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Reciprocal Space Expansion in the Analysis of X-Ray Scattering Intensities from Liquid Carbon Tetrachloride

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The concept of "reciprocal space expansion" has been applied in the analysis of the X-ray scattering intensity from liquid carbon tetrachloride. The results obtained by using the bcc local lattice structure model show very good agreement with the experimental intensity in the small-s region, where ghost peaks are inevitably introduced by the "real space expansion" usually adopted.

The analysis of the X-ray scattering intensity from a liquid by constructing a "local lattice structure model" is usually carried out by means of the formulation put forward by Narten and his coworkers.[1,2] This formulation is based on the theory developed by Debye and Menke[3] and by Warren,[4] i.e., the expansion of the scattering intensity in terms of the interatomic distances, r_{ij}, in the real space (see Eq. 2). Therefore, hereafter, we will name Narten's expression for the "local lattice structure model" the "real space expansion."

This method was applied to liquid carbon tetrachloride.[5,6] The body-centered-cubic local lattice structure formed by the head-tail head-tail packing of the carbon tetrachloride molecules with a nearest neighbor distance of 5.9 Å accounted for the experimental intensity beyond $s=1.2$ Å^{-1} ($s=4\pi\sin\theta/\lambda$, 2θ: scattering angle, λ: wavelength of X-rays).

As was pointed out in a previous paper,[5] the limitations of the real space expansion for the local lattice structure model arise from the unreasonable connection of the discrete structure region and the continuum one, as the sudden onset of the continuum region inevitably leads to spurious peaks in the small-s region. The use of a larger discrete-structure region is, on the other hand, difficult practically because of the slow convergence of the real space expansion for small values of s. The small-s region, however, contains information on the long-range structure of liquids. Thus it is important to investigate the scattering intensities in this region more carefully.

In the case of the real space expansion of the bcc model for liquid carbon tetrachloride,[5] the ghost peak and valley appearing at 0.5 and 0.8 Å^{-1} respectively are distinguishable from the inherent peaks beyond $s\simeq1.3$ Å^{-1} (see Fig. 2(a)). However, in some simulation studies of the structure of liquids, ghost peaks may be misunderstood as inherent peaks. Moreover, due to the ghost peaks, the usefulness of the local lattice structure model itself has often been devaluated.[7,8]

To overcome the difficulty in the real space expansion, a method called "reciprocal space expansion" was applied to liquid carbon tetrachloride; the results were reported in a previous letter by the present authors.[6] The details are described in the present paper.

Formulation of the "Reciprocal Space Expansion"

The Poisson summation formula[10] states that, for the functions $\eta(\boldsymbol{k})$ and $\phi(\boldsymbol{r})$, that are mutually related by a Fourier transform, we have

$$\sum_{\mu} \phi(\boldsymbol{a}_{\mu}) = \frac{1}{v}\sum_{\nu} \eta(\boldsymbol{b}_{\nu}), \tag{1}$$

where $\boldsymbol{a}_{\mu}$ is the lattice-point vector in real space, $\boldsymbol{b}_{\nu}$ is that in the corresponding reciprocal space, and v is the volume of the unit cell in the real space. The notations $\boldsymbol{\mu}$ and $\boldsymbol{\nu}$ are the representations of a set of three indices.

The total coherent scattering intensity per molecule, as formulated by the real space expansion, is given by,[5]

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

where f_i is the atomic scattering factor of the i-th atom and l_{ij} is the root mean-square deviation of the mean interatomic distance, r_{ij}. The summation for j is over all atoms of the sample, while that for i is over the atoms of the central molecule. By employing the Prins relation, $l_{ij}{}^2=2Dr_{ij}$,[11] Eq. 2 becomes

$$I = \sum_{\alpha,\alpha'}\sum_{\mu} f_{\alpha} f_{\alpha'} \frac{\sin\left(s|\boldsymbol{a}_{\mu}+\boldsymbol{a}_{\alpha\alpha'}|\right)}{s|\boldsymbol{a}_{\mu}+\boldsymbol{a}_{\alpha\alpha'}|} \exp\left(-Ds^2|\boldsymbol{a}_{\mu}+\boldsymbol{a}_{\alpha\alpha'}|\right), \tag{3}$$

where $\boldsymbol{a}_{\mu}$ is the lattice-point vector and $\boldsymbol{a}_{\alpha,\alpha'}$ is the vector which connects α and α'-th atoms in a unit cell (see Fig. 1). Let us define $\phi(\boldsymbol{r})$ by means of the following relation:

$$\phi(\boldsymbol{r}) = \exp\left(-Ds^2|\boldsymbol{r}+\boldsymbol{a}_{\alpha\alpha'}|\right)\frac{\sin\left(s|\boldsymbol{r}+\boldsymbol{a}_{\alpha\alpha'}|\right)}{s|\boldsymbol{r}+\boldsymbol{a}_{\alpha\alpha'}|}. \tag{4}$$

By the Fourier transform of the $\phi(\boldsymbol{r})$, $\eta(\boldsymbol{k})$ is given as follows, where $(\boldsymbol{r}+\boldsymbol{a}_{\alpha,\alpha'})$ is replaced by $\boldsymbol{r}'$,

$$\begin{aligned}\eta(\boldsymbol{k}) &= \int \exp(-Ds^2r')\frac{\sin(sr')}{sr'}\exp(i\boldsymbol{k}\cdot\boldsymbol{r})\mathrm{d}\boldsymbol{r}\\ &= \int \exp(-Ds^2r')\frac{\sin(sr')}{sr'}\exp(i\boldsymbol{k}\cdot\boldsymbol{r}')\\ &\qquad \times\exp(-i\boldsymbol{k}\cdot\boldsymbol{a}_{\alpha\alpha'})\mathrm{d}\boldsymbol{r}'\\ &= \frac{2\pi Ds}{k}\left[\frac{1}{(Ds^2)^2+(s-k)^2}-\frac{1}{(Ds^2)^2+(s+k)^2}\right]\\ &\qquad \times\exp(-i\boldsymbol{k}\cdot\boldsymbol{a}_{\alpha\alpha'}),\end{aligned} \tag{5}$$

k being the absolute value of $\boldsymbol{k}$. Accordingly, by the use of the Poisson sum formula given by Eq. 1,

$$\begin{aligned}I = \sum_{\alpha,\alpha'}\sum_{\nu}{}' f_\alpha f_{\alpha'}\exp(-i\boldsymbol{b}_\nu\cdot\boldsymbol{a}_{\alpha\alpha'})\\ \times\frac{2\pi Ds}{vb_\nu}\left[\frac{1}{(Ds^2)^2+(s-b_\nu)^2}-\frac{1}{(Ds^2)^2+(s+b_\nu)^2}\right],\end{aligned} \tag{6}$$

is derived. The prime over the summation sign denotes omission of the $\boldsymbol{\nu}=(0\ 0\ 0)$ term[9].

Next, let us examine the term $\sum_{\alpha,\alpha'} f_\alpha f_{\alpha'}\exp(-i\boldsymbol{b}_\nu\cdot\boldsymbol{a}_{\alpha\alpha'})$ for the bcc model of carbon tetrachloride. The atoms numbered from 1 to 5 are included in the stoichiometric unit (a molecule) placed at the origin (see Fig. 1). Therefore, the summation for α is over the atoms numbered from 1 to 5, while the summation for α′ is over the atoms numbered from 1 to 10. Let $\boldsymbol{R}$ be the vector which connects the center of the molecule at the origin with that of the nearest neighboring molecule, which in this case is given by

$$\boldsymbol{R} = \left(\frac{a}{2},\frac{a}{2},\frac{a}{2}\right) \tag{7}$$

where a is the lattice constant of the bcc unit cell. Then, we obtain the following relation,

$$\begin{aligned}&\sum_{\alpha=1}^{5}\sum_{\alpha'=1}^{10} f_\alpha f_{\alpha'}\exp(-i\boldsymbol{b}_\nu\cdot\boldsymbol{a}_{\alpha\alpha'})\\ &= \sum_{\alpha=1}^{5}\sum_{\alpha''=1}^{5} f_\alpha f_{\alpha''}\exp(-i\boldsymbol{b}_\nu\cdot\boldsymbol{a}_{\alpha\alpha''})[1+\exp(-i\boldsymbol{b}_\nu\cdot\boldsymbol{R})],\end{aligned} \tag{8}$$

where the first term in parentheses corresponds to the correlation among the atoms in the central molecule (1—5) and where the second term is that between the two molecules in a unit cell (1—5 and 6—10 in Fig. 1). With a little manipulation of Eq. 8, we have

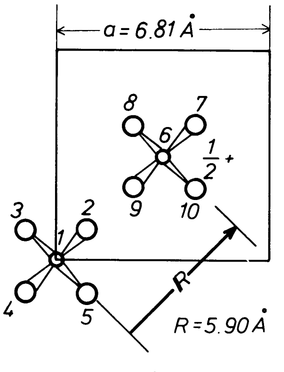

Fig. 1. The arrangement of carbon tetrachloride molecules in a bcc unit cell.

$$\begin{aligned}&\sum_{\alpha,\alpha'} f_\alpha f_{\alpha'}\exp(-i\boldsymbol{b}_\nu\cdot\boldsymbol{a}_{\alpha\alpha'})\\ &= [f_{\mathrm{C}}^2+4f_{\mathrm{Cl}}^2+\sum_{i=2}^{5}2f_{\mathrm{C}}f_{\mathrm{Cl}}\cos(\boldsymbol{b}_\nu\cdot\boldsymbol{a}_{\mathrm{C-Cl}(i)})\\ &\quad+\sum_{\substack{j,k=2\\ j>k}}^{5}2f_{\mathrm{Cl}}^2\cos(\boldsymbol{b}_\nu\cdot\boldsymbol{a}_{\mathrm{Cl}(j)-\mathrm{Cl}(k)})]\\ &\quad\times[1+\exp(-i\boldsymbol{b}_\nu\cdot\boldsymbol{R})].\end{aligned} \tag{9}$$

Finally, we must consider the correction for the term of $\boldsymbol{a}_\mu=\boldsymbol{0}$. In Eqs. 3 and 6, the mean-square deviations of the intermolecular distances are also given by the Prins relation. It is necessary to replace them by the intramolecular mean-square amplitudes, which are known more exactly. Then, the correction term, $\Delta I_{\mathrm{intra}}$, becomes

$$\begin{aligned}\Delta I_{\mathrm{intra}} &= 8f_{\mathrm{C}}f_{\mathrm{Cl}}[\exp(-l_{\mathrm{C-Cl}}{}^2s^2/2)\\ &\quad-\exp(-Dr_{\mathrm{C-Cl}}s^2)]\frac{\sin(sr_{\mathrm{C-Cl}})}{sr_{\mathrm{C-Cl}}}\\ &\quad+12f_{\mathrm{Cl}}^2[\exp(-l_{\mathrm{Cl-Cl}}{}^2s^2/2)\\ &\quad-\exp(-Dr_{\mathrm{Cl-Cl}}s^2)]\frac{\sin(sr_{\mathrm{Cl-Cl}})}{sr_{\mathrm{Cl-Cl}}},\end{aligned} \tag{10}$$

where $l_{\mathrm{C-Cl}}$ and $l_{\mathrm{Cl-Cl}}$ are the root mean-square amplitudes for the distances $r_{\mathrm{C-Cl}}$ and $r_{\mathrm{Cl-Cl}}$, respectively.

From Eqs. 6, 9, and 10, the total coherent intensity of the bcc model for carbon tetrachloride is given by

$$\begin{aligned}I &= \frac{1}{v}\sum_{\nu}{}'\frac{2\pi Ds}{b_\nu}\left[\frac{1}{(Ds^2)^2+(s-b_\nu)^2}-\frac{1}{(Ds^2)^2+(s+b_\nu)^2}\right]\\ &\quad\times[f_{\mathrm{C}}^2+4f_{\mathrm{Cl}}^2+\sum_{j=2}^{5}2f_{\mathrm{C}}f_{\mathrm{Cl}}\cos(\boldsymbol{b}_\nu\cdot\boldsymbol{a}_{\mathrm{C-Cl}(j)})\\ &\quad+\sum_{\substack{j,k=2\\ j>k}}^{5}2f_{\mathrm{Cl}}^2\cos(\boldsymbol{b}_\nu\cdot\boldsymbol{a}_{\mathrm{Cl}(j)-\mathrm{Cl}(k)})][1+\exp(-i\boldsymbol{b}_\nu\cdot\boldsymbol{R})]\\ &\quad+\Delta I_{\mathrm{intra}}.\end{aligned} \tag{11}$$

For $\boldsymbol{b}_\nu$ expressed by $\left(\frac{2\pi h}{a},\frac{2\pi k}{a},\frac{2\pi l}{a}\right)$, the value in parentheses $[1+\exp(-i\boldsymbol{b}_\nu\cdot\boldsymbol{R})]$ is equal to 2 when $h+k+l$ is even and zero when $h+k+l$ is odd. This corresponds to the extinction rule of the bcc lattice.

In practical calculation the following values were used; the intramolecular parameters, $r_{\mathrm{C-Cl}}$, $r_{\mathrm{Cl-Cl}}$, $l_{\mathrm{C-Cl}}$, and $l_{\mathrm{Cl-Cl}}$, were the values obtained by means of gas electron diffraction,[12] the lattice constant of the bcc unit cell was 6.81,[5] and D was 0.036 Å.[5] (Note that the definition of D in Ref. 5 is that of $2D$ of the present paper.)

Results and Discussion

The results of the application to carbon tetrachloride based on the bcc local lattice structure are shown in Fig. 2(b). For comparison, the results of the "real space expansion" are shown in Fig. 2(a).[5] The total coherent intensity is adopted, because it distinguishes the discrepancy between the experimental and the simulated intensities in the small-s region. The dots represent the experimental intensities,[13] while the monotonically decreasing broken curves are the calculated self-scattering intensities. The solid curve in Fig. 2(a) is the calculated intensity based on the bcc model.[5] The agreement is very good up to $s \simeq 20$ Å^{-1}, although not shown in this figure. The intensity in the small-s region ($s < 1.2$ Å^{-1}), however, shows discrepancies, which are due to the inherent ghost peaks of the "real space expansion."

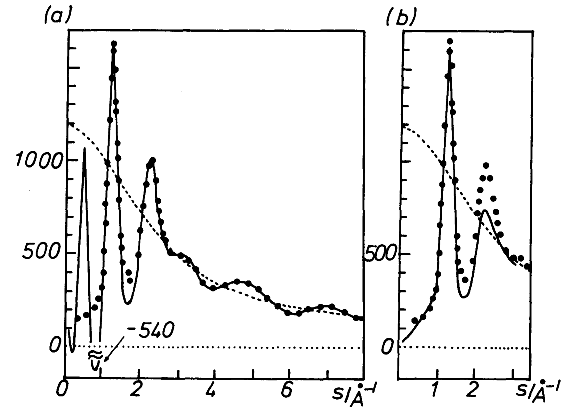

Fig. 2. Total coherent intensity (in electron unit) of liquid carbon tetrachloride. The curves described by dots are experimental intensity.[13)
(a): The solid curve is the calculated intensity based on the bcc model by the use of the "real space expansion."
(b): The solid curve is the calculated intensity based on the bcc model by the use of the "reciprocal space expansion."

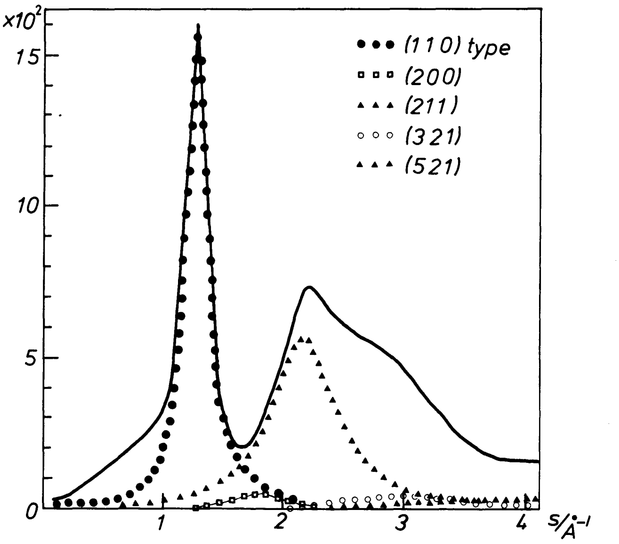

Fig. 3. contribution of each reciprocal lattice point. The solid curve is the calculated total coherent intensity. The Lorentzian-like curves are contributions from {1 1 0}, {2 0 0}, {2 1 1}, {3 2 1}, and {5 2 1} lattice points, respectively. The difference between the solid curve and the sum of the contributions from the reciprocal lattice points is the contribution of $\Delta I_{\mathrm{intra}}$.

The solid curve in Fig. 2(b) is the intensity calculated by the use of the "reciprocal space expansion" based on the bcc model. In this calculation reciprocal lattice points up to $\boldsymbol{\nu}=(6\ 0\ 0)$ ($b_\nu = 5.54$ Å^{-1}) are included. The calculated curve is in very good agreement with the experimental intensity in the region of s less than 1.5 Å^{-1}. However, the convergence becomes worse with the increase in the scattering parameter, s, contrary to the case with the "real space expansion."

Figure 3 shows the contribution of each reciprocal lattice point to the calculated total coherent intensity (solid curve). The Lorentzian-like curve with the peak at $s \simeq 1.3$ Å^{-1} is the contribution from the {1 1 0} reflections, which contain 12 equivalent reflections with the magnitude of b_ν 1.305 Å^{-1}. The next peak is due to the {2 0 0} reciprocal points, whose contribution is relatively small in this bcc structure. It should be noticed that the main feature of the total coherent intensity is almost entirely determined by the {1 1 0} and the {2 1 1} reflections; that is, the former form the first peak at $s=1.3$ Å^{-1}, while the latter form the second peak at $s=2.3$ Å^{-1}. The difference between the solid curve and the sum of the contributions from the reciprocal lattice points in the range of $s<1$ Å^{-1} and $s>2$ Å^{-1} is the contribution of $\Delta I_{\mathrm{intra}}$ (see Eq. 11). As the magnitude of b_ν increases, the widths of the Lorentzian-like curves rapidly become wider. This corresponds to the fact that the convergence becomes worse with the increase in the scattering parameter, s. By the reciprocal space expansion, the intensities for s values ranging up to about 2 Å^{-1} can be well simulated. For some molecular liquids, the scattering intensity near $s \approx 0$ Å^{-1} has a finite value. This is caused by the density fluctuation of the liquids.[14] This fluctuation was not included in the present formulation by the local lattice structure model. Thus, the calculated intensity is not necessarily in agreement with the experimental values at $s \approx 0$ Å^{-1} for a liquid with large density fluctuations.[15]

With the use of both the "reciprocal space expansion" and the "real space expansion", the observed scattering intensity of liquid carbon tetrachloride is satisfactorily accounted for over the whole range of the parameter s on the basis of the bcc local lattice model.

In simulation studies for the diffraction intensity of liquids, there have been many cases where the calculated intensities can not simulate the observed intensities. In these cases, there are two possibilities; one is that the structure model itself is not adequate, and the other is that the ghost peaks because of the inevitable result of the "real space expansion" are disturbing the inherent peaks. In this paper, the problem of the ghost peaks of the "real space expansion," which appears in the small-s region is solved by the introduction of the "reciprocal space expansion." By the use of both expansions, the application of the "local lattice structure model" becomes more promising in the study of the structure of liquids.

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