

Introduction

- The NRTL thermodynamic model is a widely-used activity coefficient model in process simulations
- Very often a “black box” approach is taken, with trial-and-error methods used to add or change parameters

The aim of this work is to **simplify and improve the parametrization procedure** for the NRTL model for common LLE, VLE, and VLLE data through the Tττ-approach:

- to replace the “black-box” approach
- to reduce computationally expensive regressions
- to elucidate the model behavior and limitations
- to incorporate a priori knowledge (incl. initial guesses)

Non-Random Two Liquid (NRTL) Model

Phase Equilibrium:

$$x_i^I \gamma_i^I P_i^{\text{sat}} = x_i^{\text{II}} \gamma_i^{\text{II}} P_i^{\text{sat}} = y_i P$$

NRTL model:

$$\ln(\gamma_1) = x_2^2 \left(\frac{\tau_{21} G_{21}^2}{(x_1 + x_2 G_{21})^2} + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right) \text{ with } G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

where:

$\alpha_{12} = \alpha_{21}$ - Non-randomness parameter ← Often fixed value: 0.20 - 0.47

τ_{12} & τ_{21} - Binary interaction parameters (BIP)

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} = a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T + d_{ij} T \leftarrow \text{Temperature dependent parameters (TDPs)}$$

LLE - Liquid Liquid Equilibrium

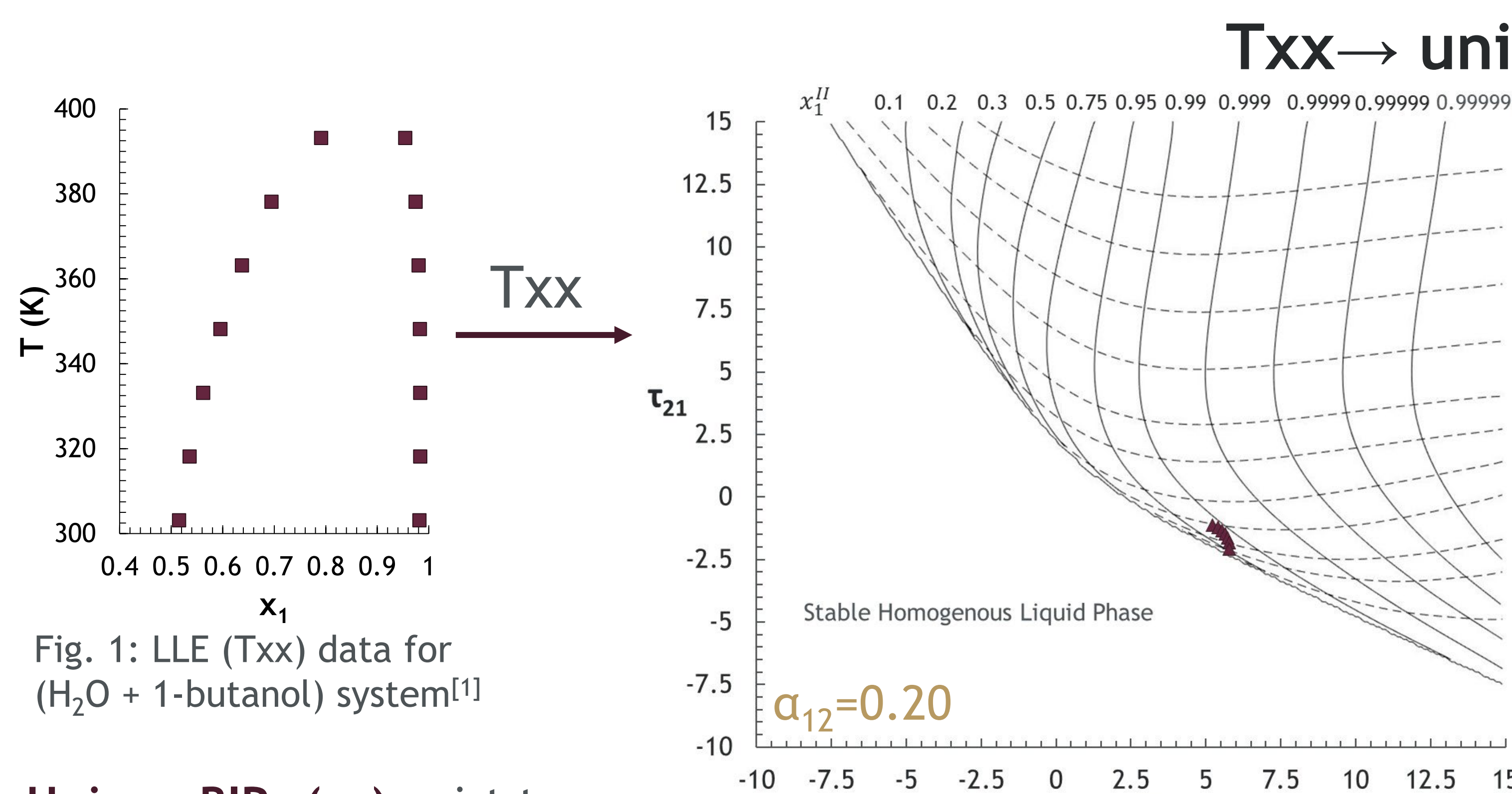


Fig. 1: LLE (Txx) data for (H₂O + 1-butanol) system^[1]

Unique BIPs (τ) exist to describe each isothermal LLE (xx) measurement

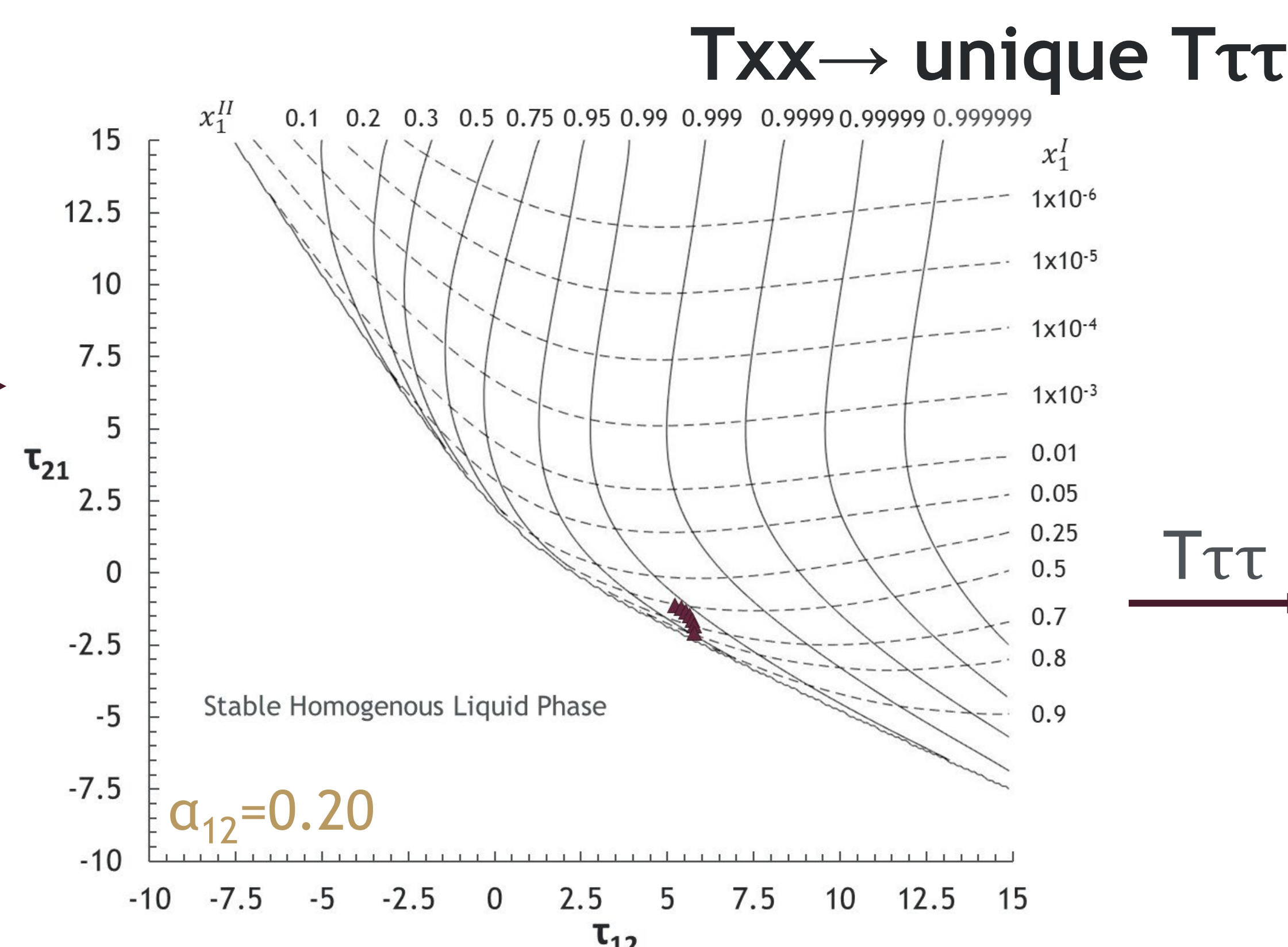


Fig. 2: Characterized *component-independent* BIP $\tau\tau$ -plane showing the unique conjugate liquid phase compositions (x_1) for $\alpha_{12}=0.20$. Redrawn from de Klerk & Schwarz (2023)^[2]

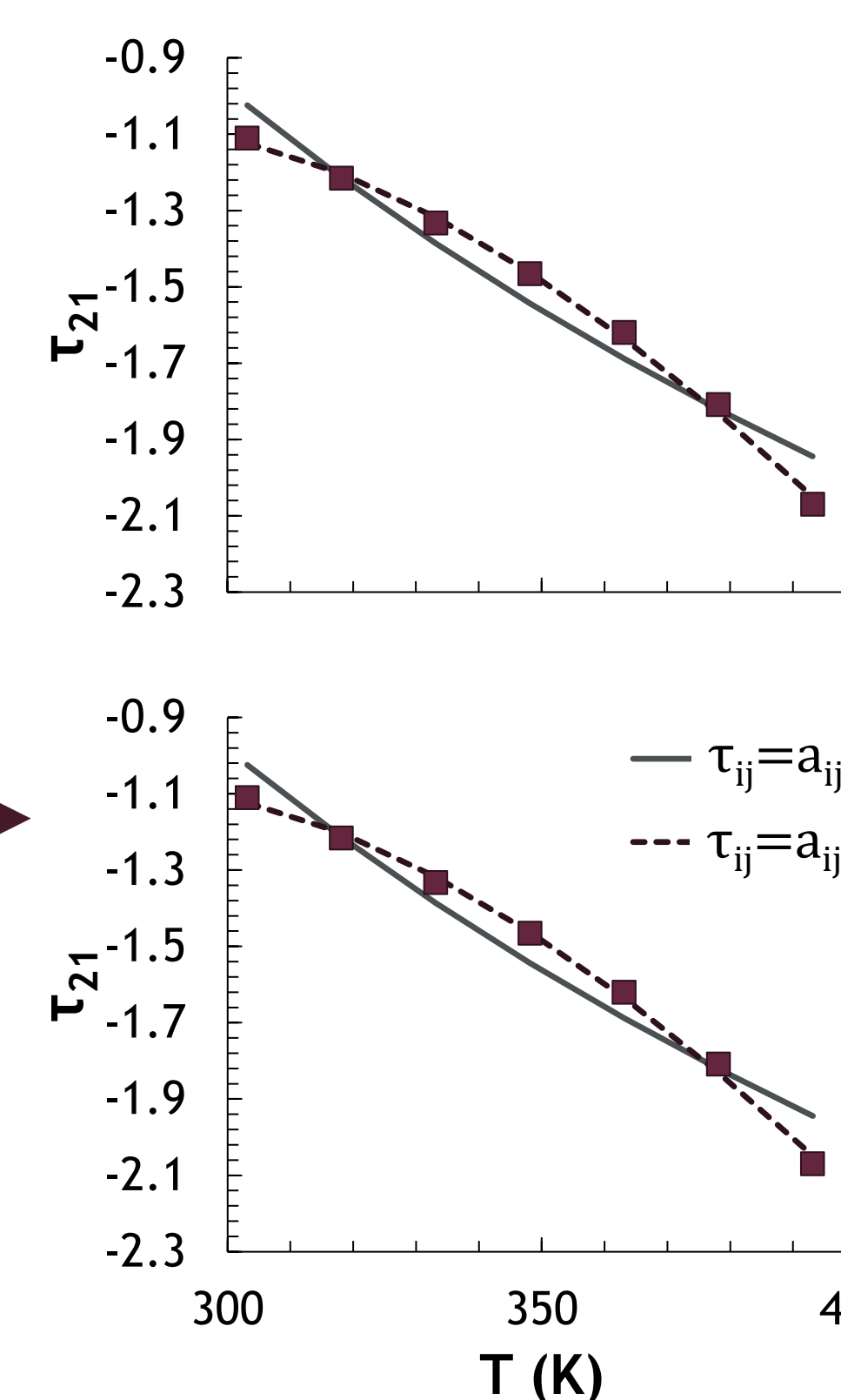


Fig. 3: Unique Tττ data and TDP correlations from Txx data

Traditional complex non-linear regression of TDPs reduced to **simple linear regression**

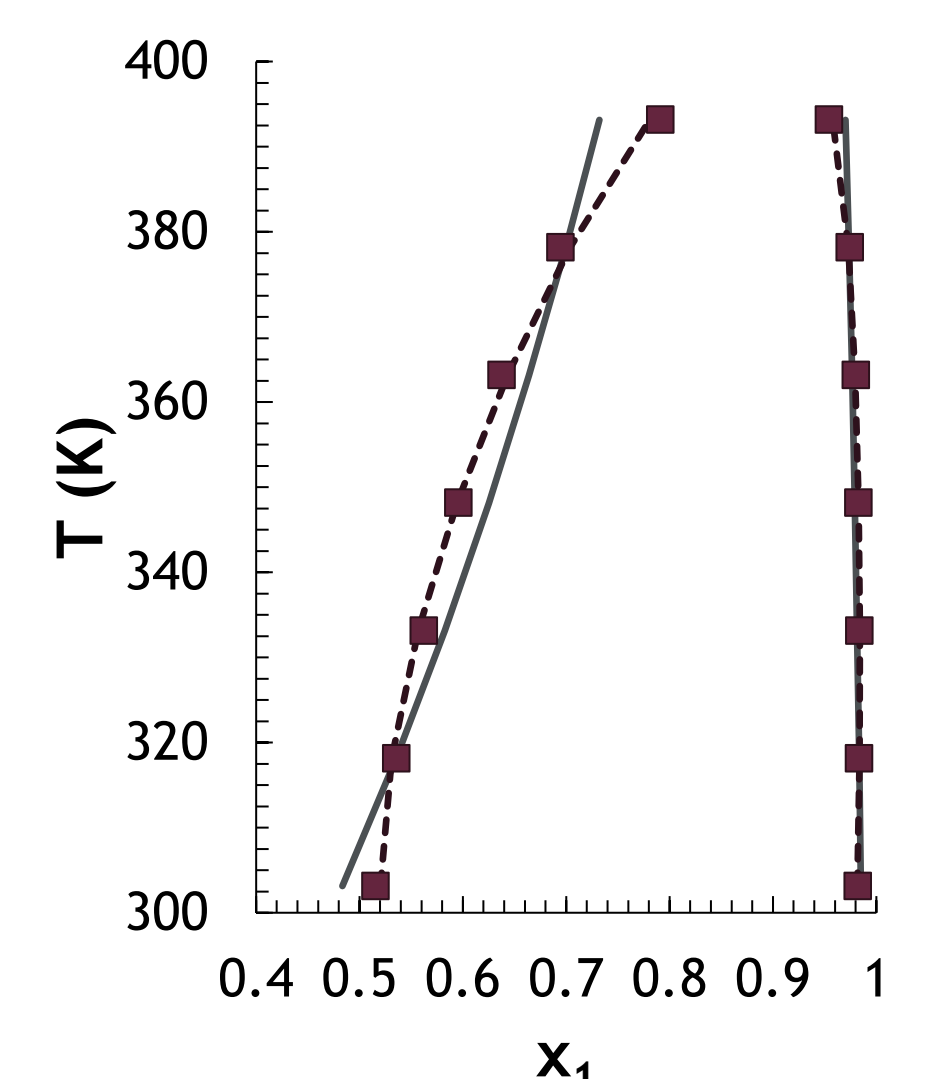


Fig. 4: LLE model predictions

VLE - Vapour Liquid Equilibrium

Azeotropic PTxy → unique Tττ

Good VLE predictions with TDPs from azeotropic BIPs and linear regression

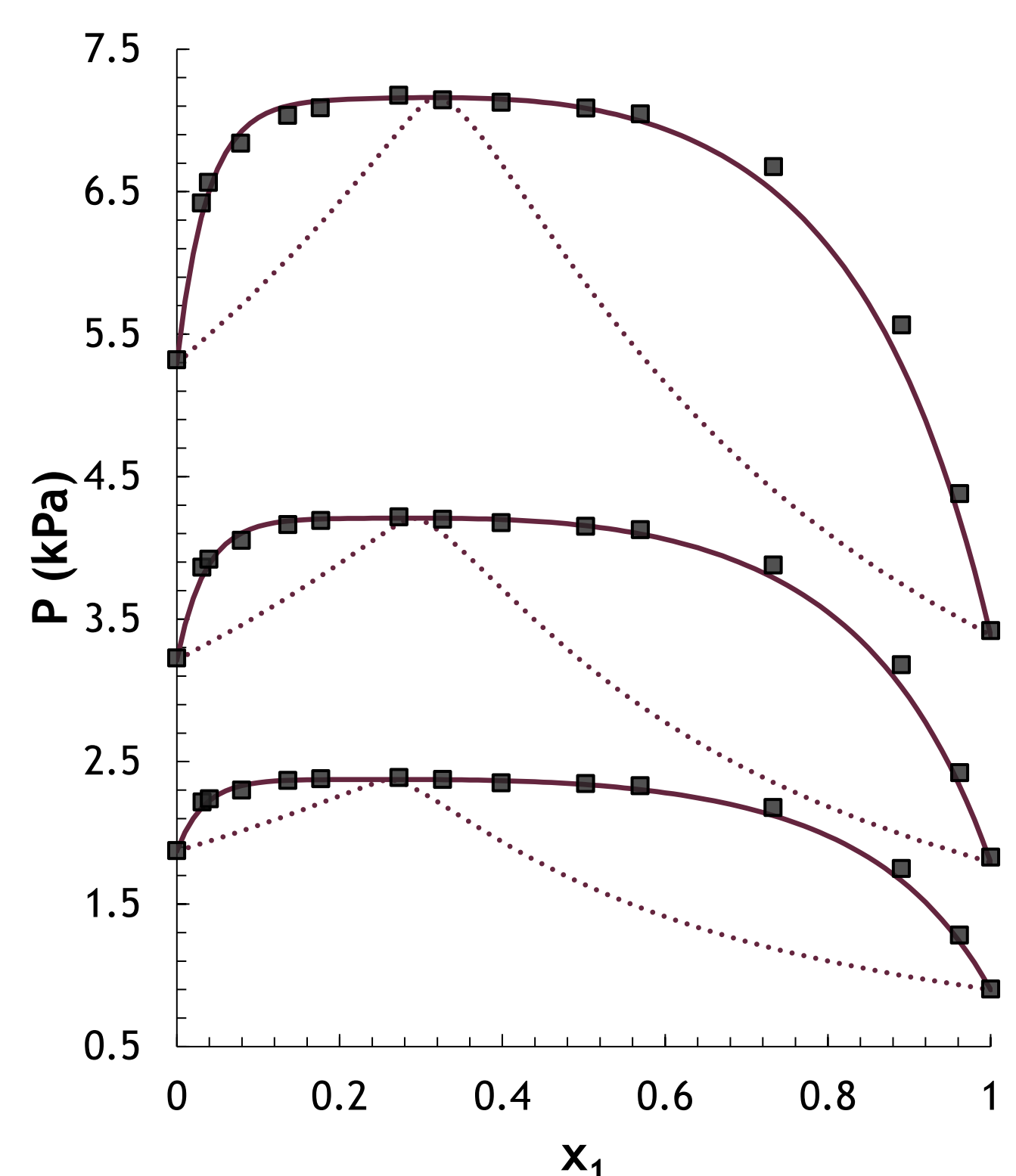


Fig. 5: Isothermal VLE data^[3], azeotropic data^[4], and model predictions ($\alpha_{12}=0.47$) of the (1-butanol + octane) system

α_{ij} selection

α_{ij} values can be **disqualified without a doubt** based on only an azeotropic point

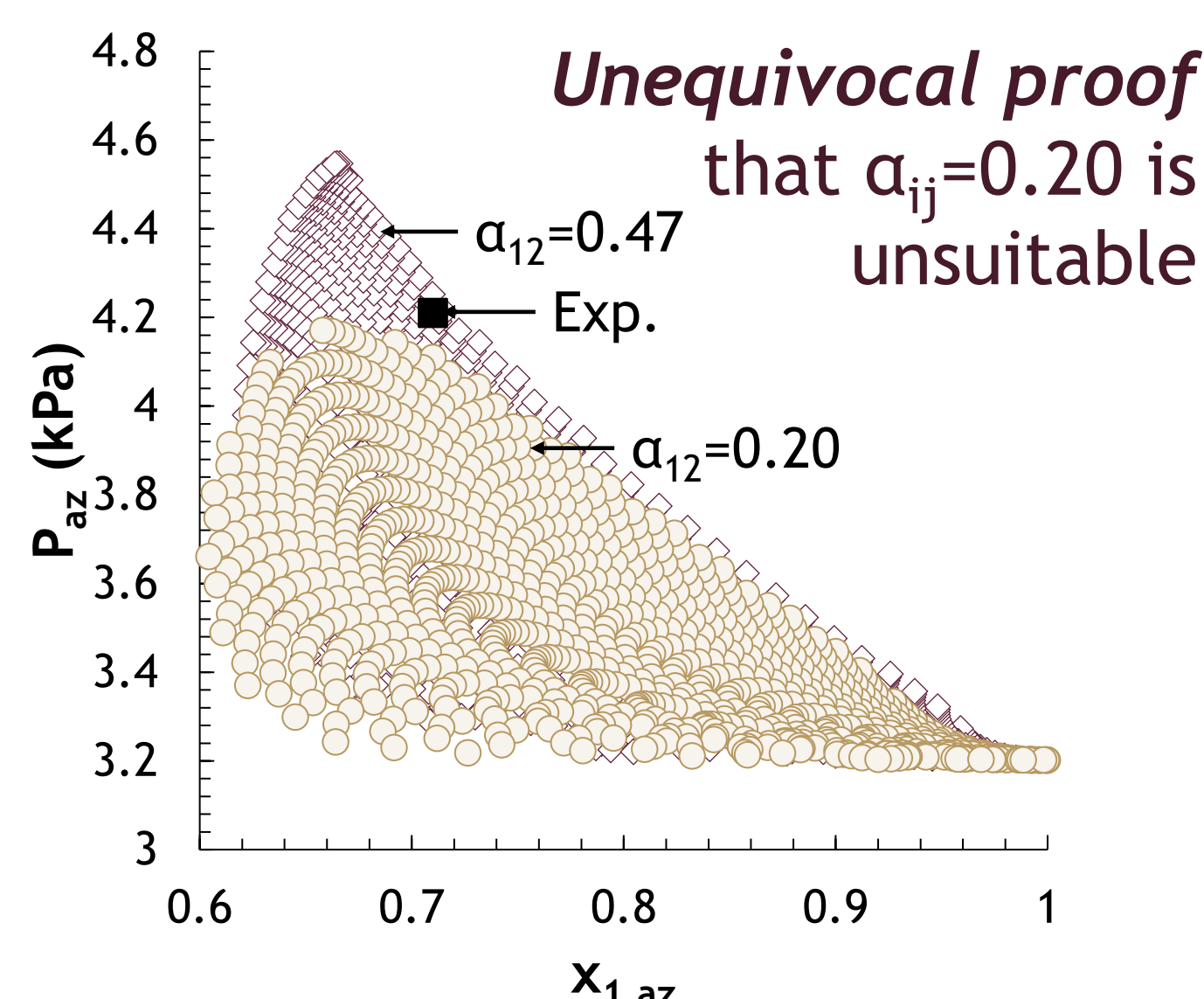


Fig. 6: Possible NRTL azeotropic predictions for the (octane + 1-butanol) system at 318 K compared to experimental data^[4]

No improvement in BIPs (or TDPs) can improve azeotropic PTxy description if α_{ij} is unsuitable

VLLE - Vapour Liquid Liquid Equilibrium

Azeotropic PTxxy → unique Tττ

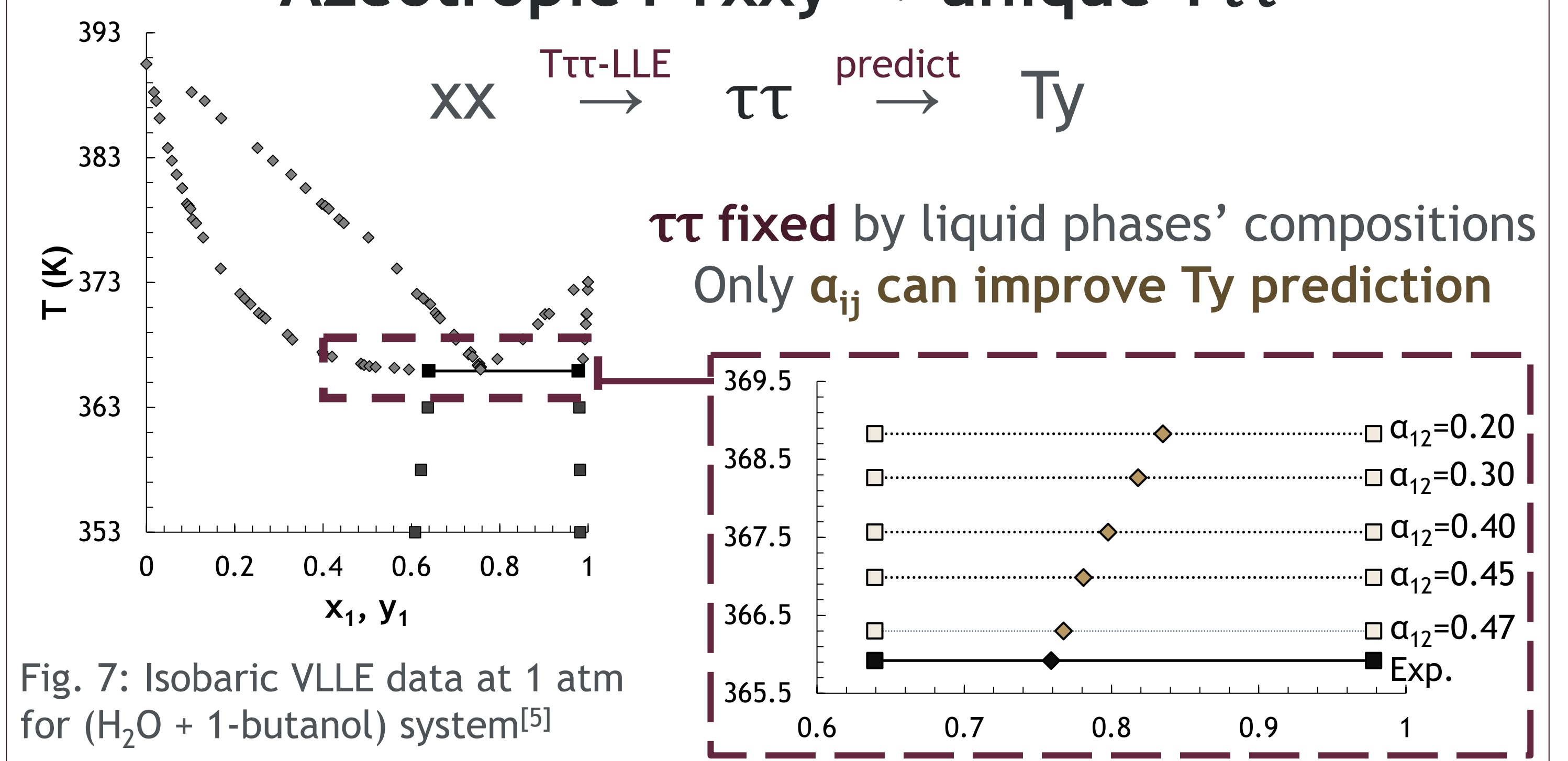


Fig. 7: Isobaric VLLE data at 1 atm for (H₂O + 1-butanol) system^[5]

Further Applications of the Approach

The approach presented can be extended/applied to:

- Combined, simultaneous binary phase equilibria description (VLE, LLE, VLLE, H^E, etc.)
- Multicomponent phase equilibria description (LLE, VLE & VLLE)
- The principles presented can be extend to other activity coefficient models, e.g. Wilson Model