

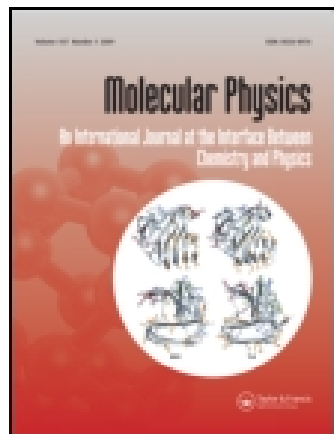
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Structural studies of liquid D-glycerol

M. Garawi^a, J.C. Dore^a & D.C. Champeney^b

^a Physics Laboratory, University of Kent, Canterbury, Kent, CT2 7NR, England

^b School of Maths and Physics, University of East Anglia, Norwich, NR4 7TJ, England

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Structural studies of liquid D-glycerol

II. Molecular conformation and long range correlations

by M. GARAWI and J. C. DORE

Physics Laboratory, University of Kent,
Canterbury, Kent CT2 7NR, England

and D. C. CHAMPENEY

School of Maths and Physics, University of East Anglia,
Norwich NR4 7TJ, England

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Neutron diffraction measurements are reported for D-glycerol at 293 K extending over a Q -value range up to 16 \AA^{-1} . Analysis of the molecular conformation yields improved values for the geometrical parameters compared with those obtained in an earlier study and enables a better estimate to be made of the systematic uncertainties arising from the analysis. The intermolecular distribution function shows local correlations due to hydrogen-bonding and long-range correlations due to molecular packing effects.

1. Introduction

Initial results for the structural characterization of liquid glycerol determined from neutron diffraction data were presented in an earlier paper [1]. The measurements were restricted to a Q -value range of $<12 \text{ \AA}^{-1}$ and although this enabled useful information to be extracted on temperature variation effects it did not enable precise values to be determined for the molecular conformation. The present measurements were made for a more extended Q -range in which the effects due to the inelasticity corrections are reduced.

Glycerol is an interesting material for detailed investigation since it is strongly hydrogen-bonded and readily passes through the super-cooled liquid phase to form a glassy solid. However, it is also a relatively complex molecule so that there are many partial pair-correlation functions contributing to the scattering cross-section. In spite of these difficulties it can be shown that careful analysis of the observations can yield valuable information on the spatial characteristics. Both X-ray [2] and neutron diffraction [1] data suggest that there is a relatively small change in the structural features with respect to temperature whereas other properties related to dynamic behaviour frequently show a very large variation.

2. Experimental procedure

The neutron diffraction experiments were made at room temperature with fully deuterated glycerol (isotopic enrichment >98 per cent) supplied by Merck, Sharp and Dohme. The basic procedure was similar to that of the earlier experiment [1] except that the diffractometer D4B at the Institut Laue-Langevin was used instead of D2. The recently re-constructed D4 diffractometer is mounted on a hot source and therefore has a high flux of short wavelength neutrons. In this case measurements were made with an incident beam of wavelength $0.694 \pm 0.002 \text{ \AA}$. A high

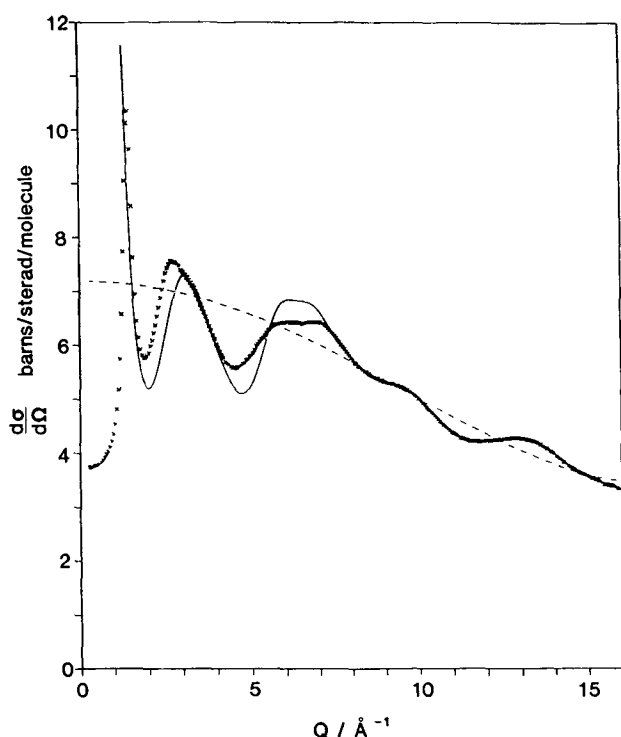


Figure 1. The differential scattering cross-section (\times) for D-glycerol at 293 K and the molecular form-factor fit (—).

statistical accuracy was obtained using the two multidetectors which were scanned to cover an angular range of $3\text{--}140^\circ$ corresponding to a Q -range of $0.2\text{--}16.0\text{ \AA}^{-1}$. After application of all the usual corrections [3] the differential cross-section was evaluated and is shown in figure 1.

3. Data analysis

(a) Theoretical formulation

The differential cross-section for coherent scattering may be related to the liquid structure factor $S_M(Q)$ which can be divided into intra- and inter-molecular contributions [4], i.e.

$$S_M(Q) = f_1(Q) + D_M(Q), \quad (3.1)$$

where $f_1(Q)$ is a molecular form factor and $D_M(Q)$ characterizes the liquid structure. The formulation of $f_1(Q)$ for glycerol is complicated due to the relatively large number of independent scattering centres. Details have been presented in the earlier paper [1] and are summarized in Appendix 1.

Subtraction of the intra-molecular contribution from the observed cross-section enables the $D_M(Q)$ function to be determined. The real-space pair correlation func-

tion can then be evaluated from the Fourier–Bessel transform relation

$$d_L(r) = 4\pi r \rho [\bar{g}(r) - 1] = \frac{2}{\pi} \int_0^\infty Q D_M(Q) \sin Qr \, dQ,$$

(3.2)

where ρ is the molecular number density and $\bar{g}(r)$ is a composite pair correlation function which depends on the relative concentrations and scattering lengths of the different nuclei.

(b) Analysis of high Q -value data

At high Q -values (typically $>10 \text{ \AA}^{-1}$) the contribution from inter-molecular terms is small and the diffraction pattern is primarily dependent on the molecular conformation. The oscillatory form of the diffraction pattern is superimposed on a monotonically-decreasing contribution from the self-terms in the expression for the cross-section. This fall-off in overall intensity is due to inelasticity effects and can be satisfactorily represented by an empirical relation using powers of Q (see Appendix 1); the constants in this expression are wavelength-dependent and must therefore be evaluated independently for the new observations. Since the neutron wavelength used in the present experiments is shorter than that of the previous study, the fall-off

Table 1. Parameter values for D-glycerol.

(a) Geometric parameters				
	Set			Others
	A	B	C	
r_{CC}	1.54(9)	1.52(2)	1.50(7)	1.54(5)
r_{CO}	1.36(6)	1.39(3)	1.41(4)	1.40
r_{CD}	1.09(0)	1.08(8)	1.10(3)	—
r_{OD}	1.11(3)	0.94(4)	1.00(2)	—
$\alpha \equiv C_2O_2D_5 = 108.3^\circ$				
$\beta \equiv C_1O_1D_1 = 107.3^\circ$ Fixed angles:				
$\gamma \equiv C_1C_2C_3 = 117.6^\circ$ $C_2C_1D_2 = D_2C_1D_3 = C_1C_2O_2 = \theta_T$				
where $\theta_T \cong 109.5^\circ$, $\phi = \theta = 0$ and $\psi = 180^\circ$				
(distances in \AA , angles in deg.)				
(b) Inelasticity parameters (Set C)				
$A = 3.66 \times 10^{-3} \text{ \AA}^2$ ($M_{\text{eff}} = 3.03 \text{ amu}$)				
$B = 6.41 \times 10^{-6} \text{ \AA}^4$				
(c) Displacement parameters, $\gamma/10^{-3} \text{ \AA}^2$				
	C_1C_2	0.64		
	C_1O_1	0.67		
	C_1D_2	2.3		
	O_1O_2	29		
	O_1D_1	5.6		
	C_1D_1	10.1		
	C_2O_1	5.4		
	D_2D_3	4.6		
	O_1D_2	3.8		
	D_2O_2	15		
	D_1D_2	20		
	C_2D_1	17		
	D_1D_4	42		

Table 2. $d_L(r)$ of D-Glycerol.

$R/\text{\AA}$	$d_L(r)$	$R/\text{\AA}$	$d_L(r)$	$R/\text{\AA}$	$d_L(r)$	$R/\text{\AA}$	$d_L(r)$	$R/\text{\AA}$	$d_L(r)$
0.00	0.0000	3.30	-0.0943	6.60	-0.0055	9.90	0.0081	13.20	0.0013
0.05	-0.0063	3.35	-0.0910	6.65	-0.0062	9.95	0.0079	13.25	0.0016
0.10	-0.0123	3.40	-0.0873	6.70	-0.0067	10.00	0.0077	13.30	0.0018
0.15	-0.0175	3.45	-0.0834	6.75	-0.0072	10.05	0.0075	13.35	0.0020
0.20	-0.0219	3.50	-0.0794	6.80	-0.0075	10.10	0.0072	13.40	0.0022
0.25	-0.0252	3.55	-0.0754	6.85	-0.0078	10.15	0.0069	13.45	0.0024
0.30	-0.0274	3.60	-0.0716	6.90	-0.0080	10.20	0.0066	13.50	0.0025
0.35	-0.0289	3.65	-0.0678	6.95	-0.0081	10.25	0.0062	13.55	0.0027
0.40	-0.0298	3.70	-0.0642	7.00	-0.0083	10.30	0.0058	13.60	0.0029
0.45	-0.0306	3.75	-0.0607	7.05	-0.0084	10.35	0.0053	13.65	0.0030
0.50	-0.0318	3.80	-0.0573	7.10	-0.0085	10.40	0.0048	13.70	0.0031
0.55	-0.0338	3.85	-0.0540	7.15	-0.0085	10.45	0.0043	13.75	0.0032
0.60	-0.0371	3.90	-0.0509	7.20	-0.0086	10.50	0.0038	13.80	0.0033
0.65	-0.0419	3.95	-0.0479	7.25	-0.0087	10.55	0.0033	13.85	0.0033
0.70	-0.0486	4.00	-0.0451	7.30	-0.0088	10.60	0.0028	13.90	0.0034
0.75	-0.0569	4.05	-0.0425	7.35	-0.0089	10.65	0.0025	13.95	0.0034
0.80	-0.0669	4.10	-0.0400	7.40	-0.0089	10.70	0.0021	14.00	0.0035
0.85	-0.0780	4.15	-0.0375	7.45	-0.0089	10.75	0.0018	14.05	0.0035
0.90	-0.0899	4.20	-0.0349	7.50	-0.0089	10.80	0.0014	14.10	0.0035
0.95	-0.1018	4.25	-0.0323	7.55	-0.0088	10.85	0.0010	14.15	0.0034
1.00	-0.1133	4.30	-0.0297	7.60	-0.0087	10.90	0.0006	14.20	0.0034
1.05	-0.1235	4.35	-0.0272	7.65	-0.0086	10.95	0.0001	14.25	0.0034
1.10	-0.1321	4.40	-0.0248	7.70	-0.0084	11.00	-0.0004	14.30	0.0034
1.15	-0.1386	4.45	-0.0227	7.75	-0.0082	11.05	-0.0009	14.35	0.0034
1.20	-0.1427	4.50	-0.0208	7.80	-0.0080	11.10	-0.0013	14.40	0.0034
1.25	-0.1444	4.55	-0.0190	7.85	-0.0077	11.15	-0.0017	14.45	0.0033
1.30	-0.1440	4.60	-0.0174	7.90	-0.0073	11.20	-0.0020	14.50	0.0032
1.35	-0.1418	4.65	-0.0156	7.95	-0.0069	11.25	-0.0023	14.55	0.0031
1.40	-0.1385	4.70	-0.0137	8.00	-0.0065	11.30	-0.0025	14.60	0.0029
1.45	-0.1347	4.75	-0.0116	8.05	-0.0060	11.35	-0.0028	14.65	0.0027
1.50	-0.1310	4.80	-0.0092	8.10	-0.0055	11.40	-0.0031	14.70	0.0025
1.55	-0.1282	4.85	-0.0066	8.15	-0.0050	11.45	-0.0033	14.75	0.0023

1.60	-0.1266	4.90	-0.0038	8.20	-0.0044	11.50	-0.0035	14.80	0.0021
1.65	-0.1268	4.95	-0.0008	8.25	-0.0038	11.55	-0.0037	14.85	0.0020
1.70	-0.1288	5.00	0.0022	8.30	-0.0032	11.60	-0.0039	14.90	0.0018
1.75	-0.1328	5.05	0.0051	8.35	-0.0027	11.65	-0.0041	14.95	0.0017
1.80	-0.1386	5.10	0.0079	8.40	-0.0022	11.70	-0.0043	15.00	0.0016
1.85	-0.1458	5.15	0.0104	8.45	-0.0018	11.75	-0.0044	15.05	0.0015
1.90	-0.1539	5.20	0.0124	8.50	-0.0015	11.80	-0.0045	15.10	0.0013
1.95	-0.1624	5.25	0.0140	8.55	-0.0011	11.85	-0.0046	15.15	0.0011
2.00	-0.1705	5.30	0.0149	8.60	-0.0007	11.90	-0.0046	15.20	0.0009
2.05	-0.1776	5.35	0.0152	8.65	-0.0002	11.95	-0.0045	15.25	0.0006
2.10	-0.1830	5.40	0.0149	8.70	0.0004	12.00	-0.0044	15.30	0.0003
2.15	-0.1862	5.45	0.0141	8.75	0.0010	12.05	-0.0044	15.35	0.0000
2.20	-0.1870	5.50	0.0130	8.80	0.0017	12.10	-0.0042	15.40	-0.0003
2.25	-0.1853	5.55	0.0117	8.85	0.0023	12.15	-0.0041	15.45	-0.0005
2.30	-0.1812	5.60	0.0104	8.90	0.0030	12.20	-0.0040	15.50	-0.0007
2.35	-0.1750	5.65	0.0093	8.95	0.0036	12.25	-0.0038	15.55	-0.0008
2.40	-0.1673	5.70	0.0085	9.00	0.0042	12.30	-0.0036	15.60	-0.0009
2.45	-0.1586	5.75	0.0080	9.05	0.0047	12.35	-0.0034	15.65	-0.0010
2.50	-0.1494	5.80	0.0077	9.10	0.0052	12.40	-0.0031	15.70	-0.0011
2.55	-0.1403	5.85	0.0075	9.15	0.0057	12.45	-0.0029	15.75	-0.0012
2.60	-0.1315	5.90	0.0073	9.20	0.0061	12.50	-0.0027	15.80	-0.0013
2.65	-0.1236	5.95	0.0070	9.25	0.0064	12.55	-0.0025	15.85	-0.0014
2.70	-0.1167	6.00	0.0064	9.30	0.0067	12.60	-0.0022	15.90	-0.0015
2.75	-0.1111	6.05	0.0057	9.35	0.0070	12.65	-0.0020	15.95	-0.0017
2.80	-0.1067	6.10	0.0047	9.40	0.0072	12.70	-0.0018		
2.85	-0.1037	6.15	0.0036	9.45	0.0074	12.75	-0.0016		
2.90	-0.1017	6.20	0.0025	9.50	0.0077	12.80	-0.0014		
2.95	-0.1008	6.25	0.0014	9.55	0.0079	12.85	-0.0012		
3.00	-0.1004	6.30	0.0003	9.60	0.0080	12.90	-0.0010		
3.05	-0.1004	6.35	-0.0008	9.65	0.0081	12.95	-0.0007		
3.10	-0.1003	6.40	-0.0018	9.70	0.0082	13.00	-0.0003		
3.15	-0.0999	6.45	-0.0028	9.75	0.0082	13.05	0.0000		
3.20	-0.0988	6.50	-0.0038	9.80	0.0082	13.10	0.0005		
3.25	-0.0969	6.55	-0.0047	9.85	0.0082	13.15	0.0009		

is reduced although it is still necessary to determine the shape accurately if precise values of the geometrical parameters are to be extracted from the observations. In the present analysis an iterative procedure is used to optimize the parameters defining the contribution from the self-terms and this permits a consistency check to be applied to the data which gives an indication of the magnitude of systematic errors.

The parameters obtained in the earlier study (set *A*) were used as a starting point in the fitting routine for the new data. It was soon apparent that the oscillatory structure above 12 \AA^{-1} was not well represented by the previous parameter values. Using a low- Q cut-off of 7 \AA^{-1} a χ^2 -fitting routine was used to re-optimize all of the parameter values and the revised values (set *B*) are given in table 1. This parameter set gives a much improved fit to the data over the whole range; the fitted curve is shown superimposed on the experimental cross-section values in figure 1. In the analysis procedure there are geometric parameters (bond-lengths and angles; r_{CC} , α etc.) nuclear parameters (scaling and inelasticity; K , A , B) and Debye–Waller factors (γ) defining the vibrational properties of the molecule. The majority of the vibrational parameters have a small individual effect on the overall fit and are therefore not well-defined by the constraints of the experimental observations. In these circumstances the fitting procedure can lead to unphysical values and some consistency must be imposed on the relative magnitudes. This restriction required the adjustment of the γ -values before the final stages of fitting so that the smallest γ -values applying to the short bond-lengths were retained for optimization and the parameters defining non-bonded distances evaluated approximately from a quadrature application across the intermediate bonds. This procedure did not lead to any worsening of the fit and the final stages of optimization were made with 13 independent parameters.

During the optimization process it was noted that the latest compilation of coherent scattering lengths due to Sears [5] differed slightly from those being used. Although the changes were only at the < 1 per cent it was found that the new values had a significant effect on the fit and it was possible to reduce the optimized χ^2 -value by a further 30 per cent without substantially changing the main parameter values. The final fit to the experimental data gave the parameter values listed in table 2 Set *C* and is not visually distinguishable from that given in figure 1.

The extrapolation of the curve to lower Q -values enables the inter-molecular component, $D_{\text{M}}(Q)$, to be extracted and this curve is shown in figure 2. The corre-

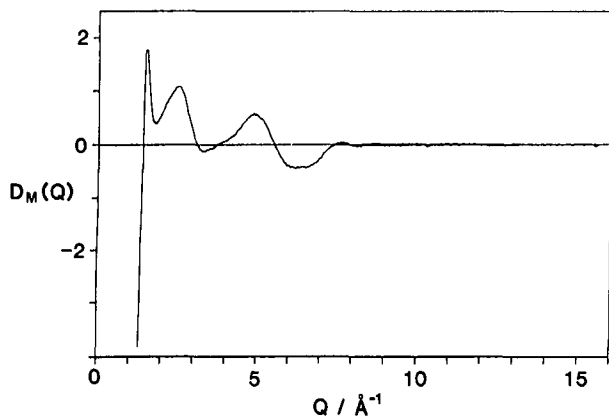


Figure 2. The inter-molecular function, $D_{\text{M}}(Q)$, for D-glycerol obtained from figure 1.

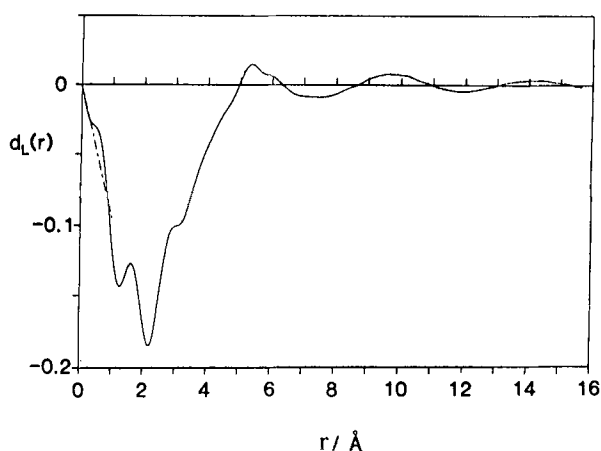


Figure 3. The intermolecular distribution function $d_L(r)$ obtained from figure 2.

sponding pair correlation function, $d_L(r)$ was evaluated from the transform relation (equation 3.2) and is shown in figure 3: a list of the data is given in table 2. It is clear from figure 2 that the subtraction of the self-terms is under-estimated in the low Q -region by the extrapolation of the fitted intra-molecular cross-section curve and is responsible for the unphysical oscillatory behaviour of the $d_L(r)$ curve at low r -values. This systematic error arises naturally from the difficulty in defining the detailed form of the self-term component of the cross-section due to the relatively large magnitude of the overall fall-off in intensity arising from the inelasticity corrections. This behaviour is a common problem in the analysis of materials containing light atoms such as hydrogen or deuterium and is discussed fully in § 4(c).

4. Discussion

(a) Comparison with other results

The refinement of the fitting procedure and the use of a wider Q -range reveals more information about the molecular conformation than was obtained from the previous analysis [1]. It is clear from the present results that it is not necessary to introduce a skew distortion to the molecule and a satisfactory fit is obtained for a symmetric structure. Furthermore the γ -values for large distances are better defined and this removes some of the sharp features observed in the inter-molecular $d_L(r)$ function (figure 3) for distances greater than 4 Å. There are some changes in the parameters defining the bondlengths but the predominant r_{CD} bond remains virtually unchanged at 1.10 Å in excellent agreement with the generally accepted values of 1.09–1.11 Å. There is a reduction in r_{OD} from the unphysical value of 1.11–1.00 Å. This general contraction of the skeletal nature of the molecule is complemented by an increase in r_{CO} from 1.37 to 1.41 Å which is also in keeping with values obtained from other sources.

(b) Resolution effects

The use of a many-parameter fitting routine can, in some circumstances, obscure the physical nature of the problem under consideration. It is therefore instructive to examine the relation between the real-space representation in the form of $d_M(r)$ and

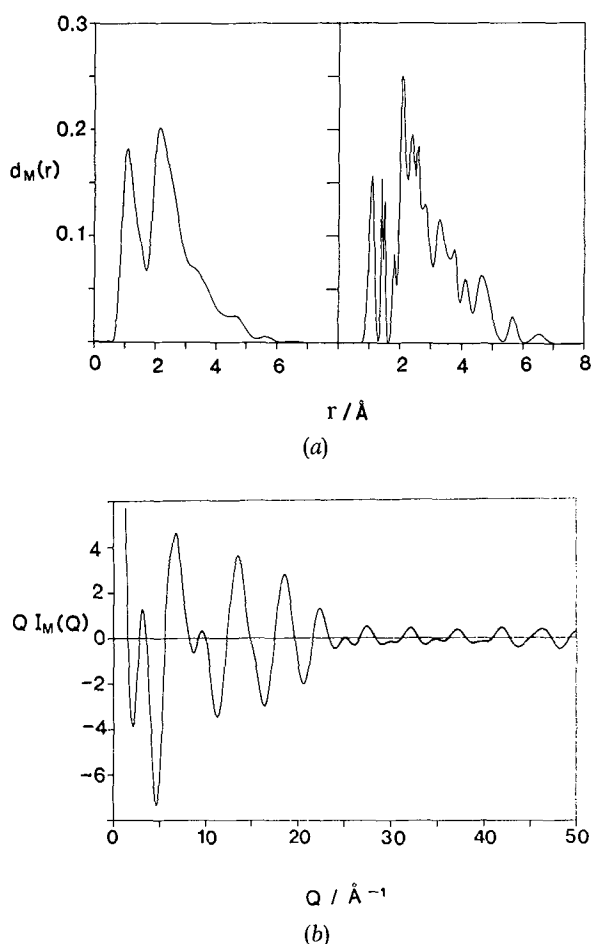


Figure 4. The effects of a finite Q -range in the observations; (a) the intra-molecular distribution function $d_M(r)$ evaluated from the fitted parameters (table 2) using a Q_M -value of 16\AA^{-1} and ∞ ; (b) the full (extrapolated) intra-molecular interference function, $Q I_M(Q)$.

the form-factor, $f_1(Q)$. Using the parameter values of table 2 it is possible to show the real-space distribution function for the intra-molecular terms corresponding to the limit of the experimental value (16\AA^{-1}) or for an unrestricted range (i.e. $Q_m \rightarrow \infty$). The resulting curves are given in figure 4(a), showing the loss of spatial resolution arising from the limited Q -range. The curve given in figure 4(b) for $Q I_M(Q)$ indicates that the oscillatory structure extends to $\sim 30 \text{\AA}^{-1}$ so that measurements over a wider range would help to define the parameter values even more accurately. This type of study should soon be possible using pulsed neutron techniques such as with the LAD instrument [6] on the Spallation Neutron Source at the Rutherford Appleton Laboratory.

(c) Separation of intra- and inter-molecular terms

It is clear from figures 1 and 2 that the $D_M(Q)$ function has an oscillatory structure which should probably extend beyond the cut-off point, at 7\AA^{-1} . In this sense the measured data are 'over-fitted' and the residual contribution from the intermolecular terms has effectively been incorporated into the fitting routine for

$f_1(Q)$. Since glycerol is a relatively large molecule it is inevitable that there will be problems in separating intra- and inter-molecular contributions corresponding to the 2–5 Å range. The choice of 7 Å^{-1} for the cut-off is a compromise in the Q -range and means that the intra-molecular terms for large distances across the molecule do not make a significant contribution to the $f_1(Q)$ function for the range of interest. The inter-relationship of the two separate components is illustrated in figure 5 where the total $d(r)$ function is compared with $d_L(r)$ for a Q_m value of 16 Å^{-1} . It is easy to see that the shape of the $d_L(r)$ curve in the range 2–5 Å is strongly influenced by the parameters defining the molecular information. However, the emergence of an inter-molecular hydrogen-bond peak at $\sim 1.8 \text{ Å}$ from this subtraction emphasizes that this type of analysis does reveal detailed inter-molecular structure over shorter distances and the regular oscillatory behaviour beyond 6 Å is also clearly defined with a periodicity of 4.6 Å. The higher statistical accuracy of the present results and

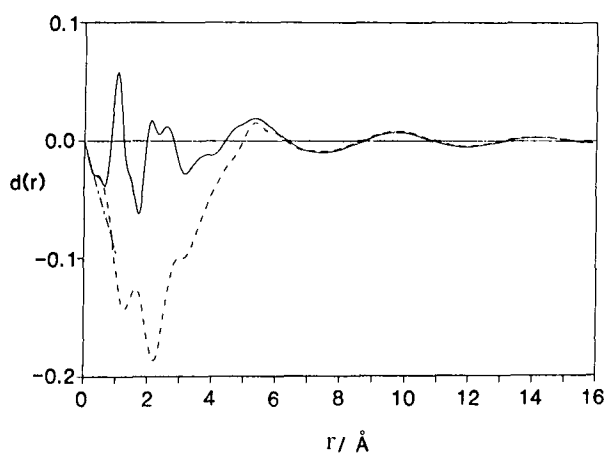


Figure 5. A comparison of the total $d(r)$ function for glycerol (—) with that for the inter-molecular $d_L(r)$ function (---) showing the removal of the intra-molecular contribution.

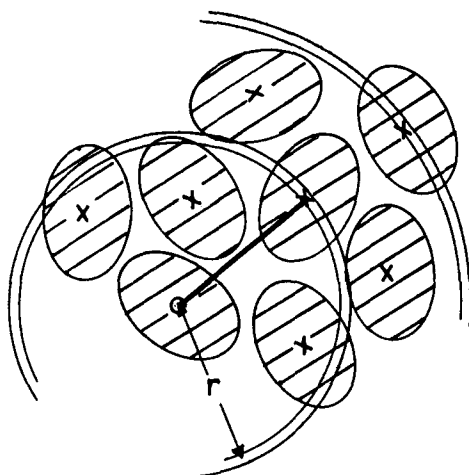


Figure 6. A schematic representation of the centres correlation function $g_c(r)$ for large molecules.

the increased truncation value leads to a much smoother curve than that obtained in the earlier measurement [1].

(d) *Inter-molecular features*

The improved fit to the intra-molecular terms does not have a large effect on the $d_L(r)$ function and the results confirm the general observations of the previous experiment. The liquid is therefore seen to be largely composed of a hydrogen-bonded network in which there are significant local inter-molecular correlations. The detailed orientational relationships cannot be deduced from the present results although further information could, in principle, be obtained from selective H/D isotopic substitution in a similar manner to that used in studies of liquid methanol [7]. The interest therefore focuses on the long range behaviour (~ 10 – 20 Å) where the specific ordering effects of the local hydrogen-bonding are less effective. At distances that are sufficiently large compared with the intermolecular distance of approximately 5 Å, the orientational correlation between molecules arising from hydrogen-bonding will be lost, and it is possible to regard the correlations in terms of the distribution of molecular centres. In this approximation the effective total pair correlation will approximate to a convolution of the centres correlation function $g_c(r)$ with an appropriately defined molecular scattering function $f_M(r)$, which becomes

$$d_L(r) = 4\pi r \rho \{ [g_c(r) - 1] * f_M(r) \} \quad (4.1)$$

at large enough r , where $*$ represents a three-dimensional convolution in r -space. The function $f_M(r)$, which is defined in Appendix 2, is radially symmetric and extends to distances comparable with the dimensions of the molecule so that, at large r , the oscillations in $d_L(r)$ simply reflect those in $g_c(r)$. An extrapolation of the $d_L(r)$ curve, figure 5, implies a main peak in the centres correlation function at about 5 Å, which would be expected from the overall dimensions of the molecule. A more detailed examination of these features using the formalism presented in Appendix 2 will be given later.

5. Conclusions

Neutron diffraction techniques have been used extensively to provide detailed structural information for simple liquids in which it is often possible to extract partial pair correlation functions. The investigation of liquid glycerol represents a huge increase in complexity such that the conventional representation as a sum of partial functions is less appropriate. The work presented in this paper shows that useful information can be obtained even in this situation provided care is taken to characterize the molecular scattering function by measurements over a suitably wide Q -range. The separation of intra- and inter-molecular contributions is possible and can readily reveal strong local correlation such as hydrogen bonds. Some residual structure in the intermediate range (2–6 Å) is often observed but the interpretation of peak positions must be treated with caution. At larger distances (> 10 Å) another type of simplification occurs such that the observed spatial distribution function can be conveniently related to the distribution of molecular centres. The successful treatment of the glycerol data indicates that neutron diffraction techniques can be applied to large organic molecules that may have specific local interactions such as hydrogen-bonds. This opens the field to a wide range of materials which have previously been regarded as too complex for detailed investigation. A combination of this approach with the use of a difference function analysis for H/D isotopic

substitution and complementary X-ray information should enable a more detailed study of the torsional effects arising from the flexibility of the molecular backbone to be conducted.

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Appendix 1

Conformation and neutron scattering by the D-glycerol molecule

The basic conformation of the D-glycerol molecule is shown in figure A 1. There are four bondlengths r_{CC} , r_{CD} , r_{CO} and r_{OD} with three significant bond angles α , β and γ ; it is assumed that the \widehat{CCC} , \widehat{CCD} and \widehat{DCD} angles for the methyl and methylene groups are tetrahedral.

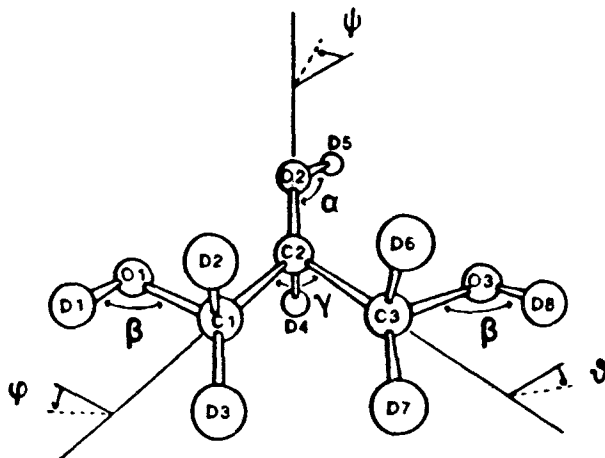


Figure A 1. Conformation of the glycerol molecule showing the parameters defining bond-lengths and angles.

The observed cross-section for scattering from the isolated molecule can be written as a sum of three terms arising from coherent self ($i=j$), incoherent and coherent distinct ($i \neq j$) terms, i.e.

$$\left(\frac{d\sigma}{d\Omega}\right)^{\text{obs}} = \left(\frac{d\sigma}{d\Omega}\right)_{\text{coh}, i=j} + \left(\frac{d\sigma}{d\Omega}\right)_{\text{incoh}} + \left(\frac{d\sigma}{d\Omega}\right)_{\text{coh}, i \neq j}.$$

The first two terms are both due to self-scattering and may be written, for D-glycerol, as

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{self}} = \left\{ 3b_C^2 + 3b_O^2 + 8b_D^2 + 8\left(\frac{\sigma_D}{4\pi}\right) \right\} (1 - AQ^2 + BQ^4),$$

where the second bracket represents the effects of inelasticity. The corresponding distinct, or interference, term involves a sum over all pairs of nuclei in each molecule

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{int}} = \sum_{i \neq j} b_i b_j \frac{\sin Qr_{ij}}{Qr_{ij}} \exp(-\gamma_{ij} Q^2)$$

and consists of 91 independent terms. The γ_{ij} values are related to mean square deviations for the corresponding separations and will include both vibrational and librational (torsional) displacements; these parameter values become larger as the distance between the centres is increased. In the previous analysis a skew displacement of the central OD-group was allowed but the analysis of the present data shows that this asymmetry is not required to obtain a satisfactory fit to the observations. Under these circumstances some simplification of the formulation is obtained by setting $\theta = \phi = 0$ and $\psi = 180$; the total number of terms then reduces to 60.

Appendix 2

The inter-relation between $\bar{g}(\mathbf{r})$ and $g_c(\mathbf{r})$ (equation (4.1)).

The experimental measurements yield the composite pair correlation function $\bar{g}(\mathbf{r})$ but it is convenient to define the long-range behaviour in terms of the correlation function for molecular centres, $g_c(\mathbf{r})$. A point C is chosen within the glycerol molecule to act as its centre which could be the centre of mass or a chosen central atom since the formalism is insensitive to the actual position of C . The individual sites within the molecule are labelled by the index i (or j) = 1 to N where N is the number of atoms; in the case of glycerol, $N = 14$. For an arbitrary molecule, with arbitrary orientation, (figure 6), the probability of finding nucleus i within the volume element dV at distance \mathbf{r} from the molecular centre is $p_i(\mathbf{r}) dV$. In a rigid molecule $p_i(\mathbf{r})$ will be zero except on a spherical shell whose radius is equal to the distance of the nucleus from the molecule centre, but in a flexible molecule $p_i(\mathbf{r})$ will be smoothed out into a continuous function of \mathbf{r} . If $g_{ij}(\mathbf{r})$ is the partial intermolecular correlation function for nuclei i and j in different molecules, and if $g_c(\mathbf{r})$ is the pair correlation function for molecule centres, then for statistically-independent molecular orientations it follows from simple probability theory that

$$g_{ij}(\mathbf{r}) = g_c(\mathbf{r}) * p_i(-\mathbf{r}) * p_j(\mathbf{r}), \quad (\text{A } 1)$$

where $*$ represents a convolution in \mathbf{r} -space. Since the average intermolecular pair correlation $\bar{g}(\mathbf{r})$ is related to the $g_{ij}(\mathbf{r})$ through

$$\bar{g}(\mathbf{r}) = \left[\sum_{i=1}^N b_i \right]^{-2} \sum_{i=1}^N \sum_{j=1}^N b_i b_j g_{ij}(\mathbf{r}) \quad (\text{A } 2)$$

it follows that

$$\bar{g}(\mathbf{r}) = g_c(\mathbf{r}) * f_M(\mathbf{r}), \quad (\text{A } 3)$$

where $f_M(\mathbf{r})$ is defined by

$$f_M(\mathbf{r}) = \left[\sum_{i=1}^N b_i \right]^{-2} \sum_{i=1}^N \sum_{j=1}^N b_i b_j [p_i(-\mathbf{r}) * p_j(\mathbf{r})]. \quad (\text{A } 4)$$

Equation (4.1) follows on combining equation (3.2) with equation (A 3) and utilizing the fact that $f_M(\mathbf{r})$ integrates, over all \mathbf{r} , to unity.

There is some convenience to working in Q -space when, assuming radially symmetric functions, we introduce the function $F_M(Q)$ as the Fourier-Bessel transform of

$f_M(r)$, i.e.

$$QF_M(Q) = 4\pi \int_0^\infty r f_M(r) \sin Qr \, dr \quad (\text{A } 5)$$

and also, from standard relations,

$$QD_c(Q) = 4\pi \int_0^\infty \rho r [g_c(r) - 1] \sin Qr \, dr, \quad (\text{A } 6)$$

where $D_c(Q)$ is the intermolecular function for molecular centres. It then follows that

$$d_L(r) = \frac{2}{\pi} \int_0^\infty Q D_c(Q) F_M(Q) \sin Qr \, dQ \quad (\text{A } 7)$$

at sufficiently large r -values.

For a rigid molecule $F_M(Q)$ can be evaluated using equations (A 4) and (A 5) and is given by

$$F_M(Q) = \left| \frac{\sum_{i=1}^N b_i j_0(QR_i)}{\sum_{i=1}^N b_i} \right|^2, \quad (\text{A } 8)$$

where $j_0(x)$ is the zero order spherical Bessel function, $j_0(x) = x^{-1} \sin x$, and R_i is the distance of nucleus i from the molecular centre.

In the case of the glycerol molecule the contribution from the 14 atoms (C, D and O) which have similar scattering amplitudes, leads to the production of a diffuse form for $f_M(r)$ which does not possess much detailed structure and therefore the behaviour of $d_L(r)$ at large r is primarily representative of the distribution function for molecular centres, $g_c(r)$. Further work on the use of this formalism will be presented in a separate publication.

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