

# Analysis to obtain precise density fluctuation of supercritical fluids by small-angle X-ray scattering

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## Abstract

A procedure of analysis for small-angle X-ray scattering (SAXS) data has been established to obtain density fluctuation of supercritical fluids near the critical point. It is indispensable for the certain analysis to utilize both of high-quality SAXS data measured under stable thermodynamic condition and accurate  $P$ – $\rho$ – $T$  data in supercritical region. As a standard example, SAXS measurements have been performed for supercritical CO<sub>2</sub>, which is a suitable sample satisfying the condition for both experiment and analysis. The measurements were carried out along four isothermal conditions at reduced temperature of  $T_r = T/T_c = 1.020, 1.022, 1.043$  and 1.064. Comparing the experimental density fluctuation with calculated one from the most reliable equation of state, the differences are within 8% at most.

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## 1. Introduction

Supercritical fluids have attracted much attention because of high operability with continuous change of density over wide range and specific behaviors for some properties. Basic studies on properties for supercritical fluids are essential for their wide and active utilization in applied technologies. It has been considered that special properties of supercritical fluids are closely related to their structural fluctuation [1–5].

Density fluctuation and correlation length are quantitative expressions of the static structural fluctuation from the standpoints of number of molecules and size of the molecular aggregates, respectively. Especially, the density fluctuation is the most fundamental quantity for supercritical fluids. It is well known that the density fluctuation diverges exponentially as approaching the

critical point [6]. Moreover, it is shown that the density fluctuation forms a ridge in the supercritical region, when the contour map of their values is drawn in phase diagram [4,5]. The “ridge” is a locus of the points where the values of the density fluctuation become maximum in isothermal changes. The ridge almost smoothly connects with the rectilinear diameter at the critical point in a density–temperature phase diagram, and the ridge drawn on a pressure–temperature phase diagram runs in the supercritical region as if it is an extension of the coexistence curve of gas and liquid. The physical meaning of these behaviors has been recently discussed in detail [7]. The ridge for the correlation length also exists, and it exactly overlaps with that for the density fluctuation in the phase diagrams. By relating the ridges to physicochemical properties of supercritical fluids, it is ensured that the ridges agree with loci of extrema for values which are related to the second derivative of the Gibbs or Helmholtz free energy [4,5,7]. From the viewpoint of utilization, much interest is attracted on the

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solubility power and chemical reactions in supercritical fluids. The rate of increase in solubility along an isotherm becomes maximum on the ridge. In many cases, the rate constants or equilibrium ones of chemical reactions in supercritical fluids show singular behavior on the ridge such as maximum, minimum or inflection points. In such ways, the density fluctuation is important parameter to discuss the properties of supercritical fluids and their examples have been described in our previous papers [4,5,7].

The density fluctuation and the correlation length are obtained by small-angle X-ray scattering (SAXS) measurements. The SAXS experiments for typical neat substances were already reported, namely  $\text{CO}_2$  [8,9],  $\text{CHF}_3$  [10],  $\text{C}_2\text{H}_4$  [11],  $\text{C}_6\text{H}_6$  [12] and  $\text{H}_2\text{O}$  [13]. By these investigations, it is found that the density fluctuation and the normalized correlation length by respective molecular sizes show fairly good agreement among them except for  $\text{H}_2\text{O}$ . It is roughly clarified that the principle of corresponding state is applicable for the structural fluctuation and the exception refers to the substances with hydrogen bonding [12]. As a result, the universality in the structural fluctuation is found from the discussion on individuality of above-mentioned substances [4,5,7–13]. For more minute discussion on the universality, the critical comparison with the results among several substances should be made with reliable values.

We have carried out SAXS experiments on above-mentioned supercritical fluids and analyzed the intensity data in trial and error [8–13]. The aim of the present study is to establish the procedure of the analysis to obtain the density fluctuation from SAXS intensity. We discussed the availability of the analysis and the reliability of the density fluctuation by SAXS measurements. The sample is supercritical  $\text{CO}_2$ . For supercritical  $\text{CO}_2$ , experimental treatment was improved in comparison with previous study [8,9] and an accurate EOS has been reported [14]. It satisfied the necessary condition for the certain analysis.

## 2. Experimental

### 2.1. Improvement of the sample cell

For the SAXS measurements to obtain the accurate values of the density fluctuation near the critical point, it is very important to keep the sample stable and to uniform the thermodynamic condition. In the present experiment, the sample cell for SAXS measurements in the previous paper [10] was improved to obtain higher-quality data than the previous studies [8,9].

Fig. 1 shows the design of the sample cell. The cell consists of three parts: a main body which includes a water-jacket to control temperature of the sample, a lid with threaded holes for high pressure piping, and a

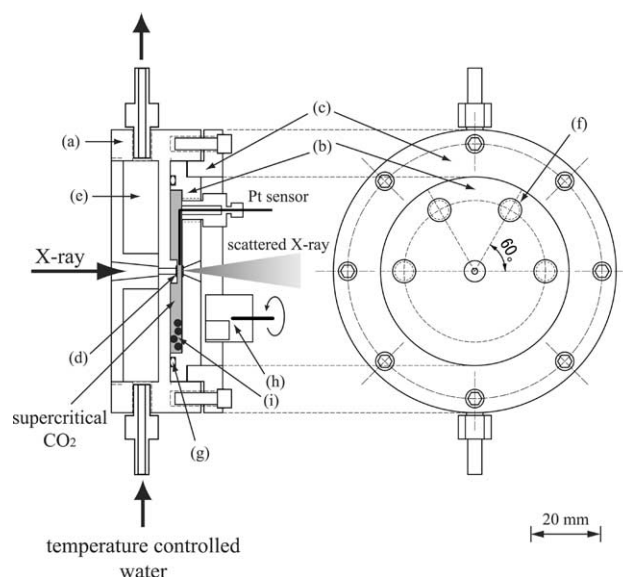


Fig. 1. Cross-section of the sample cell: (a) main body, (b) lid, (c) lid holder, (d) diamond disk for window, (e) water-jacket, (f) threaded hole, (g) silicone o-ring, (h) magnetic stirrer, and (i) iron balls.

flange-type holder for fixing the above-mentioned lid to the main body. All the parts are made of SUS 316. The internal volume of the cell is about 20 ml. Windows, through which X-rays pass, are made of two diamond disks, and they are fixed by adhesive on the main body and on the lid, respectively. The sample was injected into the cell by using a high performance liquid chromatography pump (L-7110 of Hitachi Co., Ltd.) and the value of pressure was monitored with a strain gauge (PG-200KU of Kyowa Dengyo Co., Ltd.) backed by a meter (DPM-700B of Kyowa Dengyo Co., Ltd.). To keep the temperature of the sample constant, temperature-controlled water was circulated through the water-jacket embedded in the body of the sample cell. Because the temperature of the sample was controlled by one-side heating with the water-jacket and the internal volume was large, the convection due to thermal gradient might arise, which would prevent the accurate measurement of the density fluctuation. For the improvement, some devices were adopted as follows. (1) Some iron balls were set in the sample cell to stir the sample by a magnetic stirrer from outside. For the purpose, the lid with area for setting the magnetic stirrer was newly made as shown in Fig. 1. (2) The sample cell was enveloped by thermal insulator to keep the sample temperature stable and to uniform the thermodynamic condition. (3) The values of temperature for the sample were measured down to two places of decimals with a four-wire Pt sensor (GR-0708 of Hayashi Dengyo Co., Ltd.) and the stability and uniformity were checked during each runs of measurements. As a result, deviations of the temperature and the pressure during a measurement were kept within  $\Delta T = \pm 0.02$  K and  $\Delta P = \pm 0.01$  MPa, respectively.

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