Bayesian framework for analyzing adsorption processes observed via time-resolved X-ray diffraction

In recent years, data-driven methods have attracted considerable attention in the field of materials science. One representative method is Bayesian inference, which estimates the posterior probability distribution of parameters θ from experimental data D as $p(\theta|D)$. Conventional nonlinear least-squares fitting corresponds to point estimation; however, Bayesian inference estimates the probability distribution of possible parameter values, thereby enabling the evaluation of the estimation accuracy based on the shape and width of the distribution. We can also naturally incorporate knowledge already known from previous research into Bayesian inference as a prior probability distribution. Furthermore, Bayesian inference enables the selection of the most plausible model among possible models, such as fitting functions, by evaluating the posterior probability $p(M|D)$ for each model M. By replacing conventional nonlinear least-squares fitting with Bayesian inference, the amount of information extracted from experimental data increases considerably, leading to a better understanding of materials.

Nagata and Tokuda developed the Bayesian framework for analyzing multipeak spectra [1,2]. In materials science, this method has been utilized to analyze synchrotron radiation X-ray spectra [3]. Previous studies focused on one-dimensional spectra, whereas we established a Bayesian framework for multiple spectra, such as time-series spectra. We demonstrate the effectiveness of our framework by investigating the gas-adsorption process observed via time-resolved X-ray diffraction (Tr-XRD) [4].

We selected a typical metal-organic framework as a sample, a nanoporous Cu coordination polymer [{$Cu_2(pzdc)_2(pyz)$}$_n$] (pzdc = pyrazine-2,3-dicarboxylate; pyz = pyrazine)] (CPL-1). The Ar gas adsorption process was observed using Tr-XRD at SPring-8 **BL02B2**. XRD patterns were measured continuously from $t = 0$ with an exposure time of 0.333 s. During the measurements, Ar gas molecules were injected into the sample cell at $t = 6.327$ s (t_s). We focused on the 031 reflection and analyzed the XRD patterns from 7.70° to 8.22°.

Conventional analysis based on nonlinear least-squares fitting has several limitations. Because of the poor signal-to-noise ratio of the Tr-XRD data, conventional analysis substitutes t_s for the adsorption start time (t_0). A time lag inevitably exists between the gas injection and start of adsorption, leading to a misunderstanding of the adsorption dynamics. In addition, evaluating time-evolution models describing the time variation of the diffraction peaks throughout the adsorption process is difficult; thus, a model must be determined prior to analysis, even when several model candidates exist. We aim to overcome these problems using Bayesian inference.

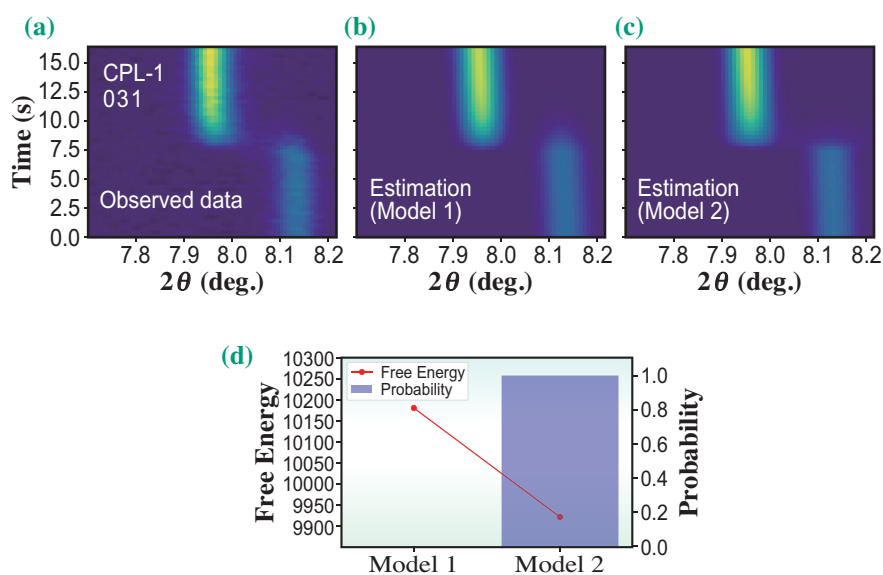Figures 1(a-c) show the color maps of the observed Tr-XRD patterns and estimated results using

Fig. 1. **(a-c)** Color maps of the observed time-resolved X-ray diffraction patterns and estimated results with Model 1 and Model 2. **(d)** Comparison between Bayes free energies of Model 1 and Model 2. The realization probability of each model is also shown. [5]

Table 1. Time-evolution models

	Model 1	Model 2
Peak area	KJMA equation	KJMA equation
Peak position	Linear	Linear
Peak width	Constant	Exponential

Model 1 and Model 2, i.e., the different time-evolution models in Table 1. Both models appeared to have good qualitative agreement with the observed data. To quantify the realization probability of each model, we calculated $p(M|D)$ using the Bayes free energy, as shown in Fig. 1(d). Because the Bayes free energy of Model 2 was approximately 300 lower than that of Model 1, $p(M=2|D)$ was almost equal to 1. Therefore, the Bayesian model selection suggested that Model 2 is considerably better than Model 1.

Based on the selected model (Model 2), we obtained the posterior probability distributions of t_0 and the rate constant (κ), as shown in Fig. 2. Using one standard deviation (1σ) of each distribution as a measure of accuracy, the adsorption start time was estimated to be $t_0 = 7.4461 \pm 0.0287$ s. The accuracy

was one order of magnitude greater than that of the conventional analysis (~0.333 s). The probability distribution also indicated that the probability of t_0 and t_s matching was almost zero, implying that the value of t_0 deviated significantly from t_s in this experiment. Because conventional analysis substitutes t_s for t_0, such a large time lag leads to a misunderstanding of the adsorption dynamics. The rate constant was estimated to be $\kappa = 0.6192 \pm 0.0235$ 1/s, whereas it was estimated to be $\kappa = 0.1535$ 1/s in the conventional analysis. We consider this difference to be owing to the time lag between t_s and t_0.

In this study, we established a Bayesian framework for analyzing the adsorption processes and demonstrated the effectiveness of our framework by investigating the Ar gas adsorption process of CPL-1. Bayesian analysis enables the selection of the most plausible model on the basis of the experimental data. The posterior probability distribution represents a more accurate estimation than the conventional analysis. Our framework can be applied to other dynamic processes, such as chemical reactions, by modifying the time-evolution models. Hence, Bayesian analysis is expected to be utilized in various areas of materials science research.
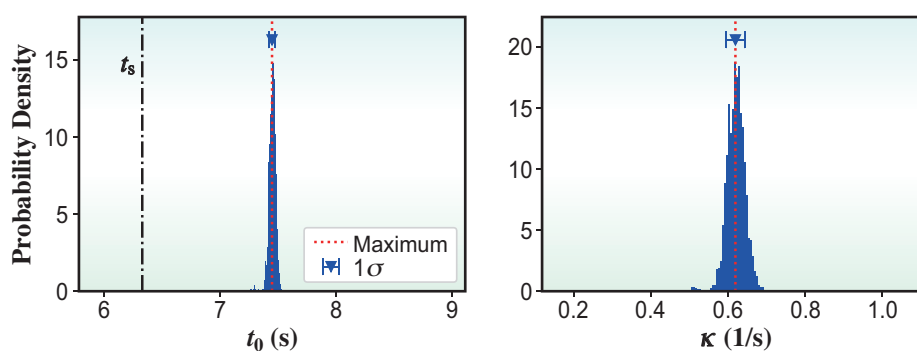

Fig. 2. Posterior probability distributions of the adsorption start time (t_0) and rate constant (κ). The dotted line and error bar correspond to the maximum and one standard deviation (1σ) of the distribution, respectively, and the dash-dotted line denotes the gas-shot time (t_s). [5]

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