A comparison of experimental and regression uncertainties in the thermodynamic modelling of 1-alkane and 1-alcohol systems

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Introduction

- Thermodynamic modelling of isobaric **ethanol (1) & heptane (2)** and **ethanol (1) & octane (2)** data with the **Non-Random Two-Liquid (NRTL) model**.
- Uncertainties in model outputs arise from **(1) experimental uncertainties** and **(2) regression uncertainties**.
- **Three modelling approaches** investigated – choice of temperature in(dependent) parameters to calculate the binary interaction parameters (BIPs).
- Compare absolute average deviation in predicted temperature and vapour composition data **(AAD)**.

Methodology

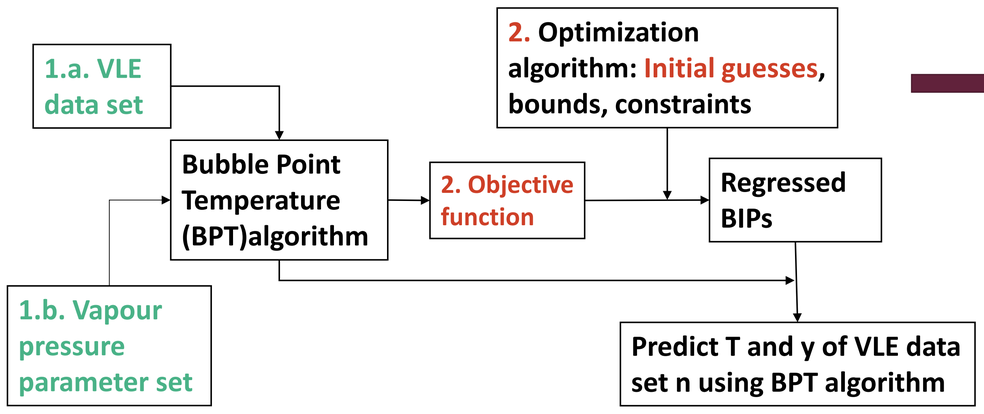
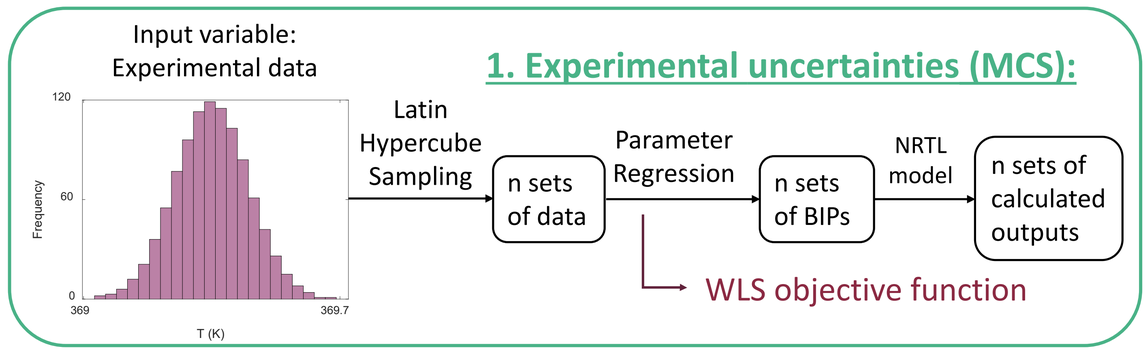


Figure 1: Parameter estimation process with investigated uncertainties highlighted

1. Assess n = 1 000 sets of **experimental data** generated by Monte Carlo Simulation (MCS). Keep all regression elements CONSTANT.
2. Assess choice of **objective function and initial guesses** while keeping experimental data CONSTANT.

Modelling approaches (calculation of BIPs): 1: $\tau_{ij} = a_{ij}$ 2: $\tau_{ij} = \frac{b_{ij}}{T}$ 3: $\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$



2. Regression elements:

Objective function:

Weighted Least Squares (WLS):

$$S = \sum_{i=1}^{N}\left[\left(\frac{T_i^{cal} - T_i^{exp}}{\sigma_{T,i}}\right)^2 + \sum_{j=1}^{C}\left(\frac{y_{i,j}^{cal} - y_{i,j}^{exp}}{\sigma_{y_j,i}}\right)^2\right]$$

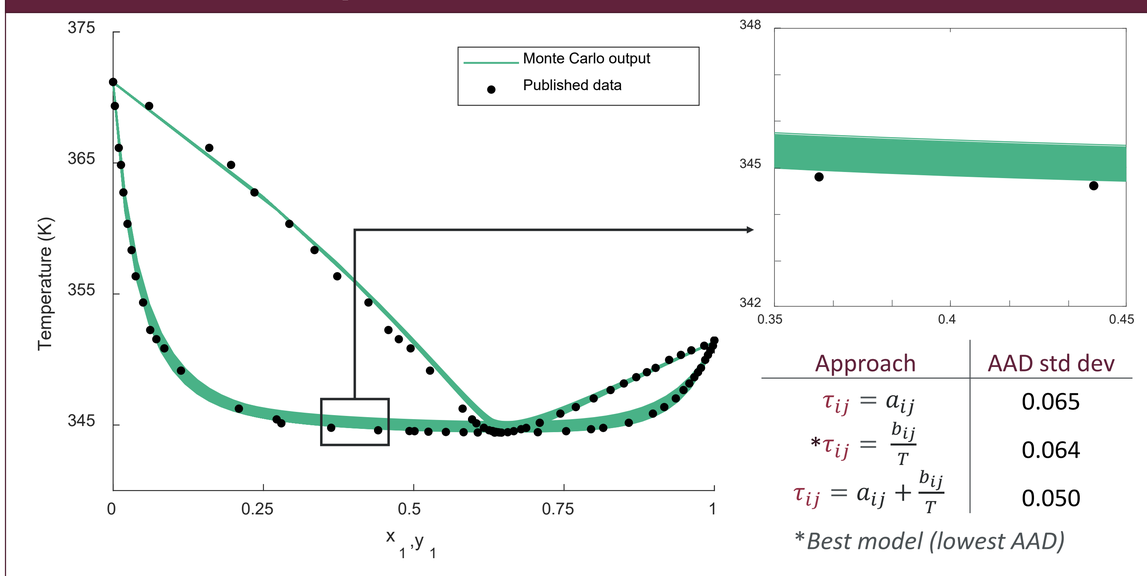
Activity coefficient:

$$S = \sum_{i=1}^{N}\sum_{j=1}^{C}\left(\frac{\gamma_{i,j}^{cal} - \gamma_{i,j}^{exp}}{\gamma_{i,j}^{exp}}\right)^2$$

Initial guesses:

- Each data set: use good initial guesses for parameters in $\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$ to calculate a range of initial guesses for approach 1: $\tau_{ij} = a_{ij}$ and approach 2: $\tau_{ij} = \frac{b_{ij}}{T}$.

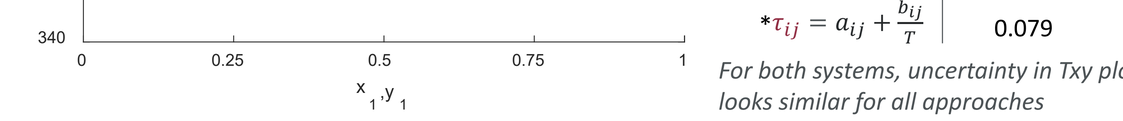
1. Experimental uncertainties



Approach	AAD std dev
$\tau_{ij} = a_{ij}$	0.065
$*\tau_{ij} = \frac{b_{ij}}{T}$	0.064
$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$	0.050

**Best model (lowest AAD)*

Figure 2: Txy plot of the ethanol (1) and heptane (2) system at 101.32 kPa [1] modelled with $\tau_{ij} = \frac{b_{ij}}{T}$ with experimental uncertainty propagation

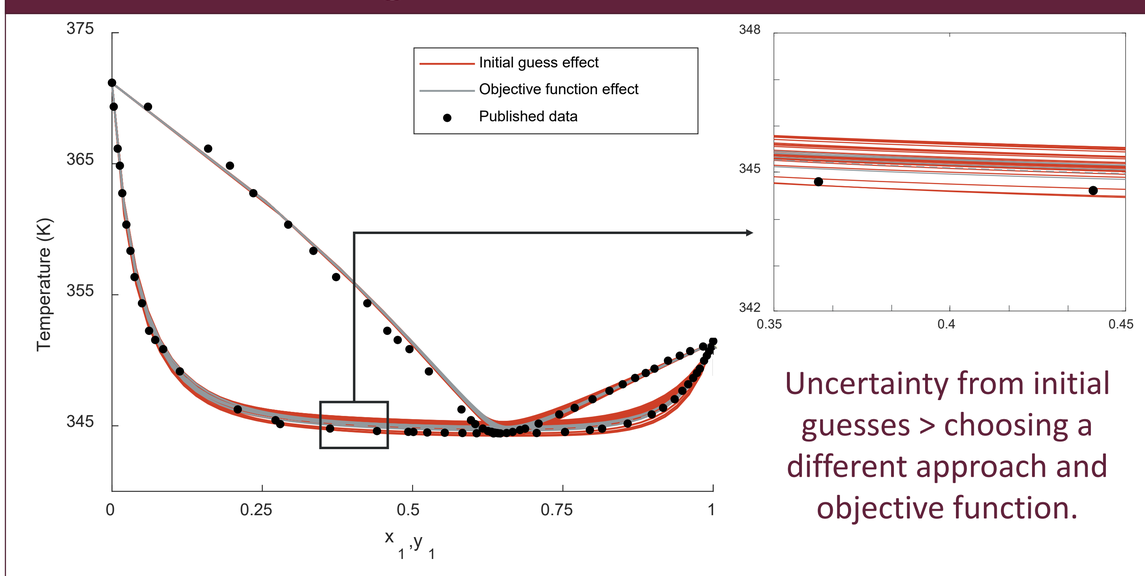


Approach	AAD std dev
$\tau_{ij} = a_{ij}$	0.083
$\tau_{ij} = \frac{b_{ij}}{T}$	0.068
$*\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$	0.079

For both systems, uncertainty in Txy plot looks similar for all approaches

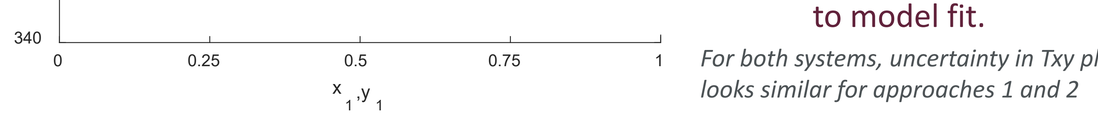
Figure 4: Txy plot of the ethanol (1) and octane (2) system at 101.32 kPa [1] modelled with $\tau_{ij} = a_{ij}$ with experimental uncertainty propagation

2. Regression uncertainties



Uncertainty from initial guesses > choosing a different approach and objective function.

Figure 3: Txy plot of the ethanol (1) and heptane (2) system at 101.32 kPa [1] modelled with different initial guesses ($\tau_{ij} = \frac{b_{ij}}{T}$) and different objective functions (for all approaches)



Ethanol (1) & octane (2): temperature dependency results in large improvement to model fit.

For both systems, uncertainty in Txy plot looks similar for approaches 1 and 2

Figure 5: Txy plot of the ethanol (1) and octane (2) system at 101.32 kPa [1] modelled with different initial guesses ($\tau_{ij} = \frac{b_{ij}}{T}$) and different objective functions (for all approaches)

Conclusion

In the regression of model parameters in thermodynamic modelling, uncertainties in both the **experimental data** and **regression elements** should be considered. Both sources of uncertainty are **specific to the modelling approach** used, the **choice of regression elements**, and are **system-specific**. The parameter estimation has been shown to be more sensitive to the choice of initial guesses, although the objective function and experimental uncertainties are also significant in the model outcomes.

[1]: Ortega, and Espiau, (2003) *IECR*, 42(20), pp. 4978

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