Visualization of Density Fluctuation of Supercritical Carbon Dioxide Using Reverse Monte Carlo Simulation

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It is well known that carbon dioxide (CO_2) molecules aggregate themselves and make clusters around a critical point (31.0 °C, 7.38 MPa, 0.468 g/cm^3). The aggregate property is considered to be an important key for understanding many characteristic features of supercritical CO_2 as a solvent. Therefore, clarification of the cluster structure in detail is absolutely necessary. Generally, small-angle neutron or X-ray scattering (SANS or SAXS) methods are used for observing the density fluctuation structure of supercritical CO_2. Although, real-space information of the cluster is very important to investigate the structural property of the cluster, it had been difficult or almost impossible to visualize the structure by previous analyzing methods. And so, to accomplish the visualization of the density fluctuation, we have tried to apply a Reverse Monte Carlo (RMC) simulation to a SANS data observing the supercritical CO_2.

The SANS experiment was performed using SANS-U of the Institute for Solid State Physics, the University of Tokyo. For measurement, the supercritical fluid (SCF) system installed at KUR-SANS is used with modification for applying to the SANS-U. In the RMC simulation, the system consists of 50 × 50 × 50 cells which are simple cubic of 5.53^3 Å^3. Up to four CO_2 molecules can be entered in each cell. Initially, the molecules are randomly put into the cells and then a scattering intensity is calculated. Next, one of the molecules randomly chosen is moved to another cell and the scattering intensity is also calculated. When the calculated intensity after moving comes closer to the experimental one, this movement is accepted. This procedure is iterated until the calculated intensity reproduces the experimental one.

Figure 1 (a) shows a SANS profile of the supercritical CO_2 at a state of 38 °C, 8.64 MPa, 0.49 g/cm^3. A correlation length which can characterize the size of cluster in this state is 16.4 Å. A solid line in the Fig. 1 (a) is the calculated scattering intensity obtained by applying the RMC simulation to the observed one. It can be confirmed that the experimental result is well reproduced by the RMC simulation. The real-space image derived from the RMC result is shown in Fig. 1(b). The structure of the density fluctuation of CO_2 molecules can be well expressed.

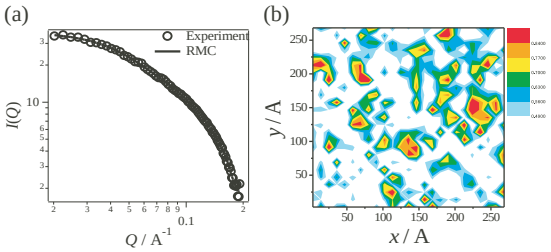

Fig. 1. (a) Open circles and a solid line indicate the experimental SANS intensity and the calculated one by the RMC simulation, respectively. (b) Real-space image of the supercritical CO_2 derived from the RMC simulation.