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Bayesian optimal experimental design for photoionization mass spectrometry experiments

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Outline

- Overview of the photoionization mass spectrometry experiment
- Bayesian optimal experimental design
- Challenges associated with high-dimensional models
  - identifying a low-dimensional representation
- Example
- Conclusion & Future work

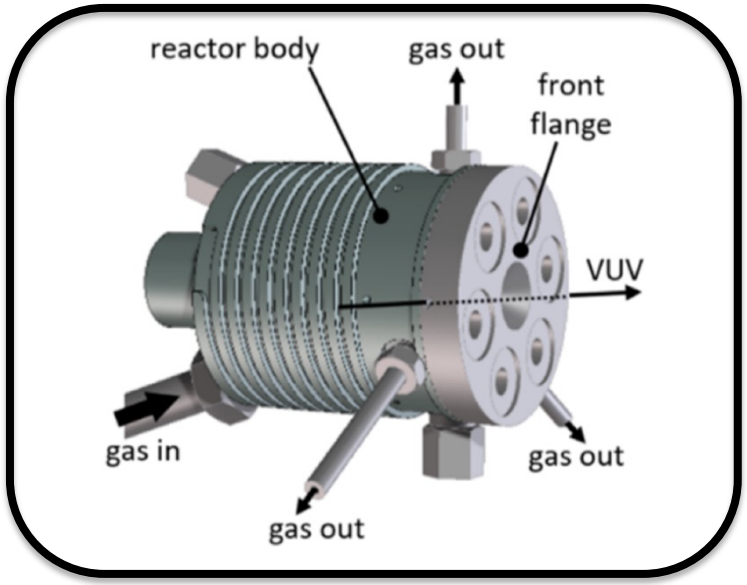
Experimental overview

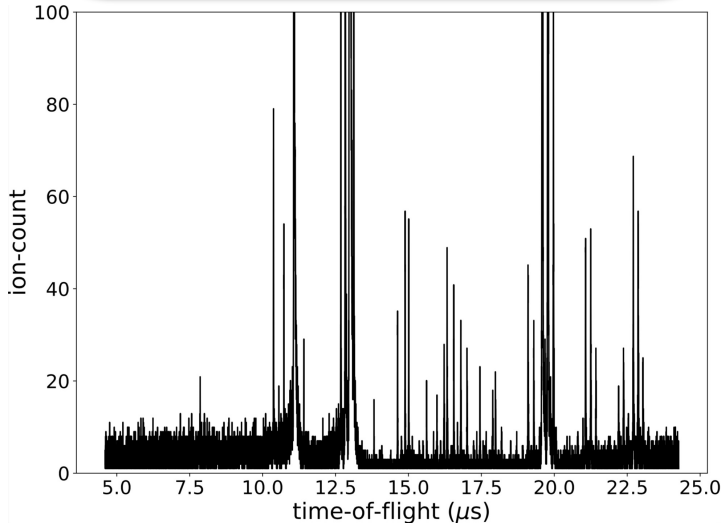
Goal: study the low-temperature oxidation of propane

- Measure the evolution of highly reactive intermediates and products

High-pressure photolysis reactor (HPR) experiment

- Premixed mixture flows into a constant pressure reactor
- Photolysis laser fires instantaneously irradiating the gas mixture
  - Chemical precursor breaks down initiating reactions
- Gas mixture exhausts out, sampled by a synchrotron tunable vacuum-ultraviolet (VUV) photoionization mass spectrometer
  - Measurement of time-of-flight mass spectrum





Time-of-flight mass spectrum at a fixed VUV energy (11.3 eV) and kinetic time (60 ms)

L. Sheps, I. Antonov, K. Au. Sensitive mass spectrometer for time-resolved gas-phase chemistry studies at high pressures. *The Journal of Physical Chemistry A* 123.50 (2019) 10804-10814.

Modeling the HPR experiment

Data model:

$$z(\boldsymbol{d}, \boldsymbol{x}) = \xi(\boldsymbol{d}, \boldsymbol{x}) + \epsilon(\boldsymbol{x})$$
$$z(\boldsymbol{d}, \boldsymbol{x}) = f(\boldsymbol{\theta}, \boldsymbol{d}, \boldsymbol{x}) + \delta(\boldsymbol{x}) + \epsilon(\boldsymbol{x})$$
$$\boldsymbol{x} = [\tau, t, E]$$
$$\delta(\boldsymbol{x}) \sim GP(\mu_\delta(\boldsymbol{x}), \Sigma_\delta(\boldsymbol{x}, \boldsymbol{x}')), \; \epsilon(\boldsymbol{x}) \sim \mathcal{N}(0, s(\boldsymbol{x})^2)$$

$\boldsymbol{d}$: design conditions

$\boldsymbol{\theta}$: model parameters

$\boldsymbol{x}$: spatial/temporal coordinates

$z(\boldsymbol{d}, \boldsymbol{x})$: ion-count data

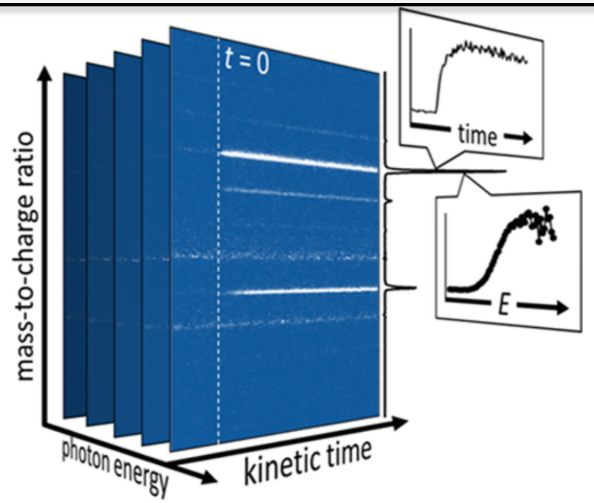
$\xi(\boldsymbol{d}, \boldsymbol{x})$: true physical process

$f(\boldsymbol{\theta}, \boldsymbol{d}, \boldsymbol{x})$: physics and instrument model

$\delta(\boldsymbol{x})$: model error

$\epsilon(\boldsymbol{x})$: observation noise

- **Physics model**
  - Zero-dimensional reactor
- **Chemical model**
  - C0-C3 mechanism, Miller et al. 2021
    - 171 species / 1143 reactions
- **Instrument model**
  - Maps species concentrations to ion counts
  - Spectrum peaks are idealized with Gaussian



Experimental measurement tensor

$z(\boldsymbol{d}, \boldsymbol{x}) \in \mathbb{R}^{25000 \times 240 \times 85}$

Miller et al., Combustion chemistry in the twenty-first century: Developing theory-informed chemical kinetics models. *PECS* (2021).

Oreluk et al., Bayesian model calibration for vacuum-ultraviolet photoionisation mass spectrometry. *Combustion Theory and Modelling* (2022).

Motivation

- Identify key operating conditions $\boldsymbol{d}$ to study specific chemical rate constant measurements (model parameters $\boldsymbol{\theta}$)

$$\boldsymbol{d} = \{T, p, \chi_{C_3H_8}, \chi_{O_2}, \chi_{pre}\}$$

Why is this important?

- Operation of the real experiment is costly and laborious
  - Initial setup time for the apparatus
  - Daily calibration experiments
- Limited time to run experiments
  - Advanced Light Source, Lawrence Berkeley National Laboratory

Bayesian optimal experimental design

Objective

Find a set of experimental conditions that maximizes the expected utility $U(d)$

- Utility function models and compares the desirability of outcomes
- Target experiments to learn specific chemical rate constant measurements

$$d^* = \arg\max_{d \in \mathcal{D}} U(d)$$

where,

$$U(d) = \int_{y \in \mathcal{Y}} \int_{\theta \in \Theta} u(y, d, \theta) p(\theta, y|d) \mathrm{d}\theta \mathrm{d}y$$

$$= \int_{y \in \mathcal{Y}} \int_{\theta \in \Theta} u(y, d, \theta) p(\theta|y, d) p(y|d) \mathrm{d}\theta \mathrm{d}y$$

Notation

d : design conditions

θ : model parameters

y : data

D.V. Lindley, On a measure of the information provided by an experiment, *The Annals of Mathematical Statistics* 27 (1956) 986–1005.
Kathryn Chaloner and Isabella Verdinelli, Bayesian experimental design: A review. *Statistical Science* (1995) 273-304.

Choice of utility function

Select a utility function that reflects the goals of our experiment

- Parameter inference
  - Information gain of an experiment is closely related to minimizing the parameter uncertainty
  - Kullback-Leibler divergence can be used to measure what we can learn from the experimental data

$$u(y, d, \theta) = D_{\mathrm{KL}}(p(\theta|y, d)||p(\theta)) = \int p(\theta|y, d) \log \left[\frac{p(\theta|y, d)}{p(\theta)} \right] \mathrm{d}\theta$$

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Nested Monte Carlo

$$U(d) \approx \frac{1}{N} \sum_{i=0}^{N} \left[\log p(y^{(i)}|\theta^{(i)}, d) - \frac{1}{M} \sum_{j=0}^{M} \log p(y^{(i)}|\theta^{(j)}, d) \right]$$

T. Rainforth et al., On nesting Monte Carlo estimators, *International Conference on Machine Learning*. PMLR, 2018.
K.J. Ryan, Estimating expected information gains for experimental designs with application to the random fatigue-limit model, *Journal of Computational and Graphical Statistics* 12 (2003) 585–603.

Maximizing the expected utility, $U(d)$

$$d^* = \arg\max_{d \in \mathcal{D}} U(d)$$

Bayesian Optimization

- Construct a Gaussian process model of the unknown objective function $U(d)$

$$U(d) \sim \mathcal{N}(\mu(d), K(d, d'))$$

- Use an *acquisition function* $\alpha(d)$ to select new samples
  - Gaussian Process upper confidence bound (UCB)

$$\alpha_t(d) = \mu_{t-1}(d) + \sqrt{\beta_t}\sigma_{t-1}(d) \quad \text{at iteration } t \text{ and } \sigma_{t-1}(d) = \sqrt{K(d,d)}$$

  - Exploits regions with a high mean and explores regions of high uncertainty

- Select next sample as: $d_t = \arg\max_{d \in \mathcal{D}} \alpha_t(d)$

- Evaluate utility function at $U(d_t)$

N. Srinivas, A. Krause, S. Kakade, & M. Seeger. Gaussian process optimization in the bandit setting: No regret and experimental design. *arXiv preprint arXiv:0912.3995* (2009).

Challenges

Computational limitations

- High-fidelity physics-based simulations can be expensive to evaluate
- Assuming no reuse of data, NM model evaluations to estimate $U(d)$
- Memory limitations storing a $(N \times J)$ sparse matrix, with $J = 5.1 \times 10^8$

- Constructing a surrogate model addresses the costly run-time
  - Total **number of outputs** remains problematic

Can we find *low-dimensional* representations of the high-dimensional output?

Reducing output dimensionality

Goal: Map high-dimensional model output to a lower-dimensional space while minimizing loss of information

Truncated SVD

At a fixed design d,

- Draw n sample of $\boldsymbol{\theta}^{(i)} \sim p(\boldsymbol{\theta})$
- Evaluate model $f(\boldsymbol{\theta}, \boldsymbol{d}, \boldsymbol{x}) + \delta(\boldsymbol{x}) + \epsilon(x)$
- Construct output matrix $\boldsymbol{Z} = \boldsymbol{U}\boldsymbol{S}\boldsymbol{V}^T$, where $\boldsymbol{Z} \in \mathbb{R}^{n \times J}, J = 5.1 \times 10^8$
- Retain only top K singular values of $\boldsymbol{S}$
- Low-rank approximation: $\boldsymbol{Z}_K = \boldsymbol{U}_K \boldsymbol{S}_K \boldsymbol{V}_K^T$

Transformation:

$$q(\boldsymbol{\theta}, \boldsymbol{d}, \boldsymbol{x}) = z(\boldsymbol{d}, \boldsymbol{x})\boldsymbol{V}_K$$

$$\underbrace{q(\boldsymbol{\theta}, \boldsymbol{d}, \boldsymbol{x})}_{(1\times K)} = \underbrace{[f(\boldsymbol{\theta}, \boldsymbol{d}, \boldsymbol{x}) + \delta(\boldsymbol{x}) + \epsilon(\boldsymbol{x}))]}_{(1\times J)} \underbrace{\boldsymbol{V}_K}_{(J\times K)}$$

Reducing output dimensionality

Construct K surrogate models, one for each of the low-dimensional QOIs

$$g_k(\boldsymbol{\theta}) \approx q_k(\boldsymbol{\theta}, \boldsymbol{d}, \boldsymbol{x}), \text{ for } k = 1, \ldots, K$$

How should we represent the likelihood in the low-dimensional space?

Reducing output dimensionality

Construct K surrogate models, one for each of the low-dimensional QOIs

$$g_k(\boldsymbol{\theta}) \approx q_k(\boldsymbol{\theta}, \boldsymbol{d}, \boldsymbol{x}), \text{ for } k = 1, \ldots, K$$

Recall,

$$z(\boldsymbol{d}, \boldsymbol{x}) = \xi(\boldsymbol{d}, \boldsymbol{x}) + \epsilon(\boldsymbol{x})$$
$$z(\boldsymbol{d}, \boldsymbol{x}) = f(\boldsymbol{\theta}, \boldsymbol{d}, \boldsymbol{x}) + \delta(\boldsymbol{x}) + \epsilon(\boldsymbol{x})$$

$$\delta(\boldsymbol{x}) \sim GP(\mu_\delta(\boldsymbol{x}), \Sigma_\delta(\boldsymbol{x}, \boldsymbol{x}')), \epsilon(\boldsymbol{x}) \sim \mathcal{N}(0, s(\boldsymbol{x})^2)$$

Therefore,

$$\mu = \mathbb{E}[z] = f(\boldsymbol{\theta}, \boldsymbol{d}, \boldsymbol{x}) + \mu_\delta(\boldsymbol{x})$$
$$\Sigma = \text{Var}[z] = \Sigma_\delta(\boldsymbol{x}, \boldsymbol{x}') + \text{diag}(s(\boldsymbol{x})^2)$$

Given a linear transformation of z,

$$\mu_q = \mathbb{E}[q] = \mu \boldsymbol{V}_k$$
$$\Sigma_q = \text{Var}[q] = \boldsymbol{V}_k^T \Sigma \boldsymbol{V}_k$$

Example: Simplified HPR model

Original data model,

$$z(\boldsymbol{d}, \boldsymbol{x}) = \xi(\boldsymbol{d}, \boldsymbol{x}) + \epsilon(\boldsymbol{x})$$
$$z(\boldsymbol{d}, \boldsymbol{x}) = f(\boldsymbol{\theta}, \boldsymbol{d}, \boldsymbol{x}) + \delta(\boldsymbol{x}) + \epsilon(\boldsymbol{x})$$

$$\boldsymbol{x} = [\tau, t, E]$$

$$\delta(\boldsymbol{x}) \sim GP(\mu_\delta(\boldsymbol{x}), \Sigma_\delta(\boldsymbol{x}, \boldsymbol{x}')), \; \epsilon(\boldsymbol{x}) \sim \mathcal{N}(0, s(\boldsymbol{x})^2)$$

$z(\boldsymbol{d}, \boldsymbol{x})$: ion-count data

$\xi(\boldsymbol{d}, \boldsymbol{x})$: true physical process

$f(\boldsymbol{\theta}, \boldsymbol{d}, \boldsymbol{x})$: physics and instrument model

$\delta(\boldsymbol{x})$: model error

$\epsilon(\boldsymbol{x})$: observation noise

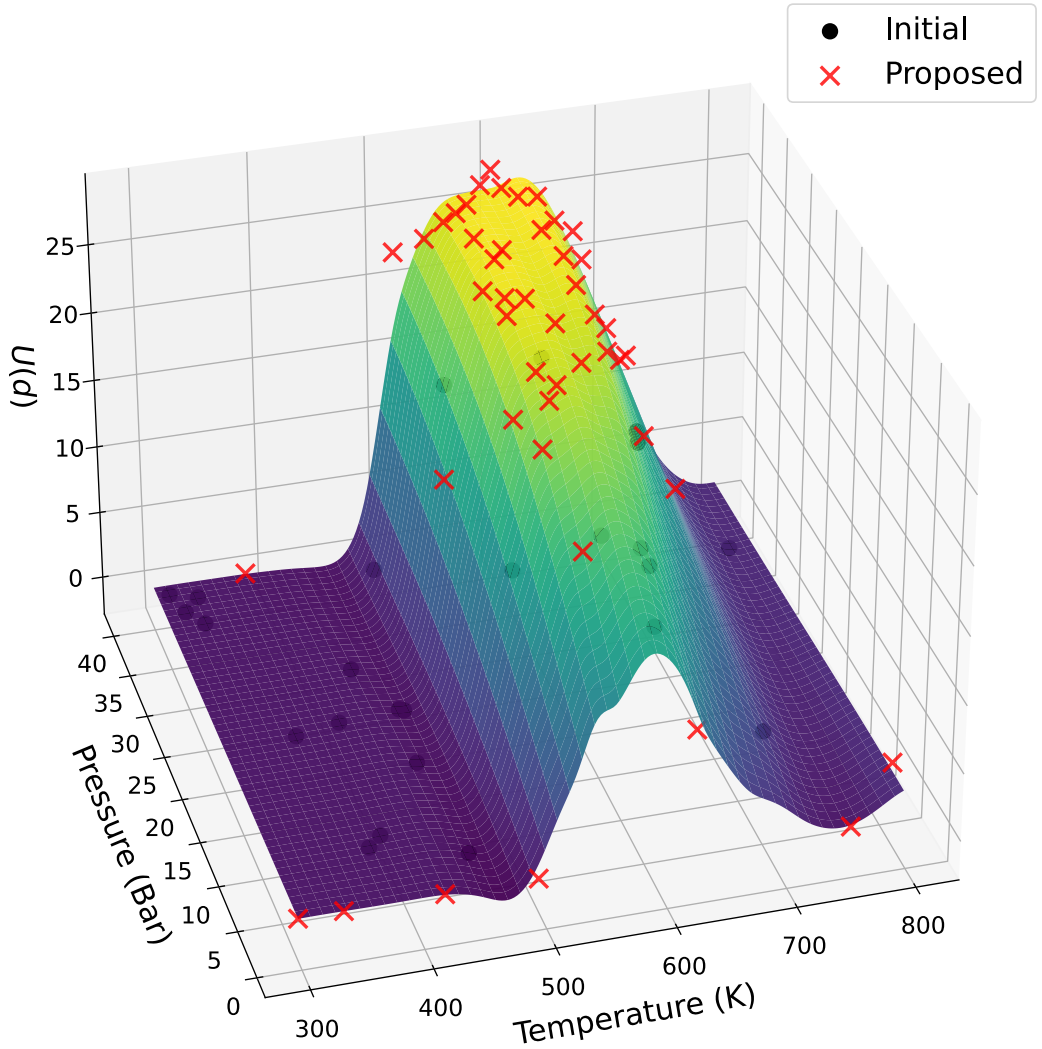
Simplifying assumption:

Only a small subset of the model parameters are considered uncertain

- 4 / 1143 reaction rates uncertain, all other reactions are at their nominal (mean) values

1) $\mathrm{O} + \mathrm{H_2} \rightarrow \mathrm{OH} + \mathrm{H}$
2) $\mathrm{C_3H_8} + \mathrm{H} \rightarrow \mathrm{CH_3CH_2CH_2} + \mathrm{H_2}$
3) $\mathrm{O_2} + \mathrm{CH_3CH_2CH_2} \rightarrow \mathrm{OH} + \mathrm{C{-}CH_2OCH(CH_3)}$
4) $\mathrm{CH_3CH(OOH)CH_2} \rightarrow \mathrm{OH} + \mathrm{C{-}CH_2OCH(CH_3)}$

Results



Solid surface is the mean function of a Gaussian process model representing $U(d)$. Evaluations from expected utility function are shown as black points or red crosses. Optimal design at **(T, p) = (598.4 K, 40 bar)**

Fixed design parameters: $\chi_{C_3H_8} = 8.3 \times 10^{-7}$
$\chi_{O_2} = 2.5 \times 10^{-2}$
$\chi_{pre} = 1.9 \times 10^{-4}$

# of utility samples: $N = 1 \times 10^4, M = 1 \times 10^4$

Optimization method: Bayesian Optimization

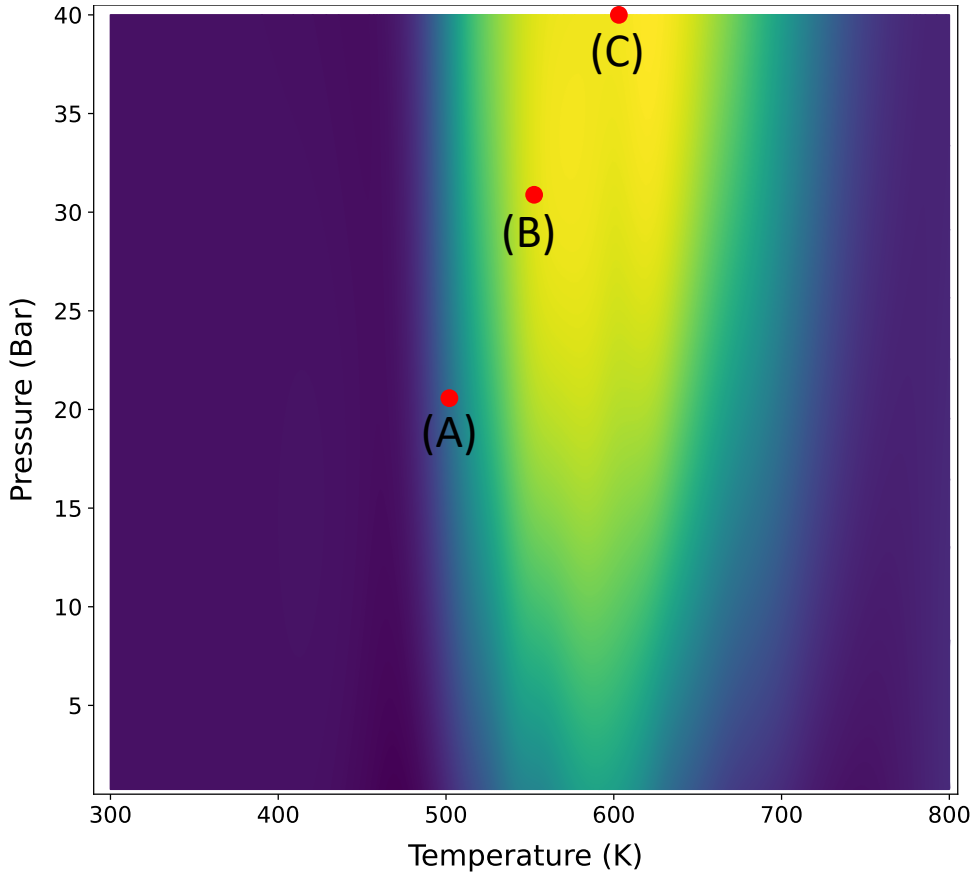
Acquisition function: UCB, with $\sqrt{\beta_t} = 2.5$

Dimension reduction: $K = 20$ components

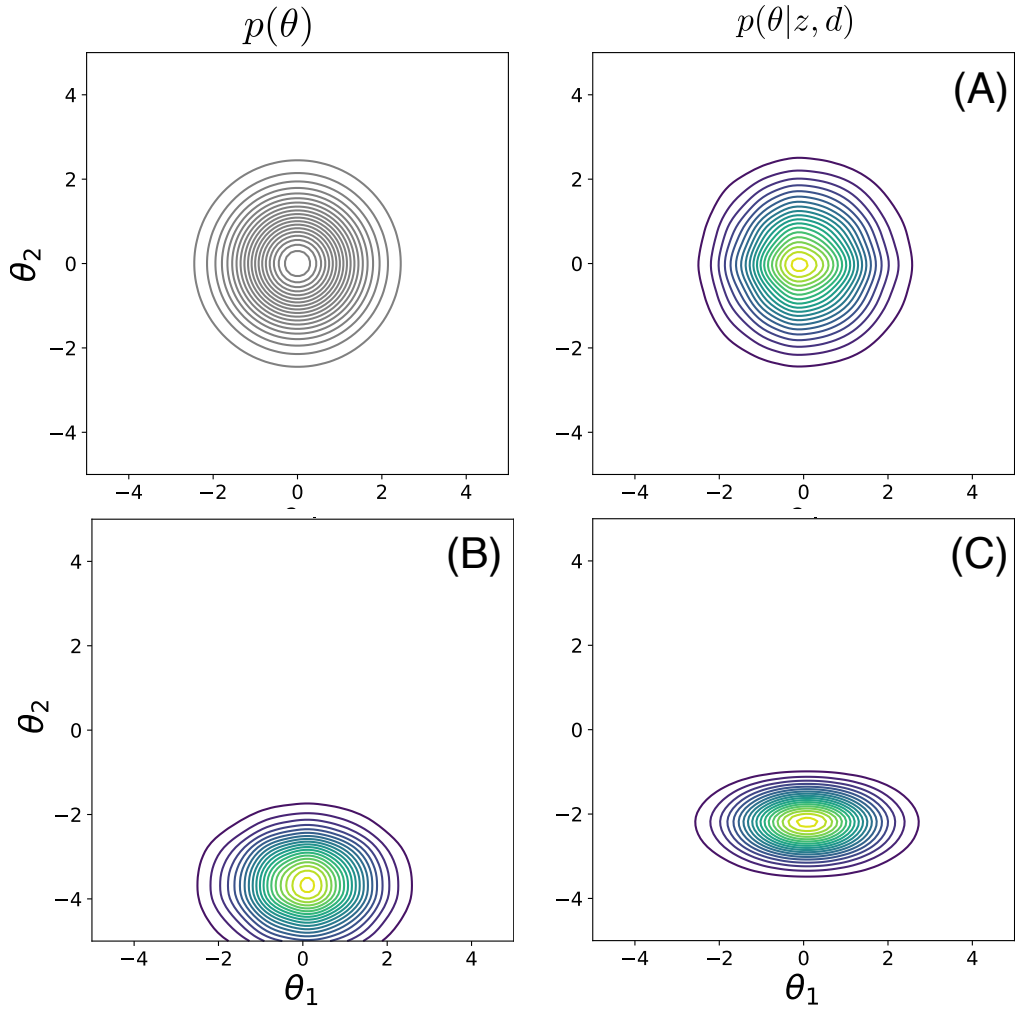
25 Latin-Hypercube samples (black points)
50 proposal samples (red crosses)

Results

Bayes' theorem: $p(\theta|z,d) = \dfrac{p(\theta)p(z|\theta,d)}{p(z|d)}$



Heatmap of the estimated utility function using a Gaussian process mean function. Data sets are generated at each of the design points (A, B, C).



Bayesian inference was performed to observe change in the joint posterior density given plausible data sets at each of the design points.

Conclusion & Future Work

- Demonstrated feasibility of OED for a HPR experiment
- Bayesian optimization efficient in optimizing noisy objective functions

- Low-dimensional representations of the model output provides significant and necessary computational savings to analyze high-dimensional combustion models

Future Work

- Relaxing assumption on total number of uncertain model parameters
  - Preliminary work shows only $\sim 40 - 100$ model parameters are influential in $\mathcal{D}$

- Run experiment at optimal design conditions
  - Collected data can inform the model error, $\delta(\boldsymbol{x}, \boldsymbol{d})$
  - Demonstrate benefit of OED by comparing information gain from an optimal design to a random designs

Acknowledgements

We would like to thank Oscar Diaz-Ibarra, Kyungjoo Kim, Arun Hegde, Cosmin Safta, and Khachik Sargsyan for helpful conversations about this work.

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Additional Slides

Modeling the HPR experiment

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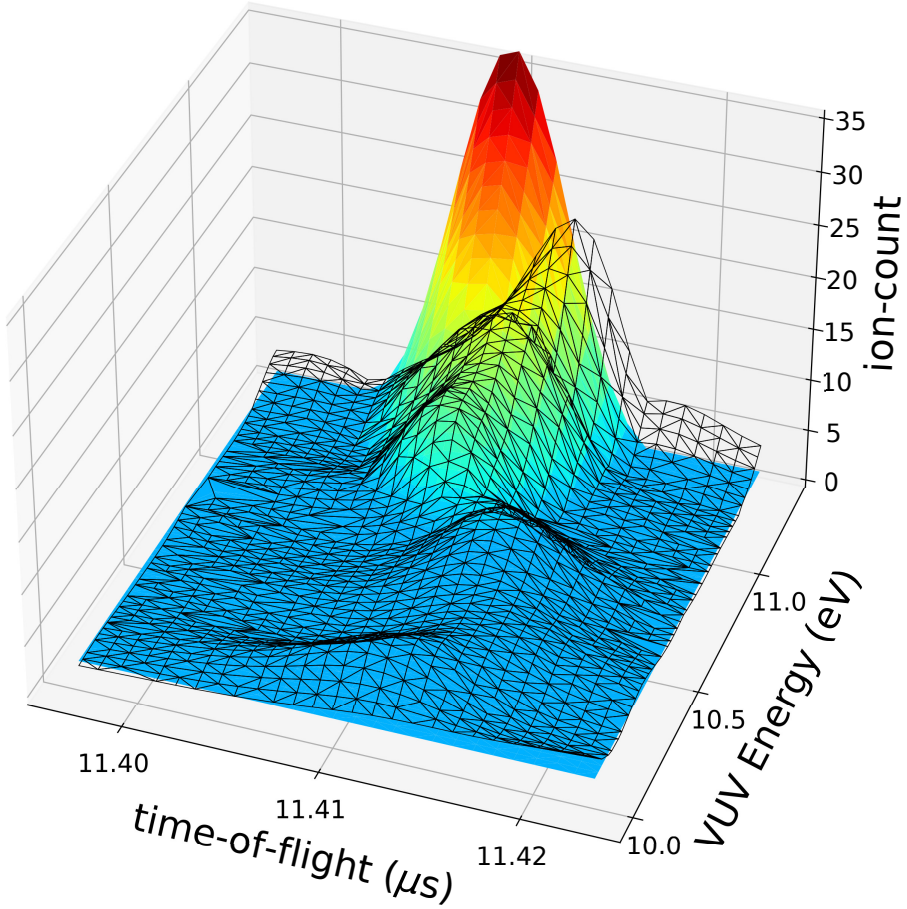
$$z(\boldsymbol{d}, \boldsymbol{x}) = f(\boldsymbol{\theta}, \boldsymbol{d}, \boldsymbol{x}) + \delta(\boldsymbol{x}) + \epsilon(\boldsymbol{x})$$

$$\boldsymbol{x} = [\tau, t, E]$$

$$\delta(\boldsymbol{x}) \sim GP(\mu_\delta(\boldsymbol{x}), \Sigma_\delta(\boldsymbol{x}, \boldsymbol{x}')), \; \epsilon(\boldsymbol{x}) \sim \mathcal{N}(0, s(\boldsymbol{x})^2)$$

- **Physics model**
  - Zero-dimensional reactor
  - Photolysis laser model
- **Chemical model**
  - C0-C3 chemical mechanism
  - 171 species / 1143 reactions
- **Instrument model**
  - Maps concentrations to ion counts
  - ***Peaks idealized as Gaussian distributions***



Solid surface is the prediction of $f(\theta_{MAP}, d, x)$ for one of the peaks in the time-of-flight spectrum (H_2O_2).
Mesh surface shows the prediction with model error, $f(\theta_{MAP}, d, x) + \mu_\delta(x)$ which increases the fidelity of the predictive model.

Numerical approximation

$$u(y,d,\theta) = D_{KL}(p(\theta|y,d)||p(\theta)) = \int_\Theta p(\theta|y,d)\log\left[\frac{p(\theta|y,d)}{p(\theta)}\right]d\theta = u(y,d)$$

$$\begin{aligned} U(d) &= \int_\mathcal{Y}\int_\Theta u(y,d)p(\theta|y,d)d\theta p(y|d)dy \\ &= \int_\mathcal{Y} u(y,d)p(y|d)dy \\ &= \int_\mathcal{Y}\left(\int_\Theta p(\theta|y,d)\log\left[\frac{p(\theta|y,d)}{p(\theta)}\right]d\theta\right)p(y|d)dy \end{aligned}$$

Using $p(\theta|y,d) = p(y|\theta,d)p(\theta)/p(y|d)$,

$$\begin{aligned} U(d) &= \int_\mathcal{Y}\int_\Theta \log\left[\frac{p(y|\theta,d)}{p(y|d)}\right]p(y|\theta,d)p(\theta)d\theta dy \\ &= \int_\mathcal{Y}\int_\Theta \left[\log p(y|\theta,d) - \log p(y|d)\right]p(y|\theta,d)p(\theta)d\theta dy \end{aligned}$$

Approximating the expected utility

Numerical approximation:

$$U(d) \approx \frac{1}{N} \sum_{i=0}^{N} \left[\log p(y^{(i)}|\theta^{(i)}, d) - \log \underbrace{p(y^{(i)}|d)}_{???} \right] \quad \text{where, } \theta^{(i)} \sim p(\theta), \; y^{(i)} \sim p(y|\theta^{(i)}, d)$$

Several approaches to estimate the marginal likelihood

- **Monte Carlo sampling**
- Laplace approximation
- Importance sampling
- Variational methods

$$p(y^{(i)}|d) = \int p(y^{(i)}|\theta, d) p(\theta) \mathrm{d}\theta$$
$$\approx \frac{1}{M} \sum_{j=0}^{M} p(y^{(i)}|\theta^{(j)}, d), \quad \text{where, } \theta^{(j)} \sim p(\theta)$$

N. Friel, J. Wyse, Estimating the evidence–a review, *Statistica Neerlandica* 66.3 (2012) 288-308.
A. Gelman, X. Meng, Simulating normalizing constants: From importance sampling to bridge sampling to path sampling, *Statistical science* (1998) 163-185.

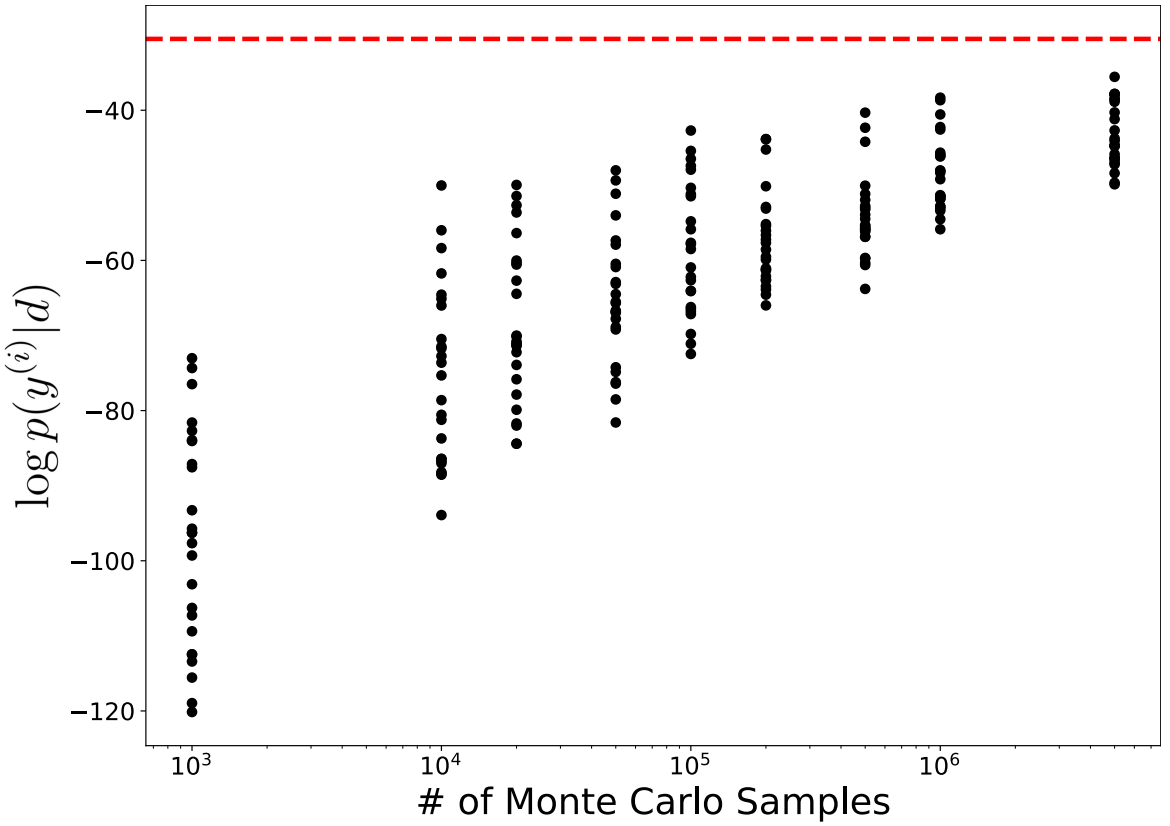
Estimating the marginal likelihood

Linear Model

$$
\begin{aligned}
y &= G(\theta) + \epsilon \\
G(\theta) &= A\theta \qquad\qquad y \in \mathbb{R}^{15} \\
\theta &\sim \mathcal{N}(\mu_0, \Sigma_0) \qquad \theta \in \mathbb{R}^{25} \\
\epsilon &\sim \mathcal{N}(0, \Sigma_\epsilon)
\end{aligned}
$$

Monte Carlo estimation

$$
\begin{aligned}
p(y^{(i)}|d) &= \int p(y^{(i)}|\theta, d)p(\theta)\mathrm{d}\theta \\
&\approx \frac{1}{M}\sum_{j=0}^{M} p(y^{(i)}|\theta^{(j)}, d), \quad \text{where, } \theta^{(j)} \sim p(\theta)
\end{aligned}
$$



Monte Carlo estimate of the log marginal likelihood converges to the true value, shown as a red dashed line, as number of samples goes to infinity.

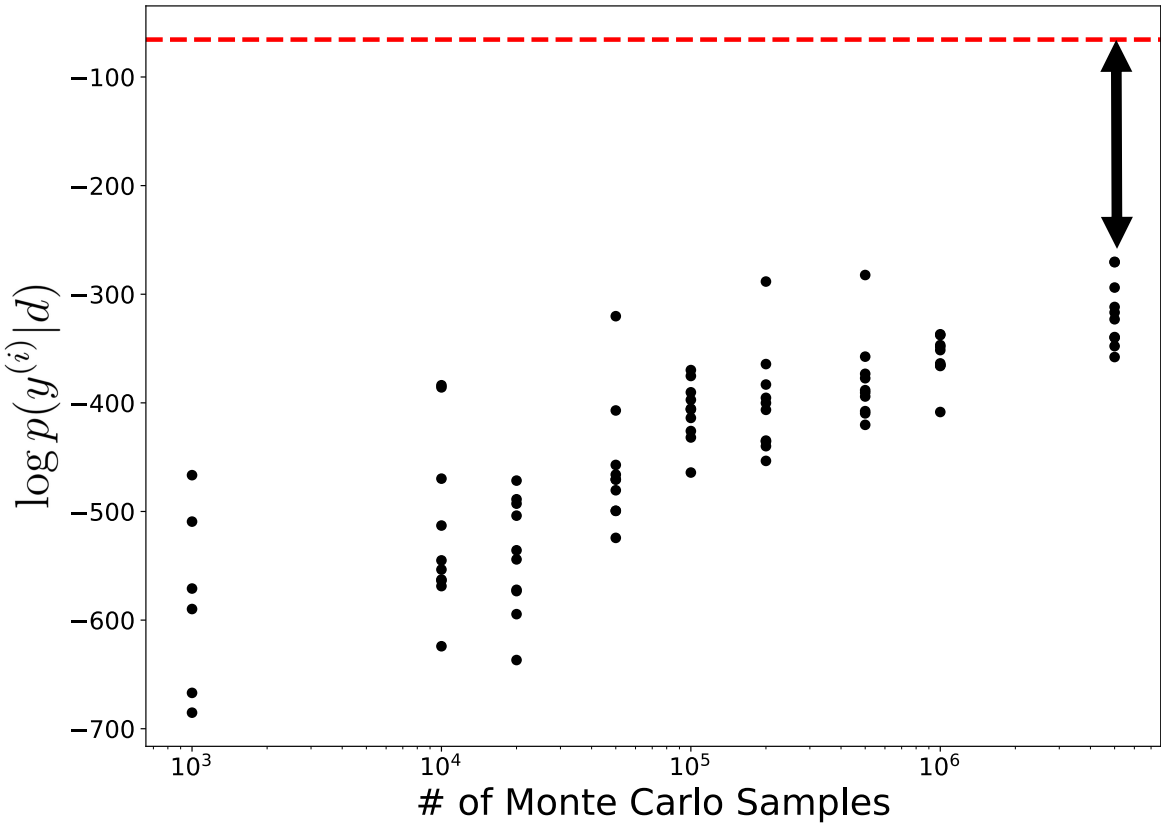
Estimating the marginal likelihood

Linear Model

$$y = G(\theta) + \epsilon$$
$$G(\theta) = A\theta$$
$$\theta \sim \mathcal{N}(\mu_0, \Sigma_0)$$
$$\epsilon \sim \mathcal{N}(0, \Sigma_\epsilon)$$

$$y \in \mathbb{R}^{30}$$
$$\theta \in \mathbb{R}^{50}$$

- As dimensionality increases, numerous samples are necessary to converge to the true marginal likelihood value



Significant error in the estimate of the log marginal likelihood as compared to the lower dimensional problem at a fixed number of samples.

Evaluating $U(d)$

$$U(d) \approx \frac{1}{N}\sum_{i=1}^{N}\left[\log p(z^{(i)}|\theta^{(i)},d) - \frac{1}{M}\sum_{j=1}^{M}\log p(z^{(i)}|\theta^{(j)},d)\right]$$

where $z^{(i)} \sim p(z|\theta^{(i)},d)$ and $p(z^{(i)}|\theta^{(i)},d) \sim \mathcal{N}(\mu,\Sigma)$.

Rewriting the data,

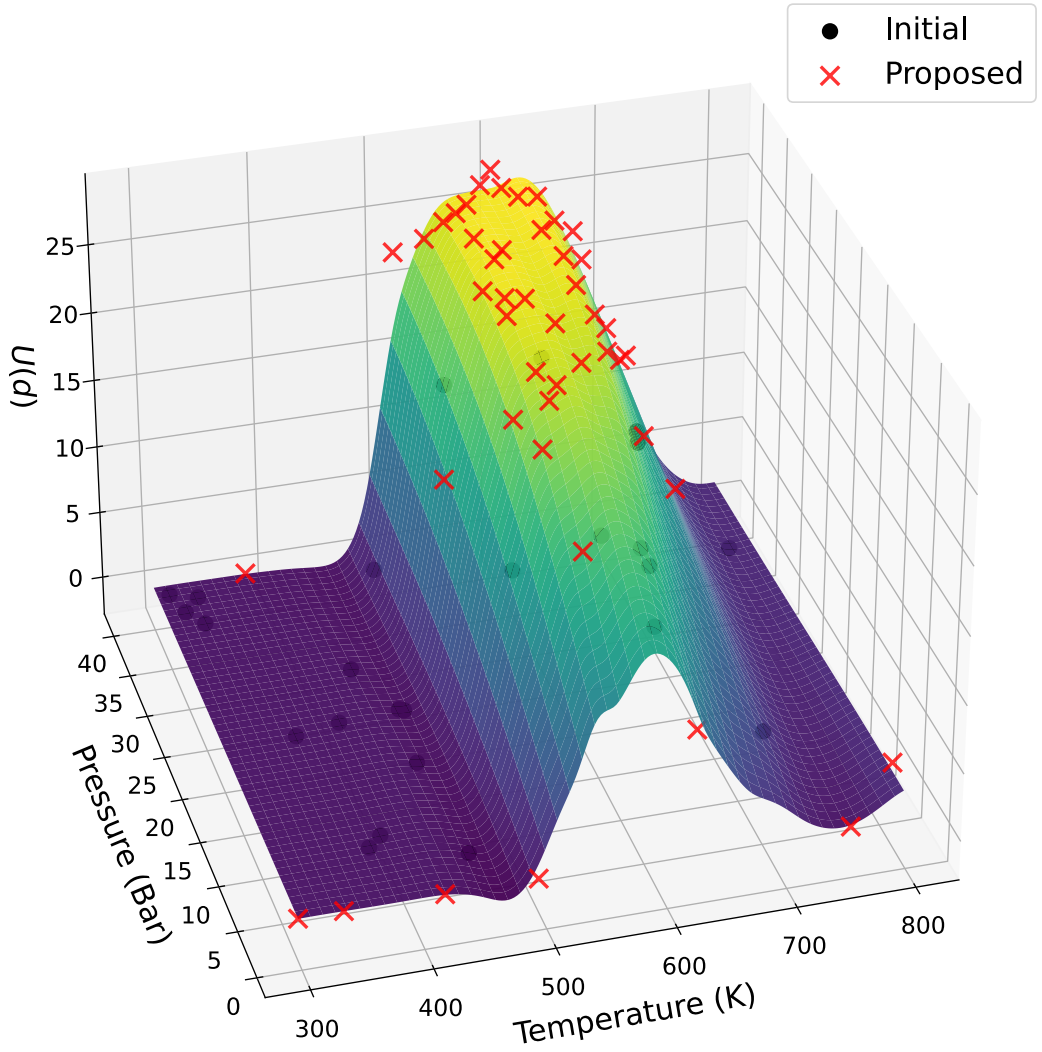
$$U(d) \approx \frac{1}{N}\sum_{i=1}^{N}\left[\log p(q^{(i)}\boldsymbol{V}_K^T|\theta^{(i)},d) - \frac{1}{M}\sum_{j=1}^{M}\log p(q^{(i)}\boldsymbol{V}_K^T|\theta^{(j)},d)\right]$$

Taking a linear combination of the data,

$$U(d) \approx \frac{1}{N}\sum_{i=1}^{N}\left[\log p(q^{(i)}|\theta^{(i)},d) - \frac{1}{M}\sum_{j=1}^{M}\log p(q^{(i)}|\theta^{(j)},d)\right]$$

where $q^{(i)} \sim p(q|\theta^{(i)},d)$ and $p(q^{(i)}|\theta^{(i)},d) \sim \mathcal{N}(\mu\boldsymbol{V}_K, \boldsymbol{V}_K^T\Sigma\boldsymbol{V}_K)$.

Results



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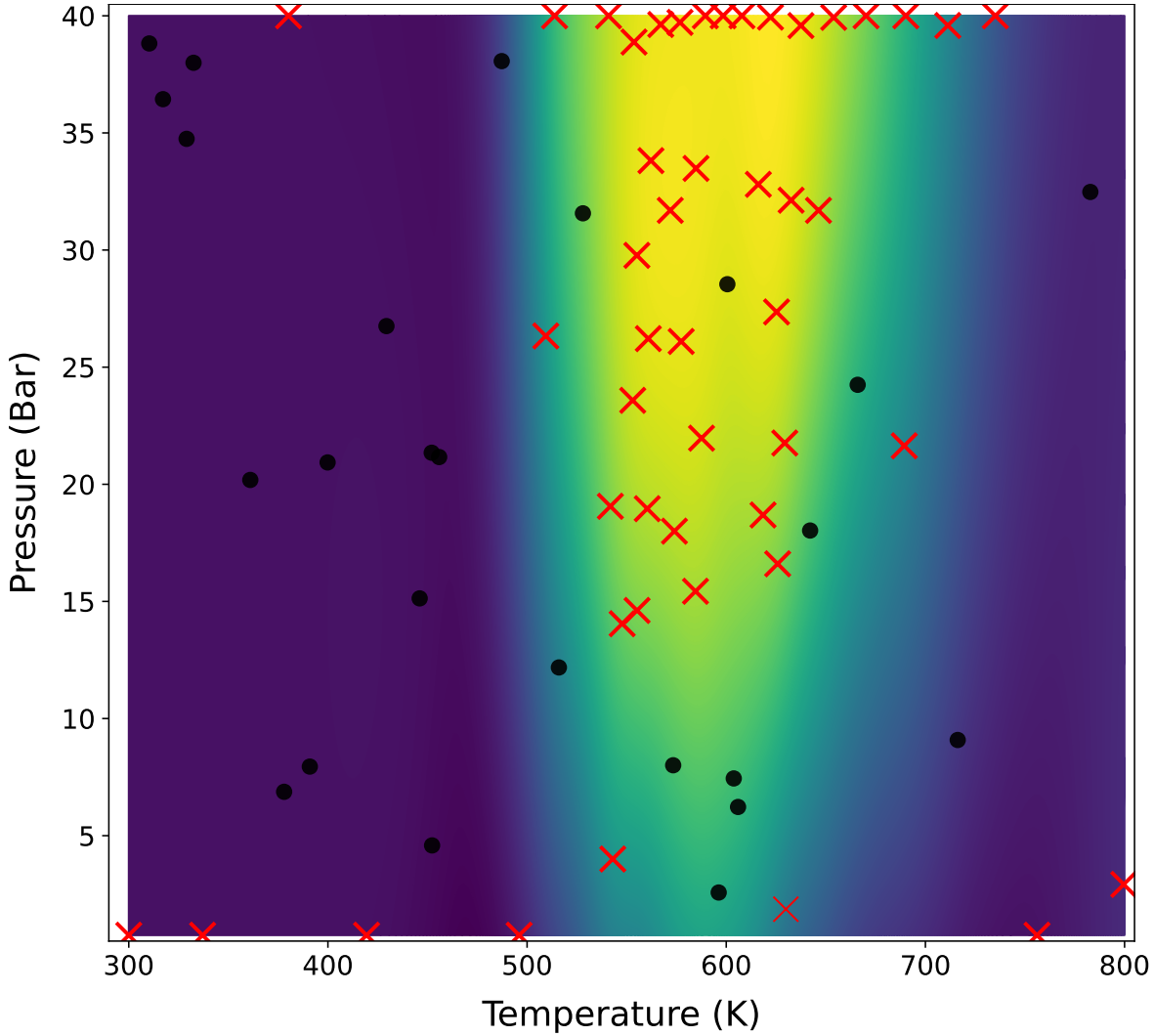

Proposals by the acquisition function were near the maximum, (T, p) = (598.4 K, 40 bar)