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Structure and allied properties of liquid carbondisulphide

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Abstract. Orientational model for liquid CS_2 has been reviewed and shown that proper selection of centre structure produces molecular structure factors comparable with reference interaction site model (RISM) for both *x*-ray and neutron data even with the parallel alignment suggested by Suzuki and Egelstaff. With this justification of orientational model next centre structure factors were calculated from measured structure data and therefrom obtained various correlation functions including the pair potential and partial structures.

Keywords. Orientational correlation; centre structure: atomic scattering; coherent scattering length; partial structure.

1. Introduction

In molecular liquids orientational correlations are strongly exhibited (Powles 1973; Egelstaff *et al* 1971; Clarke *et al* 1976). Suzuki and Egelstaff (1974) interpreted their neutron results on CS_2 using hard core model which shows how orientational model can be used to study the possible correlations. Lowden and Chandler (1974) used reference interaction site model (RISM) to interpret the neutron diffraction results. Sandler and Narten (1976) also used RISM to interpret their x-ray diffraction results. In this paper we show that comparable agreement with neutron and x-ray diffraction results can be obtained through the orientational model approach by proper selection of centre structure function even with the parallel alignment suggested by Suzuki and Egelstaff (1974). Our studies on other linear molecules N_2, O_2 (Gopala Rao and Joarder 1979) and CSe_2 (Gopala Rao and Joarder 1980) support this view. Since the parallel alignment gives a good agreement for both neutron and x-ray diffraction data we have used this orientational form factor to obtain from experimental data the centre structure factor and therefrom centre radial distribution function (CRDF), centre direct correlation function (CDCF), intermolecular potential energy function and finally partial structures in CS_2.

2. Theory

The molecular structure factor $S_m(Q)$ can be written as

$$S_m(Q) = N_m^{-1}(\Sigma b_i)^{-2} \langle \sum_{i,j} b_i b_j \exp(i\vec{Q} \cdot \vec{r}_{ij}) \rangle \tag{1}$$

where N_m is the number of molecules in the sample, b_i the mean coherent scattering length of nucleus i in neutron measurements. In the case of x-rays they are atomic scattering functions being functions of wave vector Q, the angular brackets indicate the time average and $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$ is the vector distance between the nuclei i and j.

It is convenient to separate the terms in the summation so that the nuclei in a molecule constitute a unit each with an appropriate form factor $F_1(Q)$ and all vectors $\vec{r}_{ij}$ are then referred to molecular centres. We define the molecular form factor by

$$F_1(Q) = (\sum_n b_n)^{-2} \langle | \sum_n b_n \exp(i\vec{Q} \cdot \vec{r}_{cn}) |^2 \rangle. \tag{2}$$

We also introduce another form factor $F_2(Q)$ which depends upon the molecular orientations

$$F_2(Q) = (\Sigma b_n)^{-2} \langle \sum_{ni,nj} b_{ni} b_{nj} \exp(i\vec{Q} \cdot (\vec{r}_{cni} - \vec{r}_{cnj})) \rangle. \tag{3}$$

Here $\vec{r}_{cni}$ is the distance of the nth atom in the ith molecule from its centre. Further from an analogy with atomic liquids we write the centre structure factor for molecular liquids $S_c(Q)$ as

$$S_c(Q) = 1 + N_m^{-1} \langle \sum_{i \neq j} \exp(i\vec{Q} \cdot \vec{r}_{cij}) \rangle. \tag{4}$$

Here $\vec{r}_{cij}$ is the intermolecular distance between the centres of the molecules i and j. With the definitions one can write equation (1) (Powles 1973; Egelstaff *et al* 1971; Page and Powles 1971)

$$S_m(Q) = F_1(Q) + F_2(Q)\,[S_c(Q) - 1]. \tag{5}$$

For large Q, we have $S_c(Q) \cong 1$ so that $S_m(Q) \cong F_1(Q)$. The expression (5) obtained as a formal result is only an approximation. $F_2(Q)$ introduced in this way is valid only if the radial and orientational coordinates are separable. In spherical molecules $F_2(Q)$ is the uncorrelated form factor and expression (5) is exact and $S_m(Q)$ obtained through (5) represents the isotropic part. One has to add anisotropic part to get the total $S_m(Q)$ (Weis and Levesque 1976). The anisotropic contribution is almost negligible for N_2 and in other cases this is small enabling perturbation calculations (Gubbins *et al* 1973; Wang *et al* 1973). The anisotropic part arises due to large anisotropic forces (Gubbins *et al* 1973; Streett and Tildesley 1977). Corrections to (5) due to anisotropy have been discussed by several authors (Egelstaff *et al* 1971; Gubbins *et al* 1973). Our procedure

is however different. Correction to (5) when the molecule is not spherical i.e. when radial and orientational coordinates are coupled, may be written as

$$S_m^* = S_a(Q) - [F_2(Q) - F_{2u}(Q)]\,[S_c(Q) - 1]$$

where $S_a(Q)$ is the anisotropic part which is to be added to (5) if $F_2(Q)$ is replaced by uncorrelated $F_2(Q)$, i.e. $F_{2u}(Q)$. By taking $F_2(Q)$ a linear combination of parallel and perpendicular $F_2(Q)$'s and choosing $S_c(Q)$ properly it is possible to make S_m^* very small throughout so that expression (5) becomes quite a good approximation as has been shown by our calculations (Gopala Rao and Joarder 1979, 1980 and unpublished). This is also found to be the case with equation (23) of Egelstaff *et al* (1971). If the correlation distance R_e is not too small the correction term vanishes at the maxima and minima of $S_e(Q)$ while at other points and particularly for large Q, correction is small so that (5) is a good approximation. Similar arguments have been presented in Page and Powles (1971). It is important to see what effect various assumptions about correlation of orientation have on the observed $S_m(Q)$. Since $S_e(Q)$ for water is believed to be known, the predicted $S_m(Q)$'s for two extreme models, one for which the molecular orientation is completely uncorrelated and one for which it is completely correlated as for the nearest neighbours in the ice agree quite well with small disagreement in the intermediate Q values. Thus, the coupling of translational and orientational coordinates has small effect on $S_m(Q)$.

For triatomic linear molecules like CS_2 the molecular form factor is given by

$$F_1(Q) = \frac{1}{(b_c + 2b_s)^2}\left[b_c^2 + 2b_s^2 + 4b_c b_s \frac{\sin Q r_{cs}}{Q r_{cs}} + 2b_s^2 \frac{\sin Q r_{ss}}{Q r_{ss}}\right]. \tag{6}$$

The correlated form factor $F_2(Q)$ for parallel configuration is simply given by

$$F_2(Q) = F_1(Q). \tag{7}$$

The proper selection of $S_e(Q)$ yields $S_m(Q)$ through equation (5) and this can be compared with the experimental data and also RISM values so as to test the validity of the orientational model approach. After the justification of the model we use this $F_2(Q)$ and the experimental $S_m(Q)$ data to yield $S_e(Q)$ which can be used for the calculation of various correlation functions including some angle-averaged pair potential.

2.1. *Partial structures*

The spatial correlation can be described by taking the atom as the basic scattering and geometric unit and atom-atom correlation functions $g_{\alpha\beta}(r)$ are defined so that $4\pi\rho g_{\alpha\beta}(r)r^2dr$ is the number of atoms of species β in a volume element $\vec{dr}$ at a distance $\vec{r}$ from a species a atom on another molecule. For CS_2 three correlation functions $g_{ss}(r)$, $g_{cs}(r)$ and $g_{ss}(r)$ are needed and since carbon atom is

located at the centre of mass $g_{cc}(r)$ is also the molecular centre correlation function. The spatial structure functions are defined by

$$S_{\alpha\beta}(Q) = 1 + 4\pi\rho \int_0^\infty dr\, r^2 [g_{\alpha\beta}(r) - 1] j_0(Qr). \tag{8}$$

The difference function

$$S_d(Q) = S_m(Q) - F_1(Q), \tag{9}$$

which measures the interference of radiation scattered by atom pairs in different molecules and hence dependent on the orientation effect, is given by

$$S_d(Q) = \frac{1}{(\sum_\alpha b_\alpha)^2} \sum_\alpha \sum_\beta b_\alpha b_\beta 4\pi (\rho_\alpha \rho_\beta)^{1/2} \int_0^\infty dr\, r^2 J_0(Qr) [g_{\alpha\beta}(r) - 1], \tag{10}$$

ρ_α being the bulk number density of atom α. Through equations (8) to (10) we write

$$1 + S_d(Q) = \frac{1}{(b_c + 2b_s)^2} [b_c^2 S_{cc}(Q) + 4b_c b_s S_{cs}(Q) + 4b_s^2 S_{cs}(Q)]. \tag{11}$$

The scattering amplitudes of carbon and sulphur are well-known so that for neutron case

$$1 + S_d^N(Q) = 0{\cdot}20\, S_{cc}(Q) + 0{\cdot}50\, S_{cs}(Q) + 0{\cdot}21\, S_{ss}(Q). \tag{12}$$

For x-rays the product $b_\alpha b_\beta/(\Sigma_\alpha b_\alpha)^2$ are nearly independent of Q and equation (11) becomes

$$1 + S_d^X(Q) = 0{\cdot}03\, S_{cc}(Q) + 0{\cdot}26\, S_{cs}(Q) + 0{\cdot}71\, S_{ss}(Q). \tag{13}$$

Since carbon lies here at the centre of mass and neutron scattering amplitude to carbon is significantly more than that for sulphur neutron result should yield $S_{cc}(Q)$ through the orientational model approach so that two scattering experiments can yield partials $S_{cs}(Q)$ and $S_{ss}(Q)$. The partials so obtained are definitely model-dependent. Good agreement of the calculated $S_m(Q)$ and $H_d(Q)$ values evidently shows that correction to (5) is small for this particular choice of $S_c(Q)$ and $F_2(Q)$. As shown in Egelstaff *et al* (1971) if R_c is not too small $S_c(Q)$ obtained through (5) would be correct at maxima and minima of $S_c(Q)$. At intermediate Q values some deviations from computed $S_c(Q)$ are there but this too is small if Q is large. Since $S_c(Q)$'s from two diffraction experiments agree somewhat the qualitative nature of $S_c(Q)$ computed is well justified and hence $S_{cs}(Q)$ and $S_{ss}(Q)$. The computation of isothermal compressibility from the following equation

$$\begin{aligned} \rho k_B T \beta_T &= 1 + 4\pi\rho \int_0^\infty [g_c(r) - 1] r^2\, dr \\ &= 1 + 4\pi\rho \int_0^\infty [g_c(r) - 1] r^2 \frac{\sin Qr}{Qr}\, dr \quad \text{with} \quad Q \to 0 \\ &= S_c(0), \end{aligned}$$

shows that $g_o(r)$ obtained is reasonable. The angle-averaged intermolecular potential derived also shows that $g_c(r)$ obtained should not be unreasonable. However there is a disagreement with RISM. $g_c(r)$ in RISM is a broad low height peak located at larger r. According to RISM it is expected that $S_{ss}(Q)$ would be dominant in $S_m^x(Q)$ since $S_{ss}(Q)$ should be larger in height than $S_{cc}(Q)$ (from hard sphere consideration, since $g_{ss}^{\max} > g_{cc}^{\max}$). Thus $S_m^x(Q)$ should have greater height and located at lower Q value compared to $S_m^N(Q)$. This is evident if (12) and (13) are examined. But the experimental fact is opposite; at least the neutron peak is not smaller than the x-ray peak [Data of Gibson and Dore give $S_m^N(Q)$ peak almost equal to the x-ray peak of Sandler and Narten but larger compared to Street's[17] x-ray data; all being at the same temperature].

3. Results and discussion

In the theoretical calculation of $S_m(Q)$ we have used parallel orientation and $S_c(Q)$ has been selected to be that given by Sutherland potential through random phase approximation. Sutherland potential was preferred as it is simple to handle (having inherent hard core) and has an attractive tail suitable for this type of liquid (having large entropy of melting). In the calculation of $F_1(Q)$ exponential Debye-Waller terms $\exp(-l_{\alpha\beta}^2 Q^2/2)$ were used. The quantities $l_{\alpha\beta}$ are the root-mean-square (RMS) deviations of local and instantaneous internuclear distances from the mean values $r_{\alpha\beta}$ in the liquid and were taken from Sandler and Narten (1976). With the proper selection of hard core diameter and depth of the potential, we have been able to obtain a good agreement of $S_m(Q)$ and $H_d(Q)$ curve with both neutron and x-ray data (figures 1, 2) except in the low Q region. The agreement is comparable with RISM calculations (Lowden and Chandler 1974; Sandler and Narten 1976). In the neutron case the first peak region has been produced better than that through RISM. The RISM calculation of Sandler and Narten (1976) agrees very well with their experimental data no doubt; surprisingly the distinct correlation function $G_d(r)$ from RISM differs much with the Fourier inversion of the experimental data particularly in the peak region. This large difference points to the weakness of the RISM equation. It must be also pointed out in this connection that atom-atom potential approach fails (Agarwal *et al* 1978) in the case of Br_2, another linear molecule having large quadrupole moment (CS_2 has also quite a large quadrupole moment, although the corresponding values of Q vary considerably in the literature ranging from $Q = 1{\cdot}8 \times 10^{-26}$ (Stogryn and Stogryn 1966) to $6{\cdot}8 \times 10^{-26}$ e.s.u. cm^2 (Hung and Spurling 1970). The Raman spectra experiments also indicate that polarisability of CS_2 is very high. Although RISM theory satisfactorily predicts the molecular structure for CS_2 and CH_3CN having large electrostatic forces, it is however unable to explain $(CH_3)_4C$ and $C(CH_3)_3OH$ (Narten *et al* 1978). $(CH_3)_4C$ however can be explained satisfactorily by apollo-type orientational model (Gopala Rao and Joarder, unpublished). The paper by Bertucci *et al* (1977) clearly shows that the intermolecular forces arising from the charge distributions have effect in correlating the orientation of molecules in liquid state over a short range. In addition, the thermodynamic data suggest that CS_2 is a rather flexible molecule, deviations from the rigidity being large. With this idea Monte Carlo

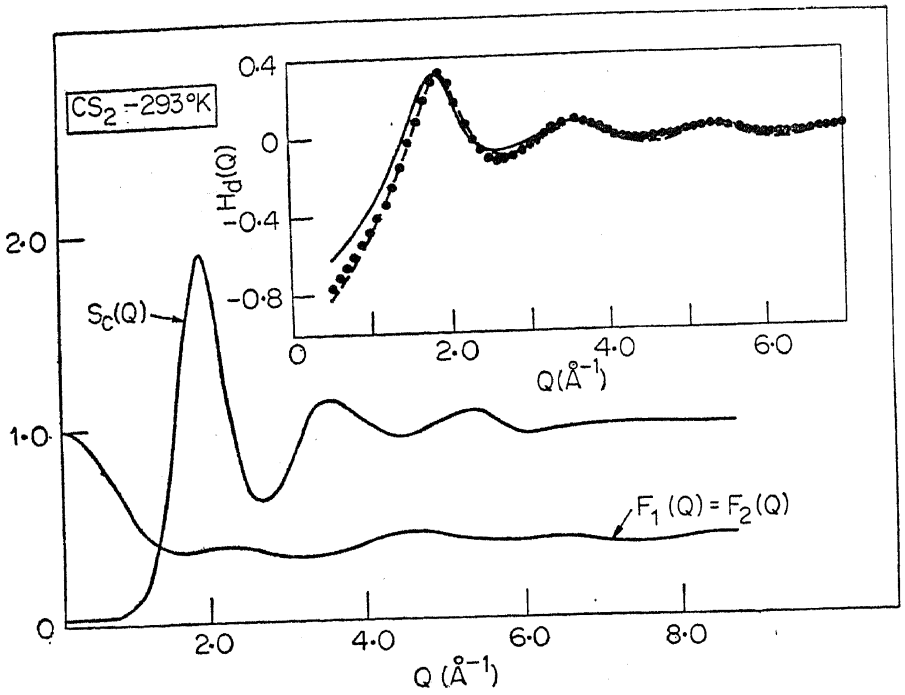

Figure 1. Distinct structure function $H_d(Q)$, molecular centre structure $S_c(Q)$ and form factors $F_1(Q)$ and $F_2(Q)$ of liquid CS_2 (x-ray data ; parallel configuration assumed). ————$H_d(Q)$, calculation with $\sigma = 3{\cdot}6$ Å, $\epsilon/K_B\,T = 0{\cdot}6$, $r_{es} = 1{\cdot}57$ Å. ····experimental points (Narten *et al* 1976). Bottom curve of the inset figure (- - - -) Calculation on RISM (Narten *et al* 1976).

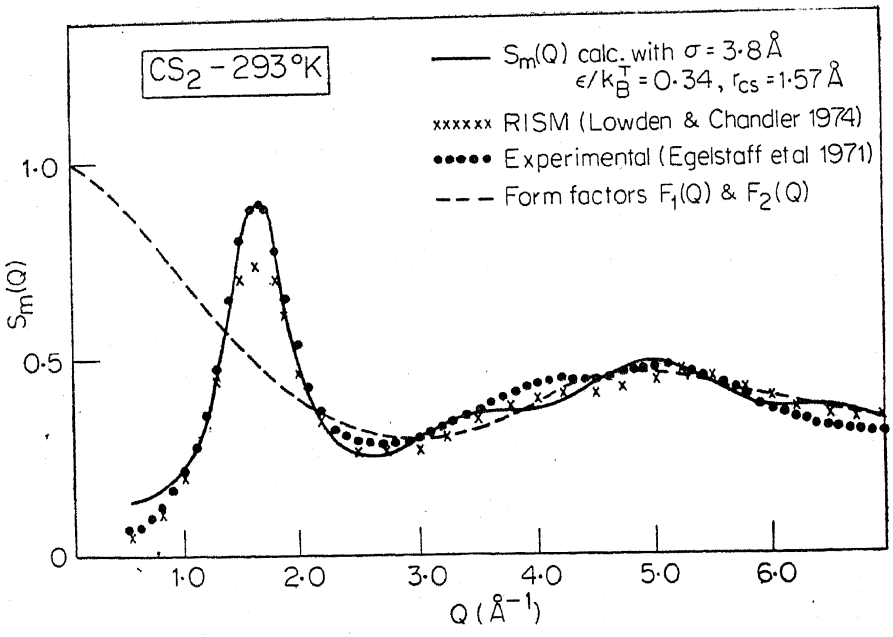

Figure 2. Molecular structure factor $S_m(Q)$ and form factors $F_1(Q)$ and $F_2(Q)$ of liquid CS_2 (Neutron data ; parallel configuration assumed).

simulation for CS_2 with L–J potential (Steinhauser and Neumann 1979) has been performed. All the three $g_{\alpha\beta}$ functions differ conisderably from the ones given by RISM. Monte Carlo simulation with quadrupole-quadrupole term may reveal the actual $g_{\alpha\beta}$ functions to some extent. That this very simple orientational model approach gives a good agreement in $S_m(Q)$ or $H_d(Q)$ is really interesting. The low Q discrepancy may be attributed to the typical model potential used in the calculation. Our other calculations (Gopala Rao and Joarder 1979, 1980) also confirm this procedure. In both neutron and x-ray calculations the bond distance r_{cs} has been taken to be 1·57 Å. The hard core diameter and depth of the potential have been taken slightly different in two cases. Parameters used in the calculations have been listed in table 1. In the subsequent calculations of $S_c(Q)$ from experimental $S_m(Q)$ data and therefrom various correlation functions including the pair potential, we have used x-ray data since neutron data are of uncertain quality particularly at large Q. The centre structure factor is shown in figure 1 and the various correlation functions including the pair potential are shown in figures 3 to 5. The pair potential was calculated following the method discussed in Gopala Rao and Joarder (1978). For comparison the potential based on mean spherical model approximation (MSM) is also shown. To test the qualitative accuracy of the potential obtained the isothermal compressibility was also computed from the potential using the approximate method of Born and Lande (Moelwyn-Hughes 1961). The accuracy of the correlation function including the pair potential depends on the accuracy of the structure factor data. The experimental data of Street (1972) on CS_2 (x-ray) differ considerably from those of Sandler and Narten (1976). The latter's data have been claimed to be very accurate and as such we have used these data for our calculations.

Table 1. Parameters used in the calculation of Sm (Q).

$T = 293°\ K$	$\rho = 0{\cdot}00997/Å^{-3}$	and parallel configuration assumed
Neutron case	$\sigma = 3{\cdot}8$ Å and	$r_{cs} = 1{\cdot}57$ Å
	$\epsilon/k_B T = 0{\cdot}36$	$b_0 = 0{\cdot}663 \times 10^{-12}$ cm
		$b_c = 0{\cdot}285 \times 10^{-12}$ cm
x-ray case	$\sigma = 3{\cdot}6$ Å and	$r_{cs} = 1{\cdot}57$Å
	$\epsilon/k_B T = 0{\cdot}6$	$l_{cs} = 0{\cdot}09$/Å
		$l_{ss} = 0{\cdot}082$/Å

Intermolecular potential parameters with compressibility values

σ (Å)		ϵ/K (°K)		Isothermal compressibilities $\times 10^{12}$			
Present	L–J	Present	L–J	Through x-ray data	$S_c(O)$ neutron data	Through potential function	obs.
5·45	4·438	446	458	72	112	161	90

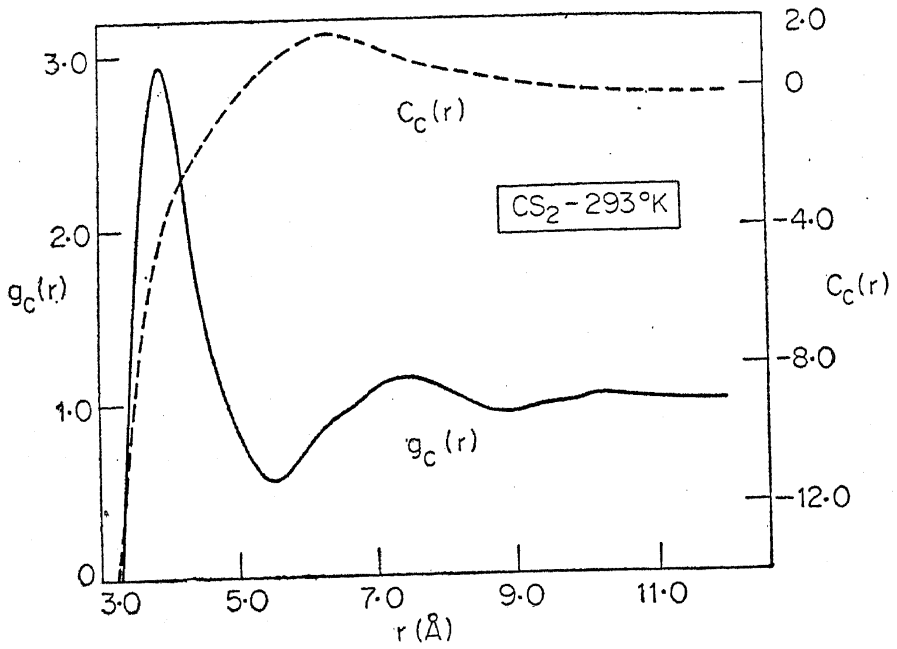

Figure 3. Centre radial distribution function (CRDF) $g_c(r)$ and central direct correlation function (CDCF) $C_c(r)$ of liquid CS_2.

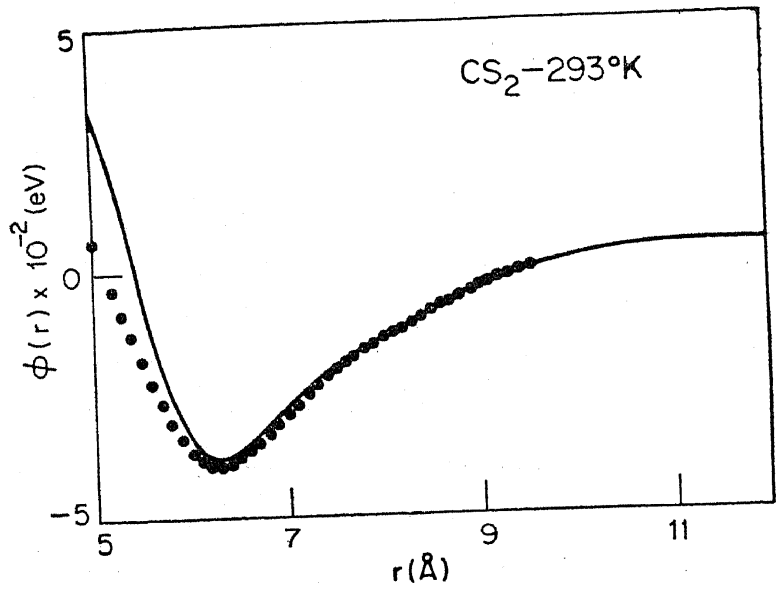

Figure 4. Intermolecular potential energy function of liquid CS_2. Dots are potential given by MSM approximation.

The CS_2 molecule possesses quadrupole moment and therefore the most probabl pair configuration at low temperature is a T configuration. However the molecules of CS_2 with large entropy of melting move rapidly above their melting point and the well-known DCKerr effect also points to the same conclusion (Deby 1936). Thus the average configuration differs markedly from that expected i the solid form at low temperature.

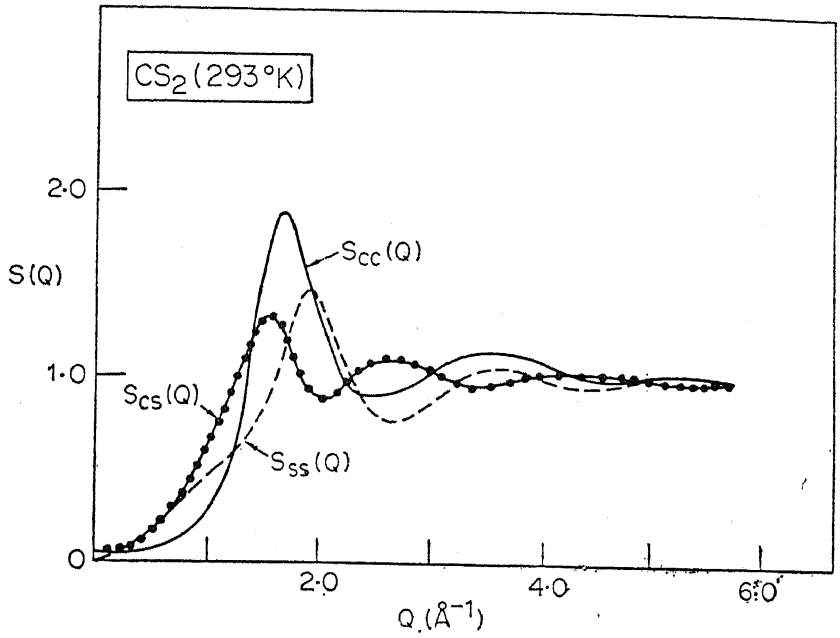

Figure 5. Partial structures of liquid CS_2.

The $S_c(Q)$ and hence $S_{cc}(Q)$ obtained from experimental $S_m(Q)$ (neutron data) are shown in figure 5 along with the computed $S_{cs}(Q)$ and $S_{ss}(Q)$ from equation (12) and (13). The $S_c(Q)$ values obtained from x-ray and neutron data agree somewhat although the two curves are displaced slightly relative to each other. The discrepancy may be due to the large error in neutron data and to some extent in x-ray data. Fourier transform of the partial structure is not justified because of their low accuracy owing to the fact that the accuracy of neutron data is only 10%. But since first peak height of $S_{cc}(Q)$ is more than that for $S_{ss}(Q)$ it is expected that (from hard sphere consideration Ashcroft and Lekner 1966) packing density would be more for $S_{cc}(Q)$ and hence $g_{cc}(\max) > g_{ss}(\max)$. Thus a preference definitely exists for carbon atoms to be in contact. This contradicts the RISM results where one of the assumptions was that the liquid structure was determined only by the size and shape of the molecules and no multipole moments were considered. The quadrupole moment of CS_2 may influence correlations of molecular orientations possibly bringing carbon atoms closer together. Further, the Fourier transform procedure of Sandler and Narten (1976) to give a total distribution function have fundamental physical objections to it (Page and Powles 1971). In the light of this the present procedure is important.

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