The liquid-state structure of octafluoropropane and decafluoro-*n*-butane as determined by

neutron diffraction

The liquid-state structure of octafluoropropane and decafluoro-n-butane as determined by neutron diffraction

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Abstract. The liquid-state structures of octafluoropropane (perfluoropropane, R218) and decafluoro-n-butane (perfluorobutane) have been determined at 150 K, 250 K and 299 K using neutron scattering techniques. Analysis of the results has shown that there is no observable difference between the intramolecular structure of octafluoropropane observed in this work and that determined by electron diffraction. Noticeable intermolecular structure has been observed including a distinct peak at 0.320 nm that must be due to a close intermolecular F . . . F separation. Interpretation of the structure of decafluoro-n-butane has been hampered by the existence of more than one conformation at equilibrium. The close, intermolecular, F . . . F separation is clearly visible.

1. Introduction

Perfluorinated alkanes have been of interest for many years: their extremely inert behaviour has led to their use as solvents, and recently as medical tools—octafluoropropane is recognized as a useful liquid in the repair of detached retinas [1] and is also used in heart surgery [2]. Their physical properties have been of significant interest, in particular in terms of using the principle of corresponding states to predict properties along a homologous series [3]. In addition, the intramolecular structure of the fluorinated alkanes has been of interest because there are significant differences between the structures of a perfluoroalkane and the corresponding hydrogenated alkane. The strength of fluorine–fluorine repulsion results in a twisted *trans* structure being the most stable conformation (see figure 1) [4]. In addition, the same work predicts that a twisted *gauche* structure will exist with a lower energy than the corresponding *gauche* structure. For long-chain perfluoroalkanes, this twist generates a helix structure. In the extreme, polymerized fluorinated alkanes have physical properties that are very different from polymerized alkanes, due to the lack of the coiled forms that are created when large populations of *gauche* isomers occur [5, 6]. Finally, mixtures of alkanes with fully fluorinated alkanes are far from ideal, leading to an interest in the intermolecular forces between the different species [7].

In this paper, we report the liquid-state structure of octafluoropropane (C_3F_8) and decafluoro-n-butane (C_4F_{10}) as determined by neutron diffraction studies.

A considerable amount of work has been performed on the interpretation of the liquid-state structure of n-butane (C_4H_{10}) as measured by neutron diffraction [8]. The interpretation of these measurements was hampered by the existence of measurable populations of both the
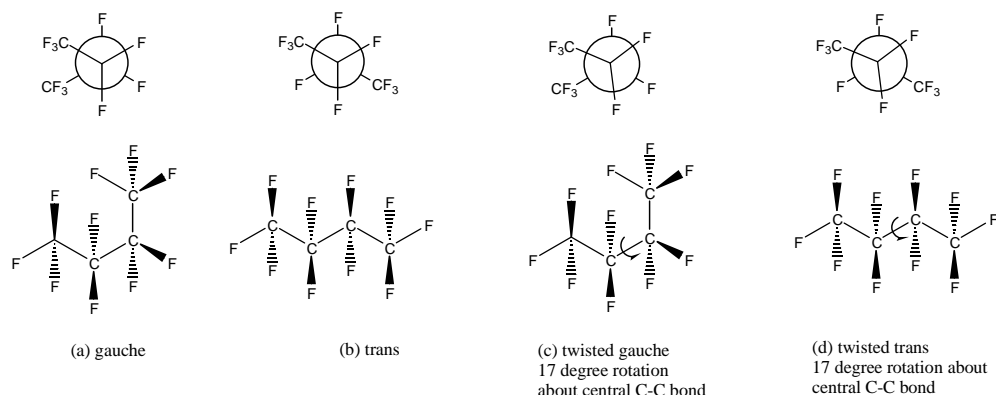
Figure 1. Possible conformations of a decafluoro-*n*-butane molecule. The twisted *trans* conformation is predicted to be the most stable [4].

gauche and *trans* isomers. In decafluoro-*n*-butane, it is predicted that the proportion of *gauche* isomers will be much smaller than in *n*-butane but the possible existence of a twisted *trans* and *gauche* conformation may introduce other complications. As a minimum, this work should demonstrate the feasibility of observing the various conformations in the liquid state.
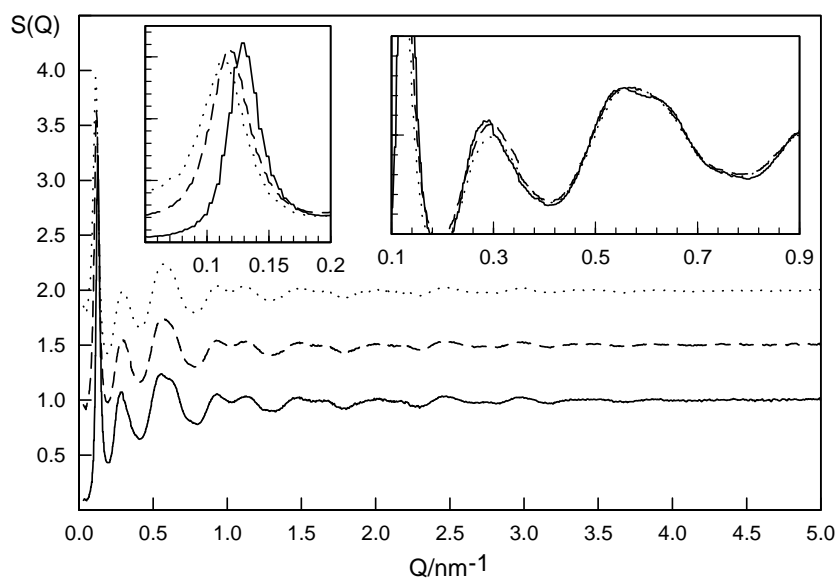
2. Experiment

Time-of-flight neutron-diffraction experiments were performed using the liquids and amorphous materials diffractometer (LAD) on the ISIS pulsed neutron source at the Rutherford Appleton Laboratory. Samples of C_3F_8 and C_4F_{10} were supplied by Fluorochem and had a stated purity of better than 99%. The fluids were contained in the same thin-walled pressure vessel as used in our previous work [9]. This cell was fabricated for Howe *et al* [10] and became part of the standard equipment available on the ISIS facility. Measurements were made on the coexisting liquid phases at three temperatures for each sample. (C_3F_8—149 K, 0.5 bar; 250 K, 8.0 bar; 299 K, 8.3 bar. C_4F_{10}—150 K, 0.7 bar; 249 K, 1.6 bar; 299 K, 2.8 bar.) The densities were taken from the published values for coexisting liquid densities [11–13]. For each run, neutrons were collected for a minimum of 1600 μA h. For all measurements, the temperature in the cell was kept constant to better than ± 0.1 K. To complete the series of experiments, spectra were also recorded for the empty cell, for the background with the cell removed and for a vanadium calibration rod.

3. Data reduction

The diffraction results were analysed using the standard package available on LAD [14]. In this way, due allowance was made for the contribution to the spectra from the background, from the empty cell, from multiple scattering and from inelastic scattering. Results from all the detector banks were merged to produce a final $S(Q)$ for each sample as illustrated in figures 2 and 3. In the main diagrams the measured $S(Q)$ at 250 K and 299 K have been increased by 0.1 and 0.2 respectively so that the variation in $S(Q)$ with temperature can be observed. Although variation is slight, the insets demonstrate that there is a significant difference between the results at differing temperatures for both octafluoropropane and decafluoro-*n*-butane.
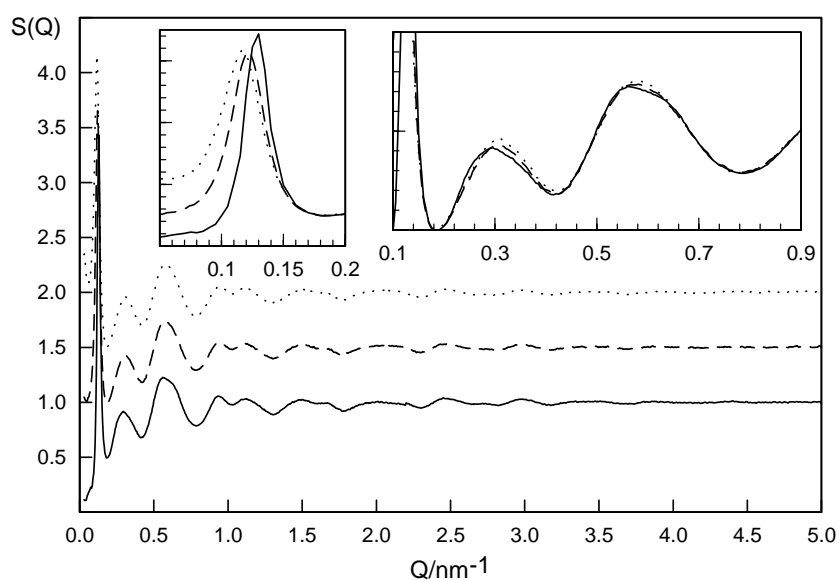
Figure 2. The total atomic structure factor $S(Q)$ of octafluoropropane at the three temperatures of the experiment. The insets illustrate the variation in the structure factor with temperature. In the main figures, the results at 250 K and 299 K have been offset by 0.5 and 1.0 respectively, so that the curves are more readily observed. ——: 150 K; - - - -: 250 K; · · · · · ·: 299 K.


Figure 3. The total atomic structure factor $S(Q)$ of decafluoro-*n*-butane at the three temperatures of the experiment. The insets illustrate the variation in the structure factor with temperature. In the main figures, the results at 250 K and 299 K have been offset by 0.5 and 1.0 respectively, so that the curves are more readily observed. ——: 150 K; - - - -: 250 K; · · · · · ·: 299 K.

The experimental $S(Q)$ were transformed to a pair distribution function $g(r)$ using MCGOFR [15]. In this method, $g(r)$ is calculated using a minimum information method
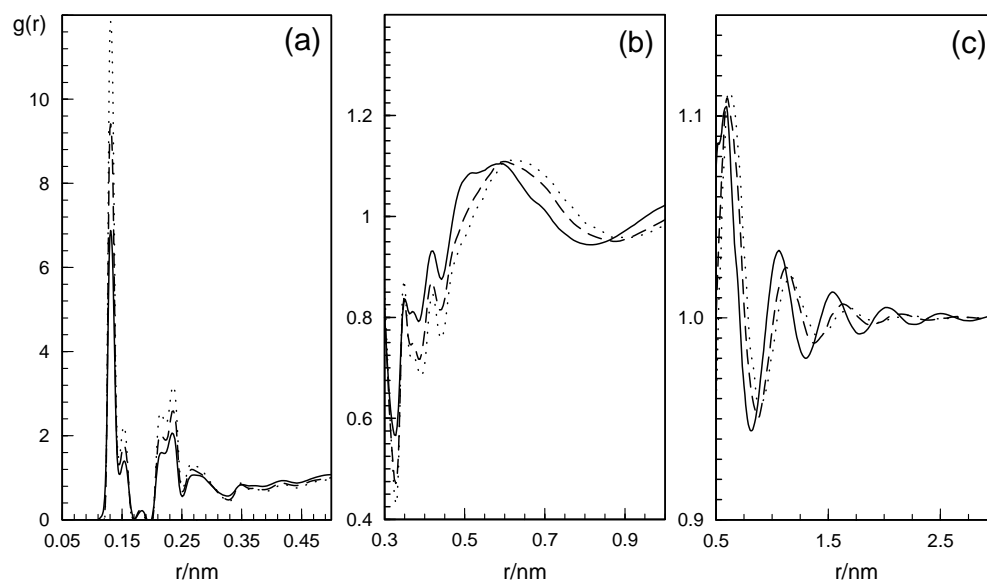
Figure 4. The total pair distribution function for octafluoropropane. (a) Intramolecular region; (b) first co-ordination shell, (c) long range order. ———: 150 K; - - - -: 250 K; ·····: 299 K.
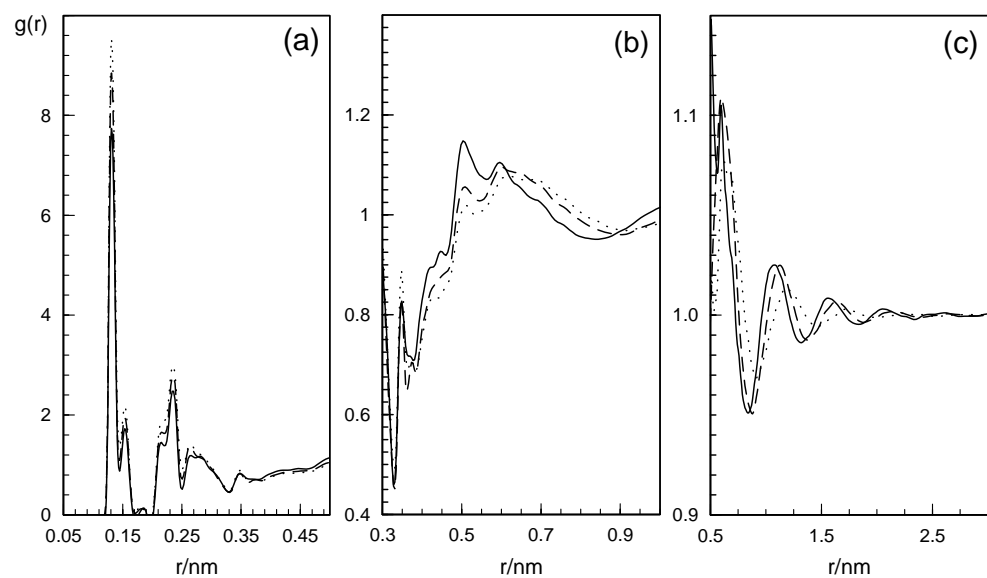
Figure 5. The total pair distribution function for decafluoro-*n*-butane. (a) Intramolecular region; (b) first co-ordination shell, (c) long range order. ———: 150 K; - - - -: 250 K; ·····: 299 K.

in which certain constraints can be incorporated. In particular, $g(r)$ was set to zero at $r < 0.095$ nm. The resulting pair distribution functions are illustrated in figures 4 and 5. Inspection of figures 4(a) and 5(a) shows that the intramolecular peaks below 0.5 nm are well defined. The first two peaks can be fitted to Gaussians to obtain the intramolecular C–F and C–C bond lengths. The next pair of peaks can be assigned to nearest neighbour F ... F and

C . . . F and can be determined by visual inspection. At higher separations, the peaks begin to overlap with the intermolecular structure as expected. However, two other observations can be made, first that that there is no free rotation about the C–C bond in either C_3F_8 or C_4F_{10} as demonstrated by the fact that the peaks at 0.35 nm and 0.42 nm are well separated, and second that there is a variation in the liquid-state structure of both of these molecules with temperature. The latter is most readily observed in the 0.3–1.0 nm region, as illustrated in figures 4(b) and 5(b).

4. Discussion

Inspection of the total pair distribution functions confirms that the bond lengths and nearest neighbour separations observed in liquid-state octafluoropropane and decafluoro-*n*-butane are the same, and, further, are not significantly different from the intramolecular separations obtained from electron diffraction studies of octafluoropropane in the gas phase [16]. However, unsurprisingly, the neutron results do not have sufficient resolution to be able to distinguish between the two types of C–F bond.

To analyse the intramolecular structure further, in particular to see whether there are any measurable contributions from the various conformations of decafluoro-*n*-butane, it is necessary to obtain further information from other sources. If intramolecular separations are obtained from gas phase data, the contributions to the total pair distribution function can be calculated and compared to the neutron diffraction data. Such a calculation has been completed for both octafluoropropane and decafluoro-*n*-butane. In this calculation, the total intramolecular pair distribution function was given by a suitably weighted sum of partial pair distribution functions using equation (1),

$$g(r) = \frac{N\sqrt{2\pi}}{8\pi^2 \rho r} \sum_{i \neq j} \frac{n_{ij} b_{ij} \exp[-(r - r_{ij}^2)/2\gamma_{ij}^2]}{r_{ij}\gamma_{ij}} \tag{1}$$

where r_{ij} is the intramolecular separation between atom i and atom j, γ_{ij} is the Debye–Waller factor which allows for the movement of the atoms in the molecule by assuming harmonic oscillation and n_{ij} is the number of interactions between atoms of type i and j. b_{ij} is the contribution to the neutron scattering length of the molecule from atoms i and j and is given by

$$b_{ij} = \frac{b_i b_j}{\left(\sum_i^{-1} b_i\right)^2}. \tag{2}$$

ρ is the atomic number density of the fluid and N is the number of atoms in the molecule.

4.1. Octafluoropropane

Table 1 gives the values of r_{ij} and γ_{ij} that were used for octafluoropropane. r_{ij} was taken from the gas-phase structure [16]; this also constrains the relative magnitude of the peaks. γ_{ij} was treated as an adjustable parameter; a correct value of γ_{ij} was considered to be the one which predicted peaks of the correct height in the liquid-state pair distribution function. Figure 7 illustrates the results of these calculations for the measurements at 300 K. The resulting total 'gas-phase' pair distribution function is compared with the 'liquid-state' structure in figure 7(a) and the difference between the two structures (assumed to be the intermolecular structure) is given in figure 7(b). It is clear that there is some well defined structure in the intermolecular liquid structure. The well defined structure occurs in the region where we would not expect

Table 1. The intramolecular structure of octafluoropropane. The atoms are identified in figure 6.

|	Structure used in this work		Gas-phase electron-diffraction structure [16]	
	r_{ij} (nm)	γ_{ij} (nm^{-1})	r_{ij} (nm)	γ_{ij} (nm^{-1})
C_2–F	0.132	0.58	0.132	0.44
C_1–F	0.132	0.58	0.134	0.44
C–C	0.154	0.65	0.155	0.56
F . . . F′	0.215	0.75	0.209	0.59
F_1 . . . F_2	0.215	0.75	0.217	0.59
C_1 . . . F_1	0.235	0.8	0.234	0.69
C_1 . . . F_2	0.235	0.8	0.235	0.69
C_2 . . . F	0.235	0.8	0.235	0.69
C_2 . . . C_2'	0.263	0.7	0.263	0.70
F_1 . . . F′	0.268	1.3	0.268	1.28
F_2 . . . F′	0.277	1.3	0.277	1.28
C_2 . . . F_2'	0.299	1.3	0.299	1.3
C_2 . . . F_1'	0.375	0.8	0.375	0.8
F_2 . . . F_3'	0.273	2.6	0.273	2.6
F_2 . . . F_2'	0.349	2.2	0.349	2.2
F_1 . . . F_2'	0.418	1.3	0.418	1.3
F_1 . . . F_1'	0.467	1.0	0.467	1.0
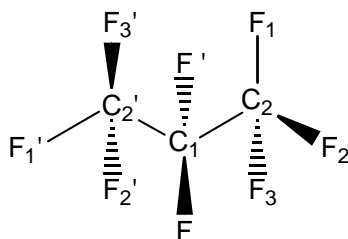
Figure 6. The intramolecular structure of octafluoropropane. The atoms are identified for table 1.

to observe any intramolecular structure. In particular there is a well defined peak at 0.320 nm which is not an artefact of the analysis. This separation is likely to be the closest approach of two fluorine atoms from different molecules.

A similar analysis was completed for octafluoropropane at all three temperatures; the resulting intermolecular structures are shown in figure 8. The variation in the first shell with temperature (and hence density) is well observed. More interestingly the additional intermolecular structure (in particular the peak at 0.320 nm) is less clearly defined at the low temperature than the high temperature. This interesting result may be worth exploring further.

4.2. Decafluoro-n-butane

Decafluoro-*n*-butane has not been studied by electron diffraction and so a gas-phase structure is not available. Instead, the geometry of octafluoropropane was used as a starting point for the analysis. Once again, γ_{ij} was used as an adjustable parameter. The analysis of the structure of decafluoro-*n*-butane is further complicated by the possibility of four different conformations, the *gauche*, the twisted *gauche*, the *trans* and the twisted *trans* structures. If the energy
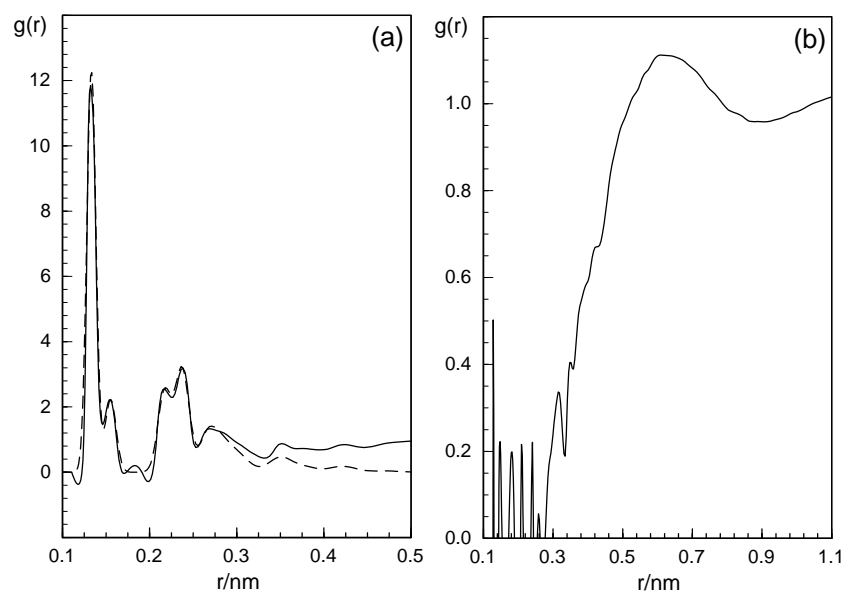
Figure 7. A comparison between the 'gas-phase' (dashed line) and liquid-phase (solid line) structures of octafluoropropane at 299 K. (a) The intramolecular region. (b) The gas-phase structure has been subtracted from the total liquid-state structure to obtain the intermolecular structure.
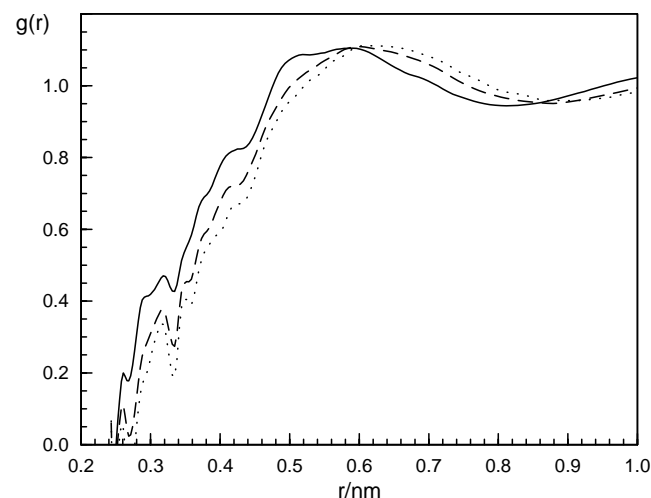
Figure 8. The intermolecular structure of octafluoropropane. ——: 150 K; - - - -: 250 K; ·····: 299 K.

separations predicted by Rothlisberger *et al* [4] are correct, then an equilibrium mixture at 150 K will consist of 71% twisted *trans*, 26% *trans* and 3% twisted *gauche*. This changes to 55% twisted *trans*, 33% *trans*, 10% twisted *gauche* and 2% *gauche* at 299 K. Fortunately, the majority of the intramolecular structure is common to all three conformations and also to octafluoropropane. The transferability of the common intramolecular structure between octafluoropropane and decafluoro-*n*-butane is illustrated in figure 9(a). The interatomic separations used for this part of the intramolecular structure are as given in table 1.
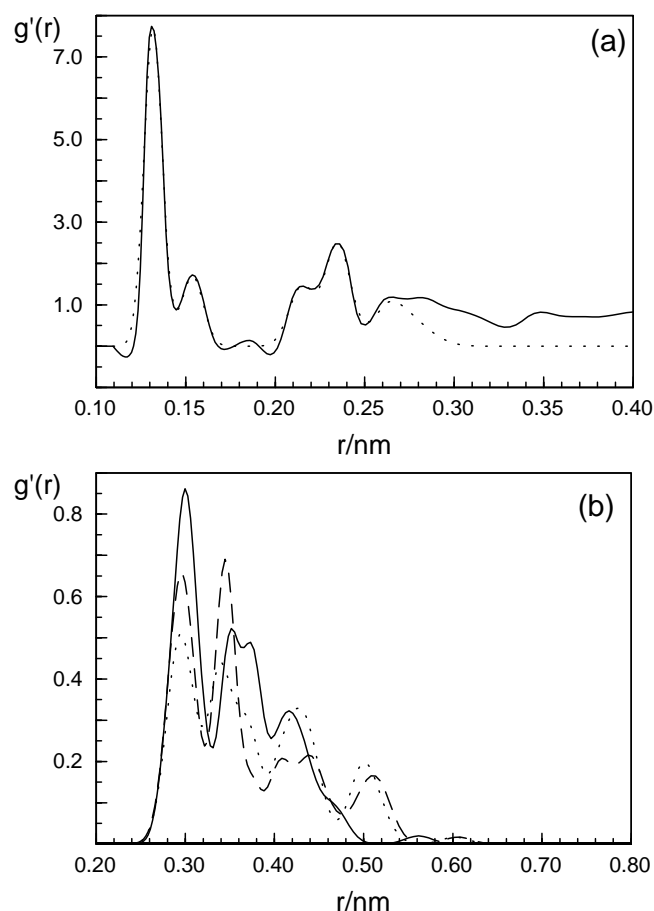
Figure 9. The predicted gas-phase structure of decafluoro-*n*-butane. (a) The measured total pair distribution function (solid line) is compared with the calculated pair distribution function (dotted line). This part of the pair distribution function does not depend on conformation. (b) The contributions to the total pair distribution function of decafluoro-*n*-butane that vary with conformation. Twisted *gauche* conformation (solid line), *trans* conformation (dashed line), and twisted trans conformation (dotted line).

Structure at separations greater than 0.27 nm is either due to intramolecular structure that depends on the conformation or due to intermolecular structure. The former is illustrated in figure 9(b) in which the contributions to the total pair distribution function at 150 K that are due to that part of the intramolecular structure which varies with conformation are plotted. In generating figure 9(b), the Debye–Waller factor has been assumed to be 1.5 nm^{-1} for all separations. Inspection of this figure suggests that, first, a peak at 0.425 nm would be due to the existence of *gauche* and twisted *trans* conformations but not *trans* conformations. Second, the existence of intramolecular structure at separations greater than 0.50 nm is either due to *trans* or twisted *trans*, but structure at separations greater that 0.52 nm must be due to straight *trans* conformations. Third, sharp peaks at 0.295 nm and 0.345 nm are due to the *trans* or twisted *trans* conformations, whereas peaks at 0.305 nm and 0.355 nm are due to *gauche* conformations. At equilibrium we would expect all three structures to be represented but would expect the majority to be either the *trans* or twisted *trans* structures. Further, as the temperature
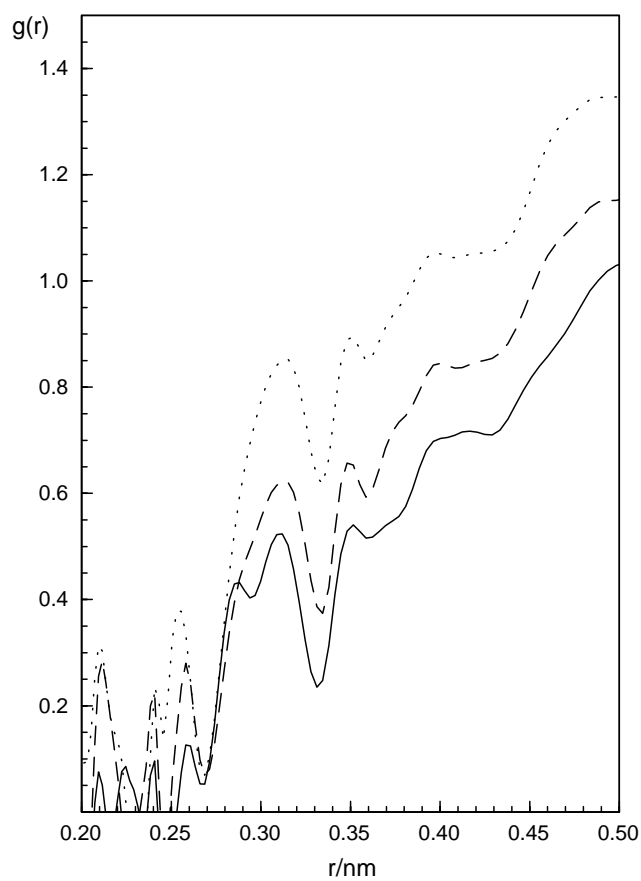
Figure 10. Possible short-range intermolecular structure of decafluoro-*n*-butane. The peak at 0.320 nm is also observed for octafluoropropane. Much of the remaining structure appears to vary with temperature and could be due to poor subtraction of the intramolecular structure. ——: 150 K; - - - -: 250 K; ·····: 299 K.

is reduced the proportion of twisted *trans* structure should increase. Inspection of figure 10 illustrates the difficulty in the analysis. This figure shows the predicted intermolecular structure of decafluoro-*n*-butane, if the analysis of the intramolecular structure described previously is correct. It is clear that, although the intermolecular peak at 0.320 nm is present at all temperatures, there is other visible structure which could be due to inter- or intramolecular structure and so the analysis of the intramolecular structure is inconclusive. Further analysis of the liquid-state structure of decafluoro-*n*-butane appears to be impossible without the use of another complementary technique such as reverse Monte Carlo [17] or empirical potential Monte Carlo simulation [18].

5. Conclusions

This work has demonstrated both the power of neutron diffraction measurements to measure the liquid-state structure and also some of its limitations. The structure of octafluoropropane has been well established and shows that there is well defined intermolecular structure in the liquid state of this molecule. The larger, decafluoro-*n*-butane molecule introduces many

more problems and in this case it is not possible to determine the intermolecular structure with any certainty. However, the analysis does show that there are similarities between the intermolecular structure of the two perfluoroalkanes studied in this work. Such a result is very important in the simulation of perfluoroalkanes.

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