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Structure Model for Liquid Carbon Tetrachloride

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The X-ray scattering intensity for the visualized structure model of a liquid is formulated. It is ascertained that by the bcc model for liquid carbon tetrachloride the experimental intensity has been simulated well.

The structures of gases and crystals have been studied extensively by diffraction methods. For liquids, however, the structure analysis is rather difficult. The fundamental difficulty is that there is no idealized abstraction of the liquid state such as an ideal gas or a perfect crystal. In the gaseous state, the interaction between molecules can be neglected in many cases and only one molecule is taken into consideration for the structure analysis. Crystals are characterized by the regularity in their configuration. So, we know the crystal structure only by studying the arrangement of molecules or atoms within a unit cell. However, in the liquid state which is a condensed phase and has no such regularity in the arrangement of molecules in crystals, it is difficult to obtain the information about the molecular arrangement immediately from experimental diffraction intensities or from radial distribution functions.

One approach to overcome the difficulty is to construct a model in which we visualize a structure of liquids,[1,2] and to calculate the diffraction intensity for the structure model, which is to be tested against the experimental intensity. In constructing a model we may describe the structure of the liquid as follows. We assume a certain nearest-neighbor configuration around a central molecule and repeat this structural unit by some specified rule. According to this model the average molecular positions, as viewed from the location of a given central molecule, conform to a certain lattice structure. Unlike the crystalline case, however, repetition of the structure unit is imperfect and therefore is accompanied by rapid loss of positional correlation as the distance between the central molecule and surrounding ones increases. This loss of correlation may be embodied in the model in the form of mean-square amplitudes of distribution of the separation between atoms which increase rapidly with the distance. At least beyond a few molecular radii away from any starting point, the structure can be regarded as a continuum. This relative distribution must obviously be independent of the choice of the central molecule. Such a structure model for liquids may be called the "local lattice structure model." Some investigators have denied such crystalline-like model for the liquids,[3] but there are in fact some examples in which diffraction intensities are explained by the "local lattice structure model." Moreover, such a lattice model may be useful in serving to keep away from the inherent difficulty of statistical theories of liquids, because such local structure of the liquid reflects directly the strong molecular interactions, which are essential to the properties of the liquid.

The analysis of the diffraction intensity for liquids by constructing a structure model has been made by several authors.[4–8] However, there has been some confusion in formulating the scattering intensities from structure models. So, we feel it necessary to reproduce the correct formulation of the scattering intensity for the visualized structure model of liquids originally put forward by Narten and Levy.[2,4]

In a preceding paper we reported improved X-ray diffraction data of liquid carbon tetrachloride.[9] So, we determine a structure model for liquid carbon tetrachloride on the basis of the correct formulation of the scattering intensity. Among the various models which have so far been suggested for the structure of liquid carbon tetrachloride,[6–8] the bcc model is confirmed to be the one that gives the best agreement between theory and experiment.

Scattering Intensity from Liquids[2,4]

In the following, we consider X-ray scattering intensity from a liquid sample. The region denoted by C in Fig. 1 shows the effective volume radiated by X-rays. The total coherent intensity scattered from this region which contains N molecules is given by[10]

$$I' = \sum_{j}^{N}\sum_{i}^{N} f_i f_j \frac{\sin sr_{ij}}{sr_{ij}} \exp\left(-\frac{l_{ij}^2}{2}s^2\right), \tag{1}$$

where f_i is the atomic scattering factor of the i-th atom and s is the scattering parameter defined by $4\pi\sin\theta/\lambda$, λ: wavelength, 2θ: scattering angle. The notation l_{ij} is the root mean-square amplitude due to the dis-

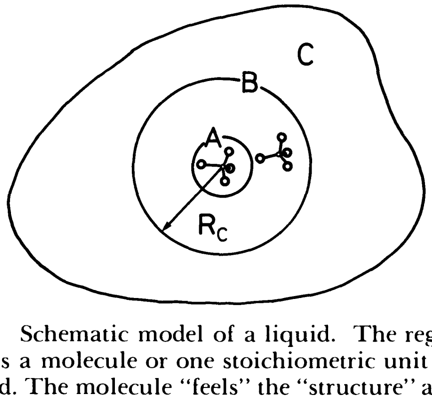

Fig. 1. Schematic model of a liquid. The region A shows a molecule or one stoichiometric unit of the liquid. The molecule "feels" the "structure" around itself up to the distance R_C. This structure region is denoted by B. The region C shows the effective volume irradiated by X-rays, and the region (C–B) is viewed as continuous from A.

tribution averaged over both time and space around the mean interatomic distance r_{ij}. The summation is over all atoms in the volume C. Here, we can define by I the scattering intensity per molecule or one stoichiometric unit in the liquid. Namely,

$$I = I'/N = \sum_{j\subset \mathrm{C}}\sum_{i\subset \mathrm{A}} f_i f_j \frac{\sin sr_{ij}}{sr_{ij}} \exp\left(-\frac{l_{ij}^2}{2}s^2\right), \tag{2}$$

where the summation is now over the stoichiometric unit A (Fig. 1) for i and over all atoms in the sample for j. The region A shows a central molecule or a unit as is mentioned in the introductory section. It is noted that any molecule or any stoichiometric unit in the liquid except for surface molecules is eligible to be this central unit.

In Eq. 2, however, it is hardly possible to perform the summation for j for the assumed liquid structure. For such a model of the liquid structure to be tractable, Narten and Levy terminated the series of terms of j at a distance R_c from a central molecule, and assumed a continuous distribution beyond this distance.[2,4] The sphere with the radius R_c is shown by the region B. Namely, a molecule or one stoichiometric unit (region A) "feels" the "structure" around itself up to the distance R_c and the region beyond R_c is regarded as a continuum in the distribution of the molecules. So, the scattering intensity per molecule in a liquid is given by

$$I = I_d + I_c, \tag{3}$$

where I_d is the contribution from the interference of a central molecule and those in the region of discrete structure B around it, given by

$$I_d = \sum_{j\subset \mathrm{B}}\sum_{i\subset \mathrm{A}} f_i f_j \frac{\sin sr_{ij}}{sr_{ij}} \exp\left(-\frac{l_{ij}^2}{2}s^2\right). \tag{4}$$

The summation for j is over all atoms in the region B. The contribution from the interference of a molecule and the continuous region is given by

$$I_c = \sum_{i\subset \mathrm{A}} f_i \langle F\rangle \rho_0 \int_{R_c}^{\infty} 4\pi r^2 \frac{\sin sr}{sr} \mathrm{d}r, \tag{5}$$

where ρ_0 is the bulk number density of molecules of the liquid and the mean scattering amplitude of the molecule $<F>$ is given by

$$\langle F\rangle = \sum_{i\subset \mathrm{A}} f_i. \tag{6}$$

On integration of Eq. 5 we obtain[11]

$$\begin{aligned} I_c &= \sum_{i\subset \mathrm{A}} f_i \langle F\rangle 4\pi\rho_0 \frac{sR_c\cos(sR_c)-\sin(sR_c)}{s^3}\exp\left(-\frac{l_c^2}{2}s^2\right) \\ &= \sum_{i\subset \mathrm{A}} f_i \langle F\rangle n \frac{3\{sR_c\cos(sR_c)-\sin(sR_c)\}}{(sR_c)^3}\exp\left(-\frac{l_c^2}{2}s^2\right). \end{aligned} \tag{7}$$

A "temperature factor" l_c is included in Eq. 7 in order to connect the continuous region to the discrete region as smoothly as possible. The notation n is the number of molecules included in region B. Using Eqs. 4 and 7, we can calculate the scattering intensity for any structure model of the liquid.

Sometimes there was confusion in making the summation for Eq. 4 in previous papers on the simulation study of the liquid structure. In some papers, the summation is taken over all the atoms in the region B, namely for i and j. The intensity thus calculated will not be the intensity of the liquid but that of a cluster floating in a continuous medium. For example, Narten and Levy described the theory correctly in deriving the scattering intensity for the model structure of water.[2,4] In the meantime, however, they gave a different expression for the scattering intensities for liquid carbon tetrachloride[6] and liquid benzene,[5] as if they had calculated the intensities of their "clusters." For the case of the simulation studies for liquid carbon tetrachloride, Reichelt *et al.*[7] and Nishikawa and Murata[8] took the summation over all the atoms in the discrete structure. Recently Arakawa *et al.* criticized[12] the correct summation of Narten and Levy.[2,4]

There is also some other confusion about the formulation of the scattering intensity mentioned in this section. Powles stated that the contribution from the continuous region diverged,[13] namely, the integration given by Eq. 5 in the present paper diverged. So he asserted that the "local lattice structure model" was inadequate for the description of the liquid structure. However, the integration of Eq. 5 coverges[14] as given by Eq. 7 excluding the term of exp $(-l_c^2s^2/2)$. Powles also remarked that the term of exp $(-l_c^2s^2/2)$ was introduced in order to circumvent the divergence of the integration.[13] However, this explanation is not correct. The problem in the "local lattice structure model" is the discontinuity between the discrete region and the continuous region. The introduction of the term $\exp(-l_c^2s^2/2)$ in Eq. 7 is only to smear this discontinuity.

The Structure Models for Liquid Carbon Tetrachloride

Many diffraction experiments for liquid carbon tetrachloride have been carried out.[6–8,15–19] However, the visualized structure models were proposed by Narten and Levy,[6] by Egelstaff *et al.*,[18] by Reichelt *et al.*,[7] and by Nishikawa and Murata.[8] Also, Lowden and Chandler proposed a model for liquid carbon tetrachloride on the basis of their RISM (reference interaction site model) calculation,[20] although it is not the result of diffraction experiments. These models have been summarized briefly in Ref. 21.

For these models, namely, the Pa3 model,[6] the monoclinic model[7] and the bcc model,[8] the respective scattering intensities were calculated, though all the calculations were imperfect as noted in the previous section. However, the imperfection did not cause any serious defect, because the calculated intensities were those for respective clusters and they are different from the correct intensities of the liquid in the weight for each atomic distance. Although some errors may have been contained in the intensities or the estimated root mean square amplitudes, the main features, especially the phases for the intensity curve, are reproduced. These three models are different from each other in three-dimensional packing, but the one dimensional scattering intensity curves happen to be similar to each other.

One cause of the difficulty in the structure analysis of liquids is that there is no general method to determine the structure of the liquid uniquely from the scattering intensity. Even if we are lucky enough to obtain a model whose calculated intensity agrees well with the experimental one, there is no assurance that the model is correct. Especially for molecular liquids, we must determine the molecular orientation and the intermolecular distances from a halo-pattern.

In the case of carbon tetrachloride, there exist plastic crystal phases. The plastic crystal can be regarded as an intermediate state between the ordered crystal and the liquid. The result of the structure analysis of the plastic crystal of carbon tetrachloride gives a helpful suggestion for the structure of the liquid carbon tetrachloride, as was mentioned in a previous paper.[21] In the structure analysis of the plastic phase Ia of carbon tetrachloride, the following result has been obtained.[21] Namely, the intermolecular distance between carbon tetrachloride molecules is 5.90 Å and the orientational correlation of neighboring molecules is explained by the head-tail head-tail packing.

Simulation of the Weighted Structure Function by the bcc Model

As is mentioned above, the most probable packing for the molecules of liquid carbon tetrachloride is the head-tail head-tail packing. By the repetition of this head-tail head-tail packing with eclipsed form for the off-axis chlorine atoms, we obtain a bcc lattice. Accordingly, we calculate here the scattering intensity from the bcc model and compare it with the experimental one.[9]

We examine how many molecules are suitable to be arranged around a central molecule with the nearest neighbor distance R of 5.9 Å.[22] For the values of the intramolecular distances $r_{\text{C-Cl}}$ and $r_{\text{Cl-Cl}}$ and their root mean square amplitudes $l_{\text{C-Cl}}$ and $l_{\text{Cl-Cl}}$, the results obtained by gas electron diffraction[23] are used. They are almost the same as the recent result for the liquid by neutron scattering experiments.[24]

Using Eqs. 4 and 7, we calculated the total coherent intensity and derived the weighted structure function $si(s)$,

$$\begin{aligned} si(s) &= s(I - \sum_{i\subset \mathrm{A}} f_i^2) \\ &= s(I_\mathrm{d} - \sum_{i\subset \mathrm{A}} f_i^2 + I_\mathrm{c}) \end{aligned} \tag{8}$$

for the bcc lattice where eight molecules are arranged as the first nearest neighbors around one molecule ($n=9$) and the distribution of molecules is assumed to be continuous beyond the distance R_c. The critical radius R_c is determined by the relationship

$$n = \frac{4}{3}\pi R_\mathrm{c}^3 \rho_0, \tag{9}$$

where ρ_0 is the bulk number density of carbon tetrachloride molecules in the liquid phase. The mean square amplitudes are determined according to the "structural diffusion" model[1]

$$l_{ij}^2 = D r_{ij}. \tag{10}$$

The calculated structure function reproduces main peaks and valleys of the experimental $si(s)$ curve, but their heights and depths can not be simulated even if the value D in Eq. 10 is changed. So, we repeat the same procedure one after another with the increase of the number n contained in B region (Fig. 1). At the number of $n=51$ (up to the fourth nearest neighbors around the central molecule), the experimental curve is simulated satisfactorily and further increase of n no longer changes the feature of the calculated curve.

Next, we investigate the root mean square amplitude l_{ij} in detail. Until now, we use the Prins relation (Eq. 10) for estimating the value of l_{ij} in relation to its interatomic distance r_{ij}. A value 0.0716 for D is suitable. This means that the root mean square variation of the distance between the nearest neighbor molecules is about 0.65 Å, which is about 11% of the equilibrium separation of the two molecules (5.9 Å). However, by only one value for D, the third peak of $si(s)$ curve at $s\approx 3.2$ Å^{-1} shifts to about 3 Å^{-1}, so we use two constants for the relation of Eq. 10. Namely,

$D_1 = 0.0716$ **for the 1-st nearest neighbor molecules.**
$D_2 = 0.1224$ **for the 2-nd, 3-rd, and 4-th nearest neighbor molecules.**

The result is shown in Fig. 2 by the solid curve with the experimental $si(s)$ curve[9] denoted by circles. The region from $s=0$ to 6 Å^{-1} is shown, because the $si(s)$ curve in the region of s larger than 6 Å^{-1} is approximately represented by a free carbon tetrachloride molecule and is hardly affected by intermolecular interference.

By theoretical investigations on the quasi-crystalline model for liquids, Medvedev *et al.*[25] and Baer[26] proposed a further modified "structural diffusion" relation

$$l_{ij}^2 = D(r_{ij} - r_0) \tag{11}$$

in place of the equation given by Eq. 10. Using this relation, we carried out the least-squares analysis for the parameters R, D, r_0, R_c, and l_c, with the number n fixed at 51. The result is shown in Table 1. The $si(s)$ curve calculated by using these parameters is in slightly poorer agreement with the experimental one in the

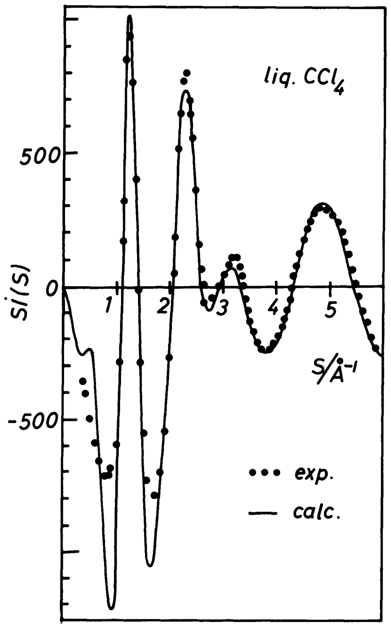

Fig. 2. The weighted structure functions $si(s)$ for liquid carbon tetrachloride. The solid curve is the calculated one for the bcc model with two D coefficients. The circles are experimental values.[9]

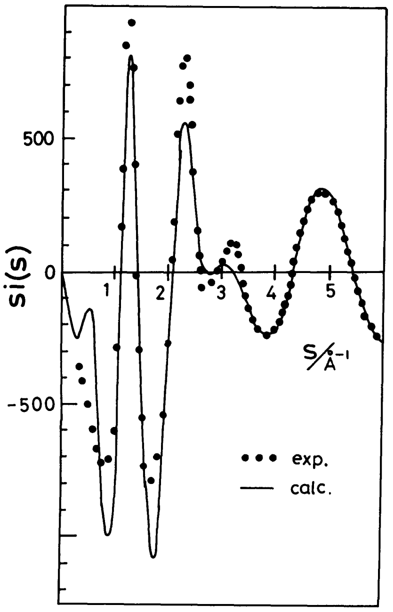

Fig. 3. The weighted structure functions $si(s)$ for liquid carbon tetrachloride. The solid curve is the calculated one for the bcc model with the relation of the root mean square amplitudes given by Eq. 11.

TABLE 1. THE REFINED PARAMETERS FOR THE BCC MODEL[a)]

R/Å	5.90 (2)	R_c/Å	12.41 (3)
D/Å	0.158 (23)	l_c/Å	1.76 (76)
r_0/Å	2.46 (74)		

a) The values in the parenthesis are standard deviations.

peak height of the first and second peak as is shown in Fig. 3, than the case of the calculated $si(s)$ curve using the two D_1 and D_2 coefficients. The result in Table 1 shows that the parameters for the distances converge very well, but not for the mean square amplitudes. This may indicate that the theoretical expression for the loss of positional correlation of the molecules from the equilibrium position in the liquid is not satisfactory. In the least squares analysis, R_c is changed as a fitting parameter, and its value has converged exactly to the value obtained by Eq. 9.

Discussion

In Fig. 2, the circles are the experimental intensities which are obtained by the improved and revised analysis of the energy-dispersive X-ray diffractometry.[9] This experimental result is in good agreement with Narten's result obtained by the angle-dispersive method.[19] In the previous work, one of the present authors (K. N.) reported that there were fine structures in the diffraction pattern of liquid carbon teterachloride,[8] but it has been proved that they are not fine structures from the liquid but are the parasitic scattering from Myler windows of the sample holder.

As is shown in Fig. 2, the calculated intensity for the bcc model is in good agreement with the experimental one except for the depth of the valley at $s=1.7$ Å^{-1} and the intensity ranging from 0 to 1.2Å^{-1}. The disagreement in the intensity at $s=1.7$ Å^{-1} has not been explained. We could not simulate the depth of the valley by changing the value of D without disturbing the balance of the other peaks and valleys in the intensity curve.

The discrepancy of the intensity ranging from 0 to 1.2 Å^{-1} between the calculated and experimental intensities is explained by the unreasonable connection of the discrete structure region (B in Fig. 1) and the continuum region. In order to connect the two regions as smoothly as possible, we introduce the "temperature factor" intentionally in Eq. 7 in the form of $\exp(-l_c^2 s^2/2)$, but there is is no physical reason for this expression. In other words, l_c is not the root mean square amplitude of the radius R_c.

In the case of liquid carbon tetrachloride, the success in modeling the structure by the "local lattice structure model" may be due to the long range correlation of the liquid; that is, the discrete region is comparably large, so the ghost peaks in the scattering curve caused by an unreasonable connection appear at small s-values and are easily distinguishable from the relevant peaks of the liquid.

The method of structure simulation of the scattering intensity mentioned above can be called "real space expansion," where we calculate the scattering intensity by summing up the contributions from each atomic distance in the liquid described by a real space. It is concluded that for the simulation method of the "real space expansion" the convergence is very poor in the small s-region of the intensity curve. To achieve a much better convergence of the simulation for the scattering intensity at the small s-region, a different formulation called "reciprocal space expansion" seems to be promising.[27]

In order to express the structural diffusion of the liquid, we tried two methods, namely, one introducing two D coefficients for Eq. 10 and the other using the relation described by Eq. 11. The former leads to a more satisfactory simulation. However, it has been reported that the latter expression is more suitable to describe the temperature factor of monoatomic liquid than the expression of Eq. 10.[25,26] In the case of a molecular liquid such as carbon tetrachloride, the shape of the molecules itself seems to play an important role. Especially for liquid carbon tetrachloride, the gear-like packing of tetrahedral molecules may be important in determining the structure. We have therefore derived a more sophisticated formulation for the mean square amplitudes for liquid carbon tetrachloride, taking into account the shape of the molecules; the result is reported in a succeeding paper.[28]

In conclusion the bcc model for liquid carbon tetrachloride explains well the scattering intensity. Of course, the bcc model may not be the only one model representing the experimental intensity. However, few other arrangements seem to be left for the structure model, because almost all the fundamental packings acceptable for tetrahedral molecules were checked in the structure study of the plastic crystal phase.[21] The head-tail head-tail packing shows that the octopole interaction is important in determining the structure of the liquid. The head-tail head-tail packing is highly stabilized for the molecules with an octopole moment.[29]

References

1) J. Frenkel "Kinetic Theory of Liquid" Dover, New York (1955).

2) A. H. Narten and H. A. Levy, *Science*, **165**, 447 (1969).

3) J. F. Karnicky and C. J. Pings, *Adv. Chem. Phys.*, **34**, 157 (1976).

4) A. H. Narten, M. D. Danford, and H. A. Levy, *Discuss. Faraday Soc.*, **43**, 97 (1967).

5) A. H. Narten, *J. Chem. Phys.*, **48**, 1630 (1968).

6) A. H. Narten, M. D. Danford, and H. A. Levy, *J. Chem. Phys.*, **46**, 4875 (1967).

7) G. Reichelt, J. U. Weidner, and H. W. Zimmermann, *Ber. Bunsenges. Phys. Chem.*, **78**, 1050 (1974).

8) K. Nishikawa and Y. Murata, *Bull. Chem. Soc. Jpn.*, **52**, 293 (1979).

9) K. Nishikawa and T. Iijima, *Bull. Chem. Soc. Jpn.*, **57**, 1750 (1984).

10) P. Debye and H. Menke, *Phys. Z.*, **31**, 797 (1930).

11) Narten and Levy used the respective distance r_{cij} in place of the radius R_c.[2,4]

12) N. Ohtomo, K. Tokiwano, and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **54**, 1802 (1981).

13) J. G. Powles, *Adv. Phys.*, **22**, 1 (1973).

14) B. E. Warren, *Phys. Rev.*, **45**, 657 (1934).

15) A. Eisenstein, *Phys. Rev.*, **63**, 304 (1943).

16) E. E. Bray and N. S. Gingrich, *J. Chem. Phys.*, **11**, 351 (1943).

17) R. W. Gruebell and G. T. Clayton, *J. Chem. Phys.*, **46**, 639 (1967).

18) P. A. Egelstaff, D. I. Page, and J. G. Powles, *Mol. Phys.*, **20**, 881 (1971).

19) A. H. Narten, *J. Chem. Phys.*, **65**, 573 (1976).

20) L. J. Lowden and D. Chandler, *J. Chem. Phys.*, **61**, 5228 (1974).

21) K. Nishikawa, K. Tohji, and Y. Murata, *J. Chem. Phys.*, **74**, 5817 (1981).

22) This distance is slightly longer than 5.77 Å, the one reported in the previous work,[8] but it is poved in the present work that the value of 5.9 Å is better to simulate the experimental intensity. Moreover, this value is consistent with the density of liquid carbon tetrachloride at room temperature.

23) Y. Morino, Y. Nakamura, and T. Iijima, *J. Chem. Phys.*, **32**, 643 (1960).

24) J. H. Clarke, J. R. Granada, and J. C. Dore, *Mol. Phys.*, **37**, 1263 (1979).

25) N. N. Medvedev and Yu. I. Naberukhin, *Phys. Chem. Liquids*, **6**, 137 (1977); *ibid.*, **8**, 167 (1978).

26) S. Baer, *Chem. Phys.*, **39**, 159 (1979).

27) T. Iijima and K. Nishikawa, *Chem. Phys. Lett.*, in press.

28) K. Nishikawa and T. Iijima, *Bull. Chem. Soc. Jpn.*, **58**, 1220 (1985).

29) T. Kihara, "Intermolecular Forces," Wiley, New York (1977).