based RMC and reference HSMC models. This behaviour is very different from what has been found for other simple molecular liquids.

Acknowledgments

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