Bayesian Methods in Multi-Scale Modeling

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CCSI™ Carbon Capture Simulation Initiative

Abstract

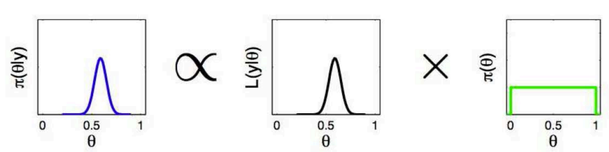
Multi-scale modeling can be viewed as a statistical problem. When moving from one scale to the next, some approximations must usually be made. This results in the introduction of uncertainty. The most effective multi-scale methodologies will be those that can best quantify the uncertainty at each scale and then propagate that uncertainty to the higher scale.

One of the goals of the US-DOE's Carbon Capture Simulation Initiative is the development of such methodologies and their application to the design and scale-up of innovative carbon capture systems. The poster contains a walk-through of the basic methodology, as applied to amine-based CO_2 sorbents.

Bayesian Calibration

- Fitting models to data in a Bayesian framework becomes a means of uncertainty quantification.
- The parameters are no longer just point estimates; there is a probability distribution of possible model values.
- In Bayesian statistics, there is a *prior* distribution and a *posterior* distribution. The prior reflects our belief about the parameters before taking account of any data. The posterior reflects our belief in light of the data.
- The relationship between the prior and posterior is given by **Bayes' Theorem**:

$$\pi(\theta|y) \propto \mathcal{L}(y|\theta) \times \pi(\theta)$$

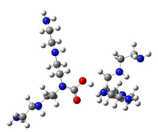


- That is, the posterior distribution for the parameters given the data is proportional to the prior parameter distribution times the *likelihood* of observing the data. (We can use this proportionality to get the actual distribution using a Monte Carlo simulation.)
- **What is / how do we get the likelihood?** First, we build a statistical model for the data. This model looks like: $Y = Z(\theta) + \delta(\xi) + \epsilon$
- This model says that the data (Y) is equal to a model prediction (Z) plus a *model form discrepancy* (δ) plus observation error (ε).
- The model form discrepancy is a very important aspect of this approach. It is a stochastic function describing the difference between our model predictions and reality. It has its own parameters (ξ), which get included in the posterior distribution.
- Because both δ and ε are stochastic, Y is also stochastic. This means given some particular Y (the actual data), and some sets of parameters θ and ξ we can use to evaluate the model Z and the discrepancy δ, we can calculate the likelihood (or probability) of observing that Y.
- All of this is called the **Kennedy-O'Hagan approach** to calibration.
- **Where do the priors come from?** Since the priors are what we know about the parameters before we take any data into account, it makes sense that they should somehow arise from first-principles considerations. Developing priors this way helps to ground our model – it keeps it a model of a physical process, and prevents it from becoming a fitting function for data.
- **How does all of this help with scale-up?** Making predictions about industrial scale-up is essentially extrapolation using a model that has (usually) been fit to experimental data at some smaller scale, like the bench scale. If we're just fitting a model to data, then we can get into trouble when we extrapolate. But through the model discrepancy, the Bayesian approach quantifies how good our model is and how much we can trust our parameters. After fitting both model and discrepancy to data, it then uses both of them to make probabilistic, extrapolative predictions. The better the model, the more certain the predictions.

Calibration of a Very Simple Equilibrium Sorbent Model

$$2R_2NH + CO_2(g) \rightleftharpoons R_2NCOOH : R_2NH \qquad \kappa = \frac{x^2}{(1-2x)^2 p} = \exp\left(\frac{\Delta S}{R}\right)\exp\left(\frac{-\Delta H}{RT}\right)/P$$

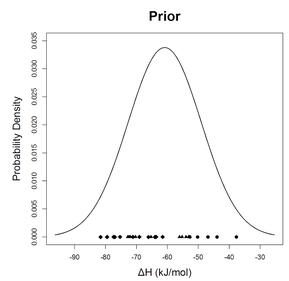
$$w = M n_v x/\rho$$



Amine chemistry

Two TEPA molecules combine to adsorb a CO_2 molecule through the formation of a bound associate.

reaction	B3LYP	PBE	MP
CO_2+2MMA→P-COOH:P	-52.72	-76.36	-62.76
CO_2+MMA+DMA→S-COOH:P	-46.86	-70.29	-62.97
CO_2+MMA+DMA→P-COOH:S	-50.21	-72.8	-62.76
CO_2+2DMA→S-COOH:S	-46.86	-70.71	-64.43
CO_2+DETA+EDA→P-COOH:S	-37.66	-69.04	-62.76
CO_2+DETA+EDA→S-COOH:P	-43.93	-68.41	-72.38

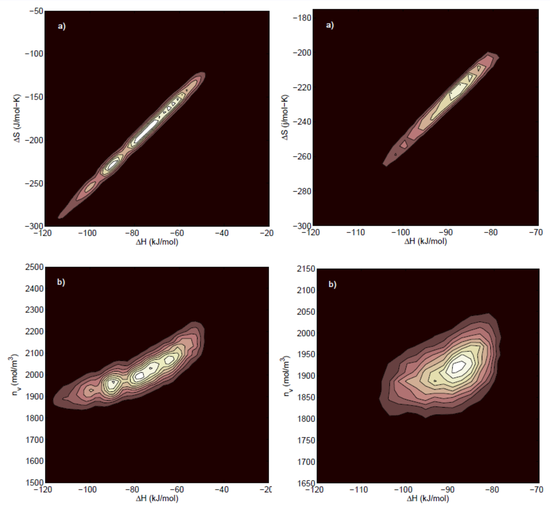


- Quantum chemistry is used to estimate the enthalpy and entropy of adsorption. Since we can arrive at different answers depending on the methods we use and how we set up the problem, this leads to a distribution.

Parameter uncertainty →

Contour plots show the bivariate posterior probability density for (top) DH-DS (bottom) DH-nv (left) uninformative (uniform) prior distributions and (right) informative priors derived using quantum chemistry.

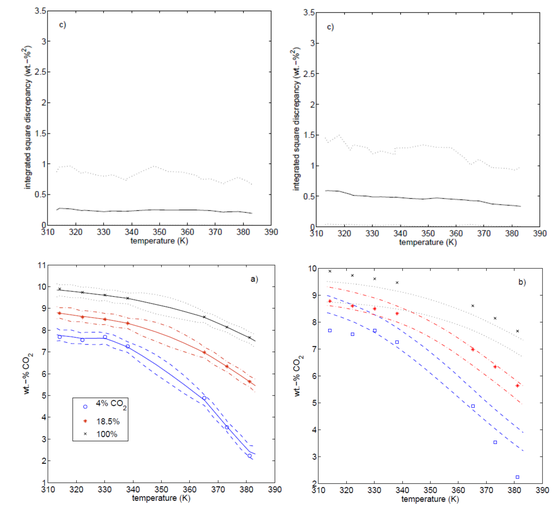
- We do the analysis twice and get two sets of posteriors: once with quantum priors and once without. The comparison shows that the quantum priors lead to a lot less uncertainty in the posterior distribution.



Model uncertainty →

Model discrepancy plotted as a function of input temperature for experiments at 1 atm CO_2 (left) with and (right) without quantum priors. The discrepancy is larger for the case with quantum priors.

- The quantum priors work hand-in-hand with the discrepancy, helping us to determine what uncertainty goes where.



Predictions →

Model-plus-discrepancy predictions (left) reproduce experimental data to within observation error. Model-only predictions do not.

Continuing Efforts

The next step is putting all of this to work in the context of a process model. Preliminary results have already been obtained, and efforts are underway to develop discrepancies that are germane to kinetic phenomena.