How Can We Determine a Non-crystalline Structure from Diffraction Data?

The determination of liquid and amorphous structures from diffraction data is by no means trivial. Diffraction data are given as a function of momentum transfer, or equivalently, wavenumber, *k*. Hence, to extract information as to structures it is necessary to convert the data from the wavenumber space to the real space. Since the diffraction data obtained from diffraction experiments yield structural information in a limited *k* range, we have to best estimate the missing information outside the *k* range so as to minimize the effects of finite truncation as far as an ordinary Fourier inversion is adopted. In this article, we report a new method for determining non-crystalline structures that relies on the maximum entropy principle.

We chose a molecular liquid, SnI_4, as a sample for developing the new method, since the intra-molecular atomic configuration of SnI_4 is well-known and we are not aware of any structural data on liquid SnI_4 at ambient pressure. The high-energy synchrotron X-ray diffraction measurement on liquid SnI_4 was performed at the high-energy X-ray diffraction beamline **BL04B2**. The scattered X-ray intensity from the sample in a glass tube measured at 433 K and that of an empty tube are shown by the black and red lines, respectively, in the inset of Fig. 1. The normalized structure factor, $S(k)$, is shown as a blue line in Fig. 1. Note that the oscillation originating from intra-molecular correlation is significant beyond 20 $Å^{-1}$. The feature of the structure factor can be satisfactorily captured by our molecular dynamics (MD) simulations [1] (as shown in the lower inset), in which the molecules were treated as rigid tetrahedra interacting via the van der Waals potential acting between the vertices. This modeling is justified because the central tin atom within a molecule is completely enveloped by the surrounding iodine atoms located at the vertex sites so that the iodine is electronically regarded as an inert gas atom. The first little peak observed at around $k = 1$ $Å^{-1}$, which is characteristic to the system, was found, by RISM calculations to the model, to be ascribed to the Sn-Sn correlation [1].

The distribution of molecules in real space as a function of radial distance, *r*, called the reduced radial distribution function (RRDF), $G(r)$, can be derived from $S(k)$ by a Fourier inversion, as mentioned above. The radial distribution function (RDF), which statistically describes how molecules are packed around one another in the radial direction, will be obtainable from the RRDF if the density of the liquid is known. Although our wavenumber window is as wide as ~ 25 $Å^{-1}$, significant oscillation can be observed up to a maximum *k* value of 25 $Å^{-1}$ (see Fig. 1), suggesting that ordinary inversion would produce spurious peaks in the RRDF.

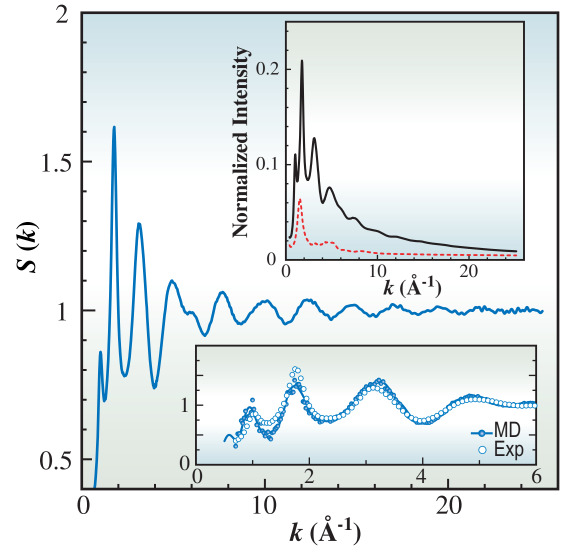

Fig. 1. Structure factor of liquid SnI_4 at 433 K and ambient pressure plotted as a function of wavenumber. The upper inset shows the normalized scattered X-ray intensities of the sample contained in a glass tube (solid black line) and from an empty tube (dashed red line). The lower inset shows a comparison of the main part of the structure factors obtained through the experiment (open circles) and our MD simulations (closed circles).

To prevent artifacts from appearing in the RRDF, a powerful inversion technique based on the maximum entropy method (MEM) has been newly devised. Here, the new method is outlined (refer to Fig. 2) emphasizing the striking differences from existing MEMs (summarized in [2]). The new inversion

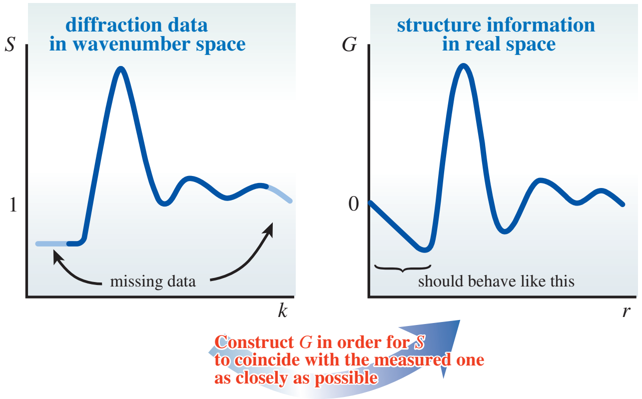

Fig. 2. Schematic diagram of the conversion from structure factor, $S(k)$, to RRDF, $G(r)$. The former information is not necessarily complete. The latter is estimated using the MEM in such a way that S predicted by G mimics the measured one as closely as possible.

process consists of two steps. In the first step, the MEM is used to transform $S(k)$ to $G(r)$ by making an unbiased estimation of the latter so that the structure factor approaches the observed $S(k)$ as closely as possible. The resultant $G(r)$ of this step obtained from $S(k)$ in Fig. 1 is delineated by a pink line in Fig. 3. The anomalies appearing below the first peak are due to systematic errors contained in $S(k)$, which were not removed even by the MEM. The true RRDF, however, should have a linear dependence on r around the region with a slope being proportional to the density. Kaplow, Strong and Averbach (KSA) claimed that an observed $S(k)$ involves ambiguity due to the finiteness of k and suggested that $S(k)$ should be modified in such a way that $G(r)$ has an initial linear part [3]. In the second step, our MEM can naturally incorporate KSA's suggestion by self-consistently determining the density within the procedure. To this end, two useful mathematical relationships were derived in which the RRDF is directly or indirectly connected with the density [2]. It becomes clear from these expressions for a reliable estimate of the density to widen the accessible k range in the experiments. The high-energy synchrotron X-ray diffraction measurements play an essential role in this context. The blue line in Fig. 3 shows the final RRDF resulting from the second step. The mass density was estimated from the initial gradient to be 3.0 g/cc, which almost coincides with the value obtained from our MD simulations, as evident from the excellent agreement between the experimental and simulated (light blue line) RRDFs. (Since SnI_4 molecule was modeled as a rigid tetrahedron in the MD simulations, the first and second peaks, which exhibit the Sn-I and I-I intra-molecular correlations, respectively, assume the form of a delta function.) The principal peaks in the RDF obtained from the final RRDF assuming the aforementioned value for the density are at 2.67 and 4.35 Å. The ratio of these distances, 1.63, implies that the liquid is truly a molecular liquid, consisting of molecules with a regular tetrahedral symmetry. For further discussion on the details of the microscopic structure, refer to [1,2].

From the above explanation, it is evident that our MEM is different from the existing MEMs in the following respects: (i) our target distribution for the maximum entropy estimator is not the RDF but the RRDF, which is not positive definite (that is, the entropy cannot be defined for the latter without an ingenious trick); (ii) the density is assumed to not be given at the outset. Finally, it should be stressed that the RRDF thus obtained through the least-biased estimation is not the final product but an initial trial, which must be interpreted using other means such as MD simulations and RISM calculations. This technique was successfully applied to the analysis of a liquid under high temperature and high pressure [4], where there are significant limitations in diffraction data, e.g., attainable k range and the reliability of background subtraction.

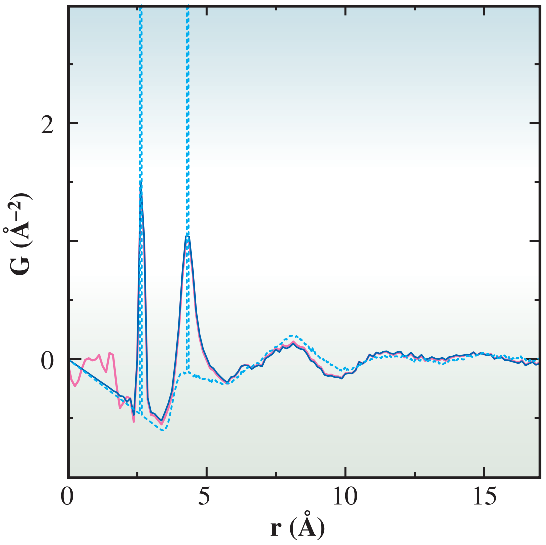

Fig. 3. RRDFs obtained using the MEM inversion in the first step (pink line) and the built-in correction procedure in the second step (blue line), and the RDF obtained from the MD simulations (light blue line) plotted against radial distance.

Kazuhiro Fuchizaki [a,b]

[a] Department of Physics, Ehime University
[b] Theoretical and Computational Molecular Science,
Institute for Molecular Science

E-mail: fuchizaki@phys.sci.ehime-u.ac.jp

References
[1] K. Fuchizaki *et al.*: to be published.
[2] *K. Fuchizaki, S. Kohara, Y. Ohishi and N. Hamaya: J. Chem. Phys.* ***127*** *(2007) 064504.*
[3] R. Kaplow *et al.*: Phys. Rev. **138** (1965) A1336.
[4] K. Fuchizaki *et al.*: to be published.