Structure and allied properties of liquid carbodiisulphide

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Abstract. Orientational model for liquid CS₂ 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 CS₂ 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 N₂, O₃ (Gopala Rao and Joarder 1979) and CSe₂ (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 CS₂.
2. Theory

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

$$S_m(Q) = N_m^{-1} \left( \sum_{i} b_i \right)^{-2} \left\{ \sum_{i,j} b_i b_j \exp \left( iQ \cdot \hat{r}_{ij} \right) \right\}$$

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 $\hat{r}_{ij} = \hat{r}_i - \hat{r}_j$ 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 $\hat{r}_{ij}$ are then referred to molecular centres. We define the molecular form factor by

$$F_1(Q) = \left( \sum_{n} b_n \right)^{-2} \left\{ \sum_{n} b_n \exp \left( iQ \cdot \hat{r}_n \right) \right\}.$$  \hspace{1cm} (2)

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

$$F_2(Q) = \left( \sum_{n} b_n \right)^{-2} \left\{ \sum_{n_i,n_j} b_{n_i} b_{n_j} \exp \left( iQ \cdot (\hat{r}_{n_i} - \hat{r}_{n_j}) \right) \right\}. \hspace{1cm} (3)$$

Here $\hat{r}_{n_i}$ is the distance of the $n$th atom in the $i$th molecule from its centre. Further from an analogy with atomic liquids we write the centre structure factor for molecular liquids $S_c(Q)$ as

$$S_c(Q) = 1 + N_m^{-1} \left( \sum_{i \neq j} \exp \left( iQ \cdot \hat{r}_{ij} \right) \right). \hspace{1cm} (4)$$

Here $\hat{r}_{ij}$ 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)

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

For large $Q$, we have $S_c(Q) \approx 1$ so that $S_m(Q) \approx F_1(Q)$. 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