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# The structure of liquid iodomethane, CH<sub>3</sub>I/CD<sub>3</sub>I

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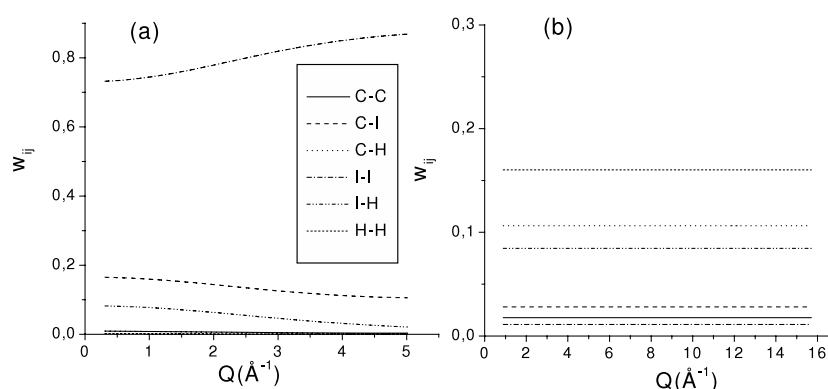
## Abstract

An x-ray diffraction measurement has been performed on liquid iodomethane using the BL04B2 beamline at the SPring-8 synchrotron radiation facility (Japan). The corrected structure factor, together with the results of an earlier neutron diffraction study, has been interpreted by means of reverse Monte Carlo modelling. This approach provides large structural models, containing thousands of atoms that are consistent with the experimental data within their uncertainties. From these models, partial structure factors and radial distribution functions were calculated. It is demonstrated that, for a satisfactory description of the intermolecular correlations, the presence of x-ray data is vital. Orientational correlations between neighbouring molecules have been found to be much better defined than if they were due to excluded volume effects only.

## 1. Introduction

Simple molecular liquids, containing highly symmetric molecules with regular shape, have been extensively and systematically studied by diffraction methods (e.g. [1–4]). The best known example of such systems is carbon tetrachloride, CCl<sub>4</sub>, for which a multitude of diffraction data sets have been published over the past few decades [1–3]. As a result of up-to-date modelling techniques, the structure of these liquids is now relatively well understood [2–4].

Molecular liquids containing molecules with a lower level of symmetry, on the other hand, have been considered much less frequently—even though there are obviously orders of magnitude more kinds of such liquids (see [5–7] for fluoroform, chloroform and methylene chloride, respectively). A possible way of systematizing the investigation of these liquids would be by distorting step-by-step the perfect symmetry of the simpler ones, so that changes in the microscopic structure induced by the changing molecular shape could be monitored. The very first step towards this direction was taken by neutron diffraction measurements reported in [8], where liquids containing molecules with slightly distorted tetrahedral symmetry were briefly considered. In the present study, we inspect in detail one of the aforementioned systems, liquid iodomethane, CH<sub>3</sub>I/CD<sub>3</sub>I.



**Figure 1.** Weighting factors of the partial structure factors when composing the totals (a) for x-ray diffraction and (b) for neutron diffraction. Note the nice complementarities between the two sets of data, particularly as far as the I–I contribution is concerned.

As an extension to the available neutron diffraction data on the deuterated compound  $\text{CD}_3\text{I}$ , here we describe a new x-ray diffraction experiment for liquid iodomethane. Due to the weighting factors of the partial radial distribution functions (prdf), neutron data sample mostly pair correlations involving hydrogen. Correlations between the ‘bulky parts’ of iodomethane molecules, which are their iodine atoms, could not be revealed. X-ray diffraction, on the other hand, is dominated by I–I (intermolecular) correlations, thus providing a complement to the neutron data (see figure 1).

As a basis for the intended detailed structural analyses, we wished to build structural models, containing thousands of particles, that are consistent with all available experimental information—in our case, the two (neutron and x-ray) total structure factors (tsf). A possible way of obtaining such models, which was also taken in [2–4], is to use the reverse Monte Carlo (RMC) method for modelling diffraction data [9]. In RMC, particles are moved around in a simulation box so that the structure factor calculated for the box approaches the experimental tsf(s). Experience shows that in most cases it is possible to achieve the desired agreement with experiment(s) to within the experimental errors (statistical and systematic). A review of RMC and related methods can be found in [10, 11].

On the route towards an understanding of the structure of more complex liquids, such as those with direct biological relevance, understanding the structure of liquids containing slightly distorted molecules is an important step. The main goal of the present study is to extend the knowledge base resulting from this ongoing research. More specific to the system in question, we wish to reveal the nature of orientational correlations found in liquid iodomethane, mainly on the basis of prdf’s and angular distributions.

## 2. Experimental details

Chemicals were obtained from Aldrich Chemical and were all of higher purity than 99%. Neutron diffraction measurements were carried out earlier, using the PSD powder diffractometer installed at the Budapest Research Reactor [12], as described in [8]. The sample here was the deuterated form of methyl iodide,  $\text{CD}_3\text{I}$ .

X-ray diffraction experiments have been performed at the SPring-8 synchrotron radiation facility (Japan), using the single-detector diffractometer setup of the BL04B2 (high-energy x-ray diffraction) beamline [13]. For the current experiments, the momentum transfer range

**Table 1.** Details of RMC models ( $r_c$ : intermolecular cutoff distance; fnc: tolerance limits of the fnc constraints). For the final HSMC calculation, the I–I cutoff was taken according to the value in parentheses.

Boxlength (Å)	Atomic density (Å <sup>-3</sup> )	fnc(C–I) (Å)	fnc(C–H) (Å)	fnc(H–I) (Å)	fnc(H–H) (Å)
59.14	0.043 85	2.07–2.19	1.02–1.14	2.55–2.79	1.67–1.91
$r_c$ (C–C) (Å)	$r_c$ (C–I) (Å)	$r_c$ (C–H) (Å)	$r_c$ (I–I) (Å)	$r_c$ (H–I) (Å)	$r_c$ (H–H) (Å)
3.3	3.0	2.5	2.5 (3.2)	2.5	2.5

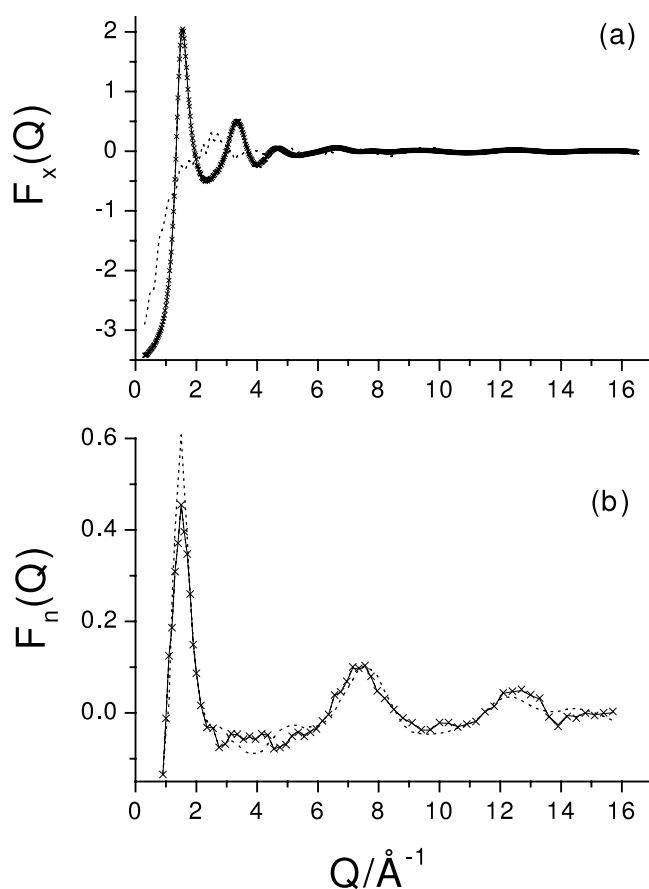
extended up to about 16 Å<sup>-1</sup>. Corrections to yield structure factors have been made by standard procedures, as described, for instance, in [13].

### 3. Reverse Monte Carlo modelling

The basic RMC modelling method has been described elsewhere (e.g. [9–11]), so only a brief summary of the relevant details is given here. We have used the flexible molecule approach, where molecules are considered to be collections of atoms which are held together by geometric constraints. The total structure factor to be modelled then contains both intra- and inter-molecular scattering, i.e. the molecular form factor (see e.g. [1]) has not been subtracted. For keeping molecules together, a method called ‘fixed neighbour constraints’ (fnc) [11] has been applied. This approach was developed specifically for dealing with flexible molecules, particularly when inter- and intra-molecular distances between the same atom types overlap. In the fnc method a neighbour list is set up for the initial configuration and each individual atom (as opposed to atom type) is given specific bonding constraints to its individual neighbours. Values for the bonding constraints for the CH<sub>3</sub>I molecule can be found in table 1. (Note that a rather similar construction is also used in the RMCProfile software, applicable for modelling diffraction data from polycrystalline materials [14].)

In order to be able to distinguish orientational correlations that arise from random packing of molecules (with a particular shape) from those that are due to specific intermolecular interactions, our results will be interpreted in terms of comparisons to ‘reference systems’. These were generated by hard sphere Monte Carlo (HSMC) simulations on the same systems (size, density, identical constraints), as were considered in the RMC runs. That is, the only difference between RMC and HSMC calculations was that in RMC the additional constraints imposed by the data were also present. This way, differences detected in terms of the local structure can only arise as a direct consequence of diffraction data. This kind of comparison proved to be extremely instructive for liquids such as CCl<sub>4</sub> [3] and SbCl<sub>5</sub> [4]. As a further benefit of the HSMC calculations, RMC modelling could be started using the HSMC models as the initial configurations.

In the present study, four (sets of) calculations have been performed: the ‘hard sphere’ Monte Carlo reference runs (denoted throughout the rest of the paper as ‘HS’), modelling the neutron data only (‘N’), modelling the x-ray data only (‘X’), and modelling both neutron and x-ray diffraction data simultaneously (‘NX’). During most of the subsequent data analyses, the NX model will be taken as representative. Several sets of the intermolecular distances of closest approaches (‘cut-offs’) have been tried before selecting the final, most appropriate values; the best I–I cutoff for the HSMC calculations could be found only after RMC modelling of the x-ray data. Details (cut-off values, fnc tolerance limits) of the reverse Monte Carlo models are given by table 1. In each calculation, 10 000 atoms (2000, flexible-molecules) have been



**Figure 2.** Total structure factors for liquid  $\text{CH}_3\text{I}$ : experimental data (symbols) and RMC with fnc (solid line); HSMC with fnc (dotted line) are also shown.

put in cubic simulation boxes with an edge-length of about  $60 \text{ \AA}$ , thus achieving the atomic number density of liquid iodomethane of  $0.04385 \text{ \AA}^{-3}$ . All calculations were run for several million accepted moves, where the ratio of accepted/rejected moves varied between 1:3 and 1:10, i.e. typically several thousand accepted moves per atom.

#### 4. Results and discussion

Experimental, RMC and HSMC structure factors for liquid  $\text{CH}_3\text{I}$  (x-rays) and  $\text{CD}_3\text{I}$  (neutrons) are shown in figure 2. The fit to the neutron data is nearly perfect, even though the counting statistics during the measurement were far from optimal, due to the non-standard diffractometer setup (see [8]). Concerning the x-ray diffraction results, it should be noted that the curve is almost flat beyond about  $7 \text{ \AA}^{-1}$ , indicating that for iodomethane the molecular structure is only very weakly represented by this type of data (cf also figure 1).

It is interesting to note that the ‘neutron weighted’ total structure factor of the HS system is in rather close agreement with the measured neutron diffraction results, suggesting that most of the neutron data concern the molecular structure. This finding is in sharp contrast with the case of liquid carbon tetrachloride, where neutron data were not even in qualitative agreement with

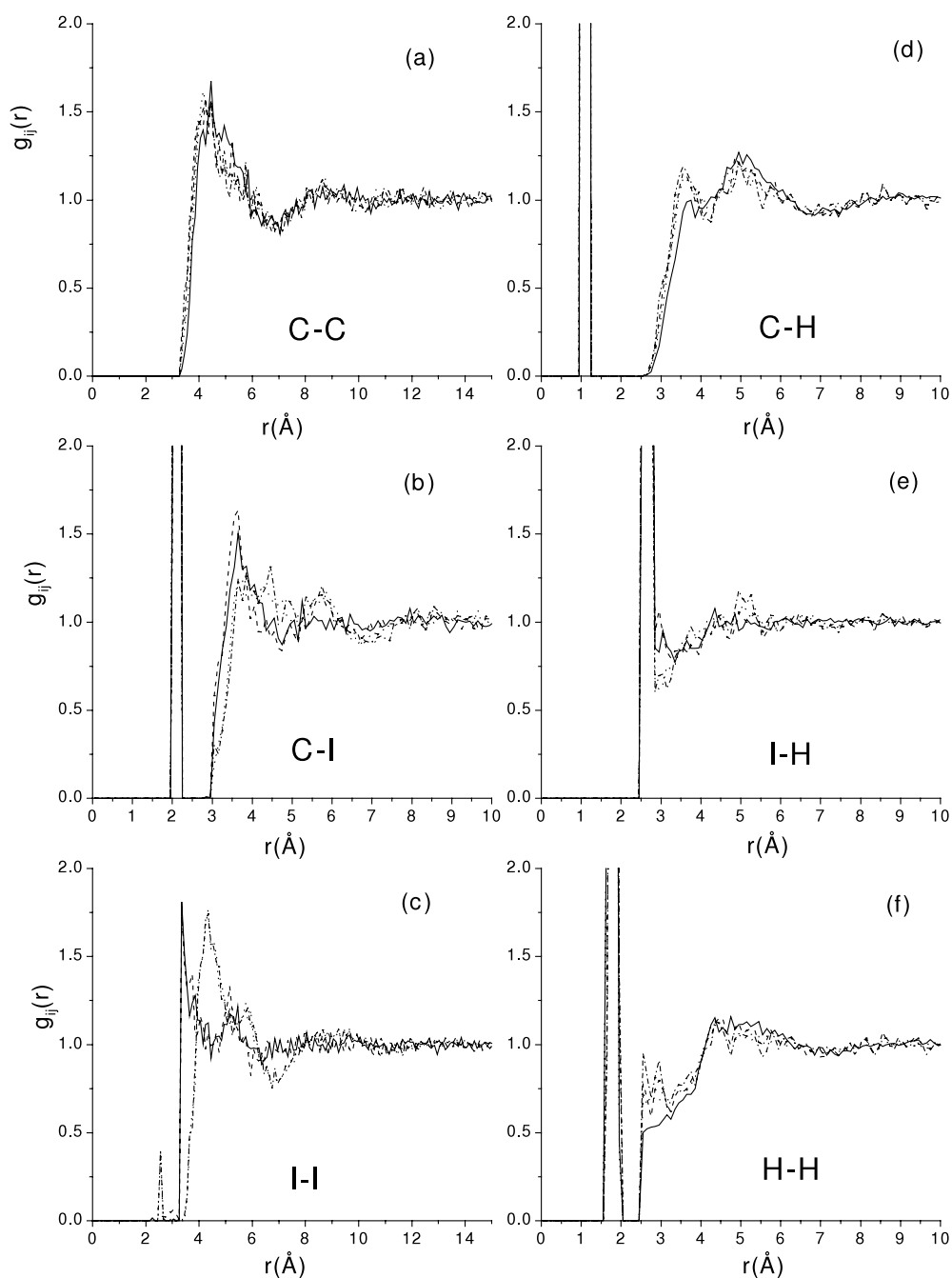
HSMC results, even though the molecular structure in that case is also weighted rather strongly by neutron diffraction results [2]. The ‘x-ray weighted’ tsf of the HS system, on the other hand, shows no resemblance to the corresponding experimental data; that is, regarding intermolecular correlations (to which I–I pair correlations may have a major contribution), neutron data are insufficient. This finding also emphasizes the need for extending the preliminary analyses of [8].

Partial radial distribution functions calculated directly from particle coordinates are shown in figure 3. Comparison with the reference system (see figure 3) shows an overall agreement between the HS and NX models, apart from the I–I pair correlations. For these latter, the—otherwise rather powerful—constraints of the excluded volume and molecular shape proved to be totally ineffective for estimating the intermolecular structure. As a result of adding the x-ray data, the shape of the I–I prdf became similar to that of the C–C prdf. The C–C prdf was estimated very well by the HS model, reflecting the fact that the C atom is the real (topological) centre of the molecule and, therefore, its position is determined by the positions of the ligands (in our case, of the three H atoms and the I atom). This is in agreement with previous findings [2–4] which pointed out that the determination of the centre–centre prdf in molecular liquids is possible when information on the ligand–ligand partial(s) can be sampled by diffraction measurements. The similarity between C–C and I–I prdfs suggests that C and I atoms share the central role within the molecules. This is not entirely surprising, taking into account the dumb-bell shape of the molecule; note, however, that if this behaviour was purely due to the molecular shape, then it should show up at the HSMC level, too.

Both the C–C and the I–I prdfs become flat beyond about 10 Å, which denotes the lack of longer-range correlations between molecular centres, found in liquid CCl<sub>4</sub> [2, 3]. This feature may be taken as the direct consequence of the molecules losing the perfect tetrahedral symmetry: the ‘sphericity’ of the molecules disappears and, with that, the long-range centre–centre ordering, too. It is worth noting that, in terms of these two prdfs, qualitative agreement is found with results of Gibbs ensemble Monte Carlo simulations that use a two-site model of the iodomethane molecule [15].

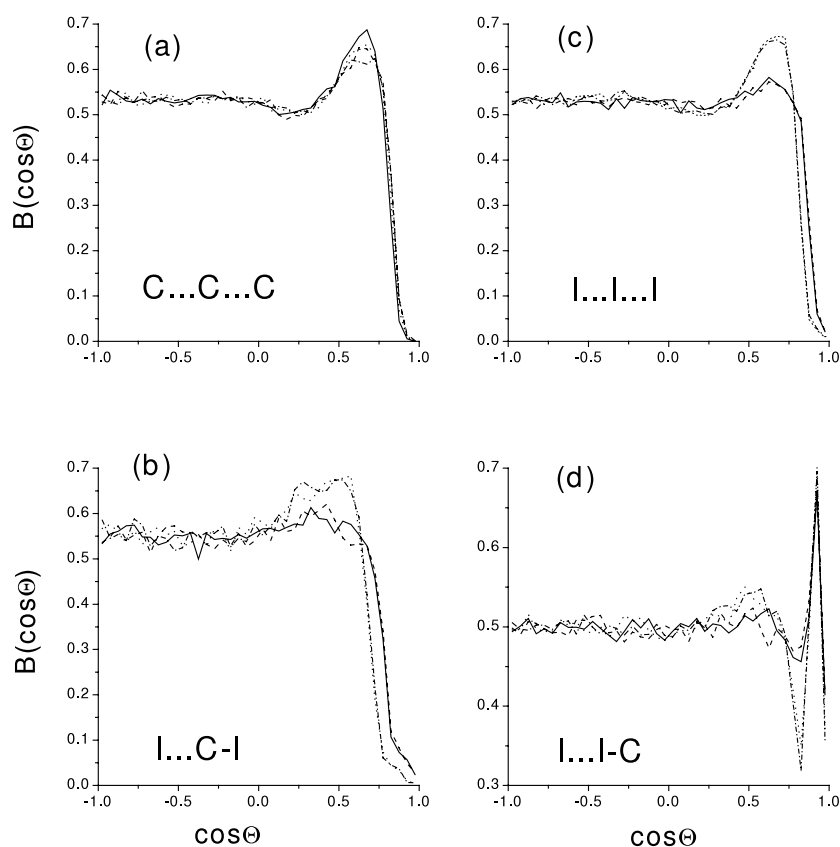
Apart from the I–I  $g(r)$ , no large deviations from the HS model can be detected in terms of the prdfs. However, a couple of small but significant alterations should be mentioned, of which the most visible is the formation of small extra peaks in the C–H and H–H prdfs, just above and just below 3 Å, respectively. These small maxima can be taken as indications of weak local correlations between methyl groups of neighbouring molecules. Finally, there is a tiny shift in terms of the position of the first intermolecular C–I peak, towards larger distances, which can be connected to the large change of the I–I prdf.

Some of the  $B(\cos \Theta_{ijk})$  (where  $i, j, k$  can be C, I or H) angular distribution functions, predominantly those containing the I–I distance, are shown in figure 4 for the four models considered in the present study. Angles have been defined by vectors joining a central atom with two of its neighbours (either intra- or intermolecular), within the first maximum of the corresponding prdf (i.e. within the first coordination shell). It is obvious that the introduction of the x-ray data, i.e. the precise knowledge of the I–I pair correlations, resulted in better defined (and in some cases, even altered) angular correlations. Angle distributions defined by C···C···C and I···I···I triplets look similar, as could be expected on the basis of the C–C and I–I prdfs, but with the I···I···I distribution peaking at a somewhat larger angle. The C···C···C distribution peaks at exactly 60°: the distribution of molecular centres seems to follow that of atoms in a simple liquid (cf, e.g., [16]). I···C–I angles exhibit an analogous behaviour to that of the I···I···I angles, which indicates that I atoms tend to surround C and I atoms in a similar fashion. The large peak in the I···I–C cosine distribution function near 0° shows that a constellation in which the intramolecular C–I axis point to the



**Figure 3.** Partial radial distribution functions of liquid iodomethane, resulting from hard sphere (solid line), neutron-only (dashed line), x-rays-only (dotted line) and neutron + x-ray (dash-dotted line) calculations: (a) C-C; (b) C-I; (c) I-I; (d) C-H; (e) I-H; (f) H-H. (Note that  $r$  axes for the I-I and C-C prdfs are the same, but different from the rest of the figure.)

I atom of a neighbouring molecule (see also figure 5) is a favourable one. Note that each angular distribution function displays a marked difference between HS and NX models: that is,



**Figure 4.** Angular distributions for liquid  $\text{CH}_3\text{I}$ , resulting from hard sphere (solid line), neutron-only (dashed line), x-rays-only (dotted line) and neutron + x-ray (dash-dotted line) calculations: (a)  $\text{C}\cdots\text{C}\cdots\text{C}$ ; (b)  $\text{I}\cdots\text{C}-\text{I}$ ; (c)  $\text{I}\cdots\text{I}\cdots\text{I}$ ; (d)  $\text{I}\cdots\text{I}-\text{C}$ . Dots between atoms mean purely intermolecular sections, whereas the hyphen denotes a possible intramolecular section.

orientational correlations between neighbouring molecules go well beyond those determined by the molecular shape and excluded volume effects only.

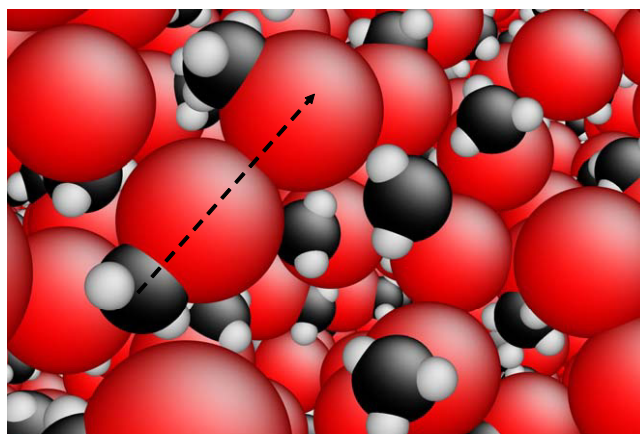
Figure 5 shows a small section of one of the particle configurations collected for the NX model (the picture was taken by the AtomEye software [17]). Some molecules in front display nicely the favourable configuration mentioned above; note that the definition of the  $\text{I}\cdots\text{I}-\text{C}$  triplets allows not only for  $\text{I}\cdots\text{I}$  but also for  $\text{I}\cdots\text{C}$  intermolecular ‘close’-contacts. It is also instructive to look at the picture just for gaining a sense of the excluded volume relations in liquid iodomethane, as the sizes of the balls are related to the covalent radii [18] of the atoms.

## 5. Conclusions

The structure of liquid iodomethane has not been studied before by x-ray diffraction. Here we provide total structure factors, as determined by x-ray diffraction, as well as partial structure factors and partial radial distribution functions calculated from RMC structural models, which are fully consistent with experimental data.

It is found that both the C atoms and the I atom can behave as the ‘centre’ of the  $\text{CH}_3\text{I}$  molecule: this phenomenon results in a quick decay of the molecule–molecule two-particle





**Figure 5.** Picture of a particle configuration corresponding to the NX model; the arrow indicates the favoured orientation of I and C atoms (see text). Big balls, I atoms; medium sized balls, C atoms; small balls, H atoms. (In colour: red, I atoms; black, C atoms; light grey, H atoms.)

(This figure is in colour only in the electronic version)

correlations. This appears to be a major difference compared to liquids containing molecules of perfect tetrahedral shape. Through the investigation of angular distributions containing the  $I \cdots I$  distance, a favoured arrangement of neighbouring molecules could be revealed, in which the C–I axis of a molecule and the I atom of a neighbour nearly lie on a straight line; this arrangement was also easy to detect visually. As a general remark, it is clear that orientational correlations in liquid iodomethane cannot be described by just molecular shape and excluded volume effects.

Finally, it is worthwhile emphasizing that starting from simple molecular liquids (containing molecules of regular shape) and moving step-by-step towards more complex molecular systems seems to be a rewarding strategy: by comparison with an earlier stage (that of carbon tetrachloride), minute details of the structure of liquid iodomethane can be understood.

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