Understanding and predicting CO2 properties

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Overview

- Parametric equations of state (pressure explicit)
- Non-parametric EoS (pressure explicit or free energy formulation).
- Molecular simulations

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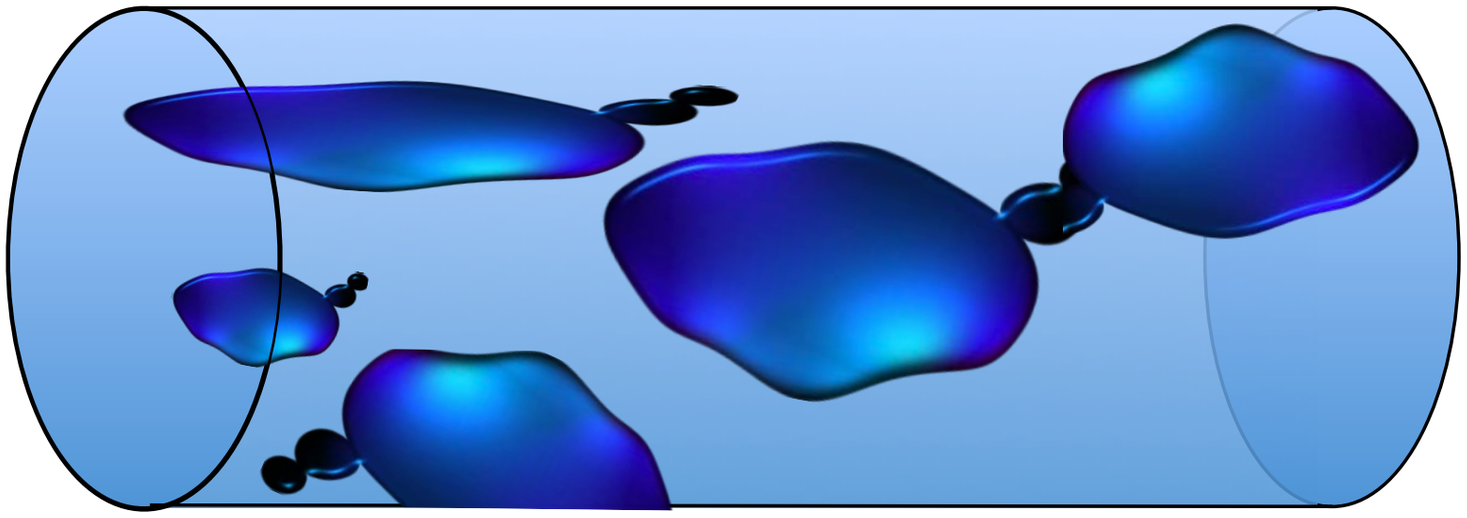
- Non-parametric EoS (pressure explicit or free energy formulation).

- Molecular simulations

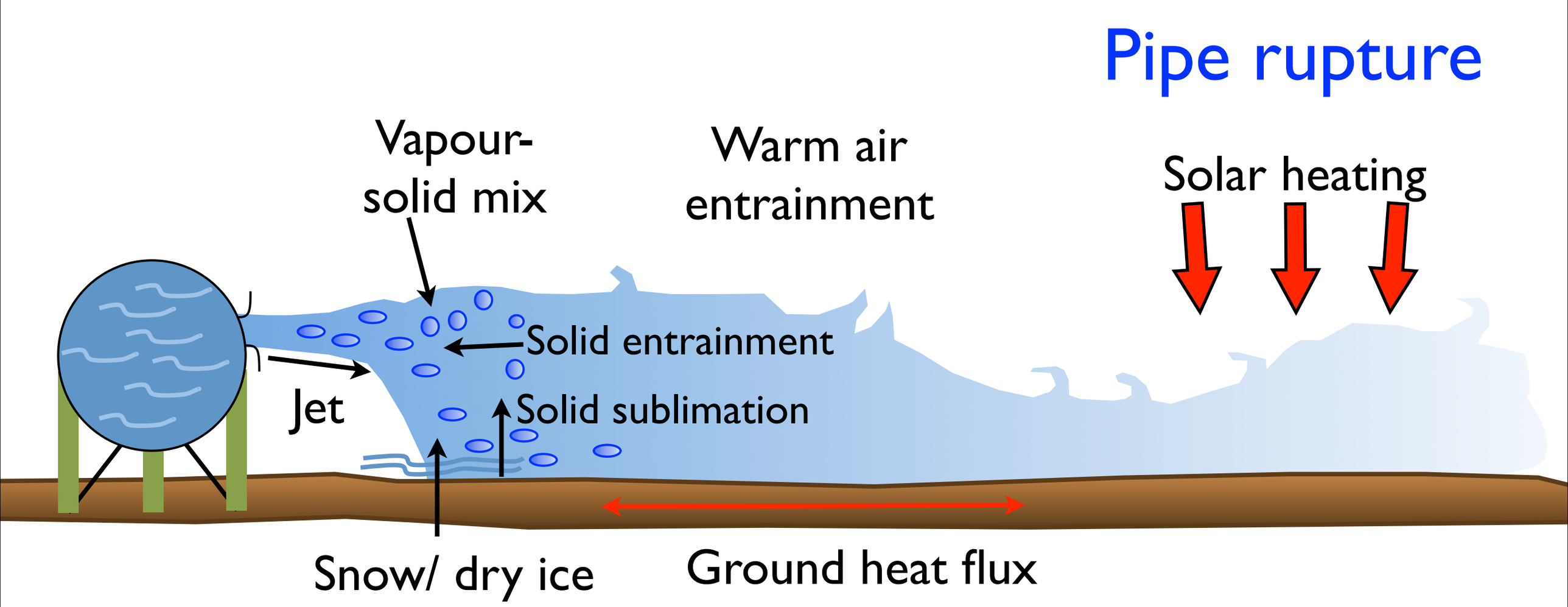
- **Uncertainty quantification**

Potential applications: Avoiding pipeline issues



Two-phase flow

Pipe rupture



Coexistence - Impurities

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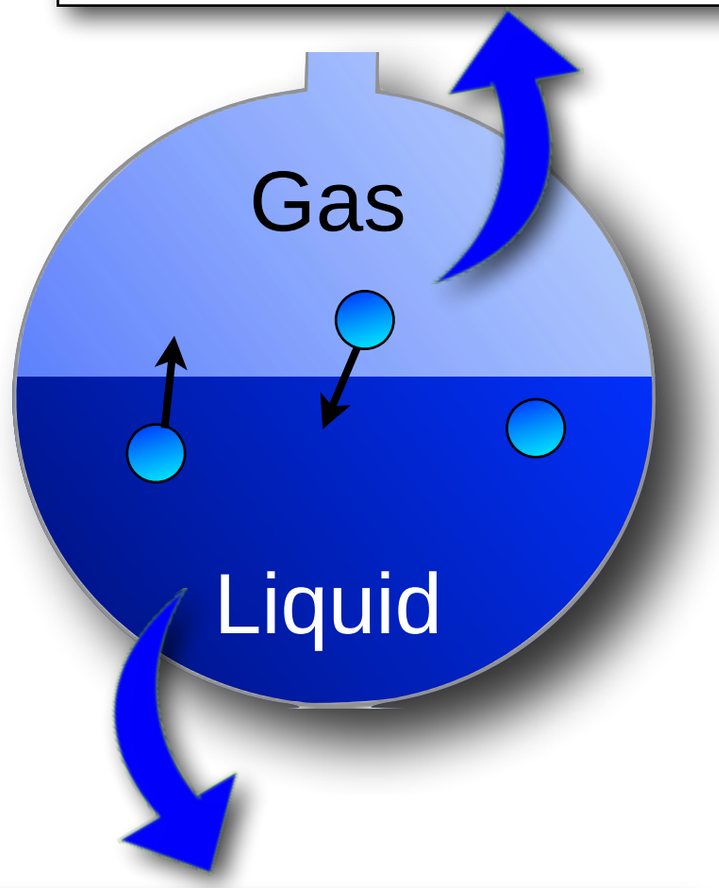
x_G: Gas composition
v_G: Gas volume



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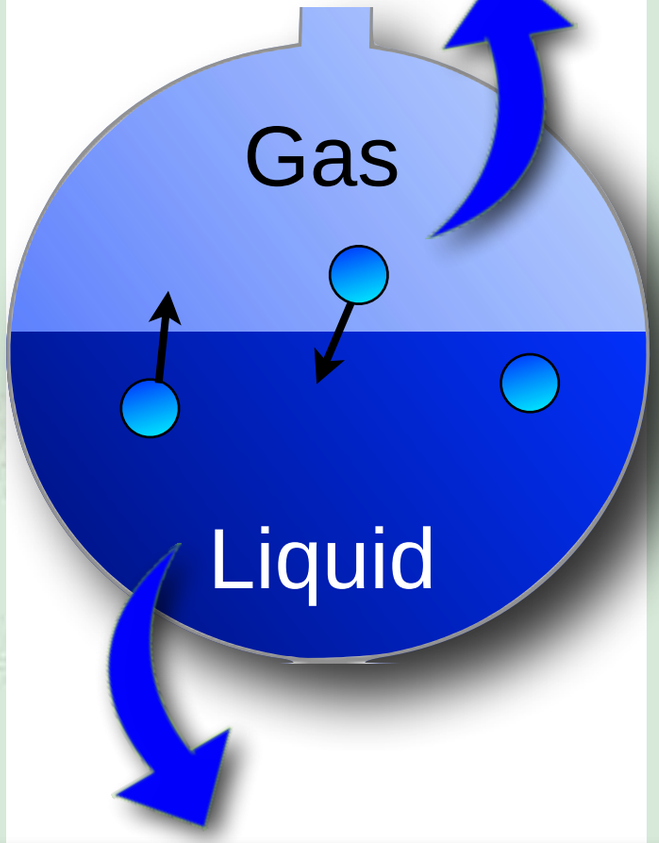

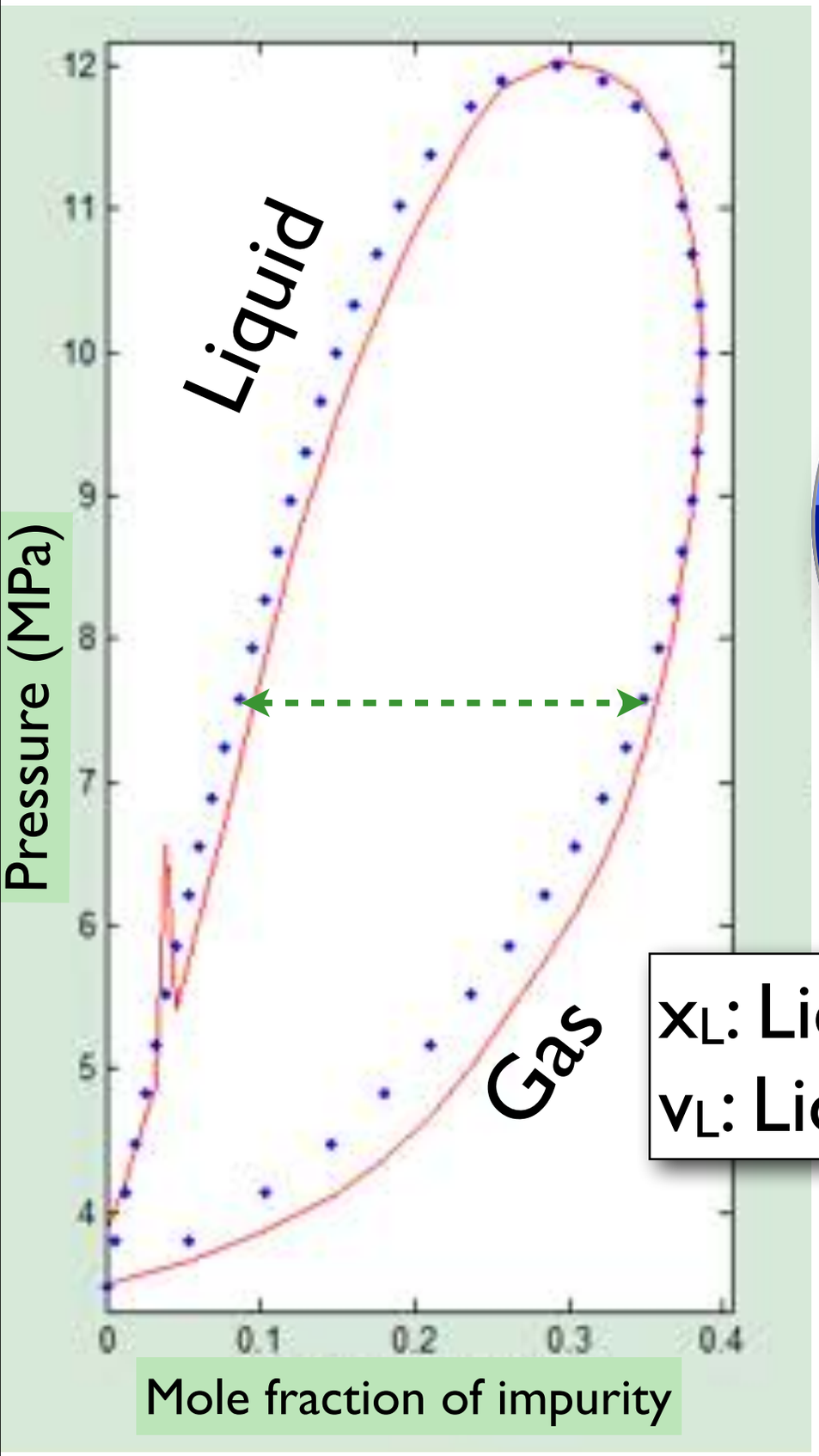

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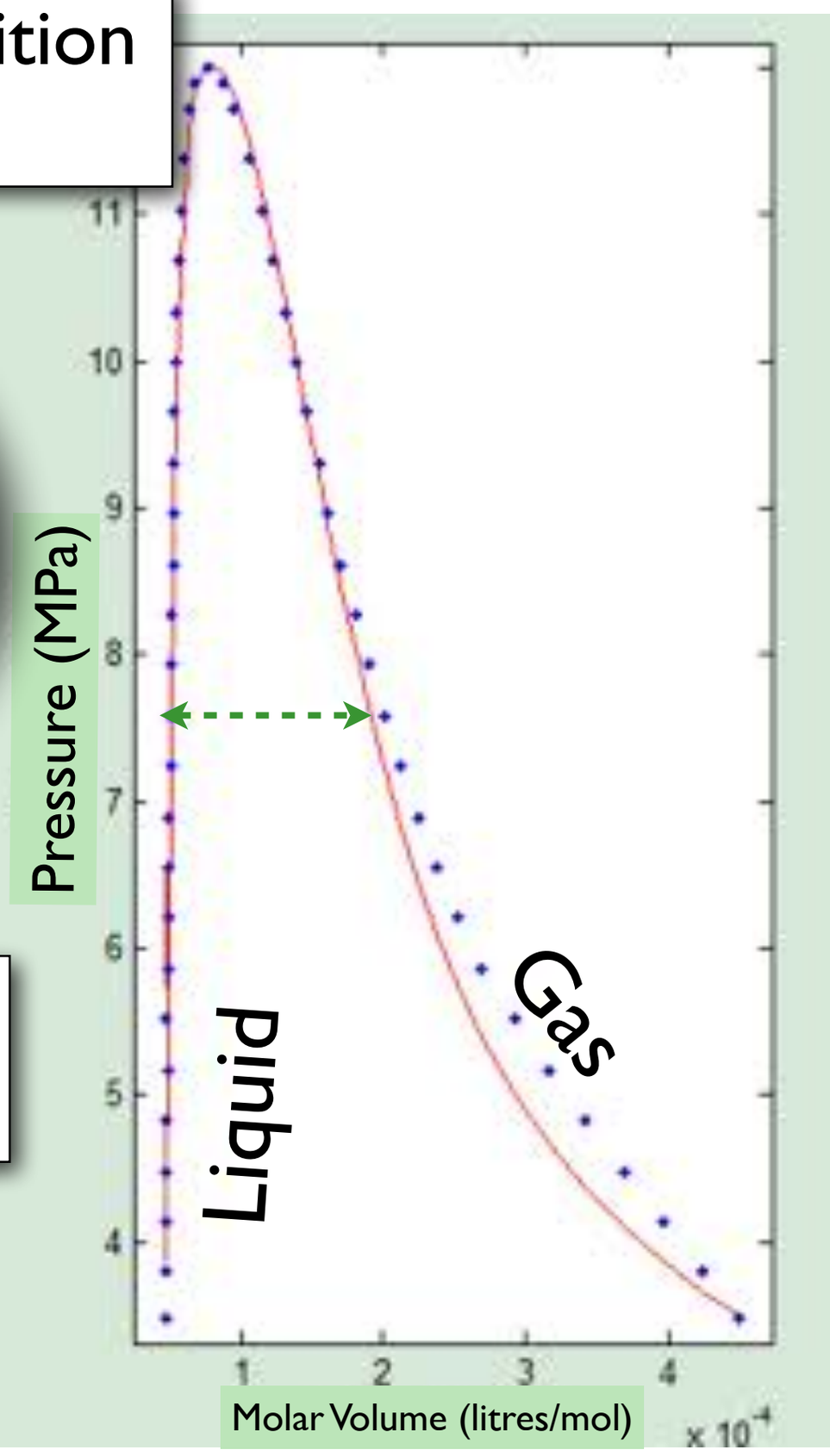
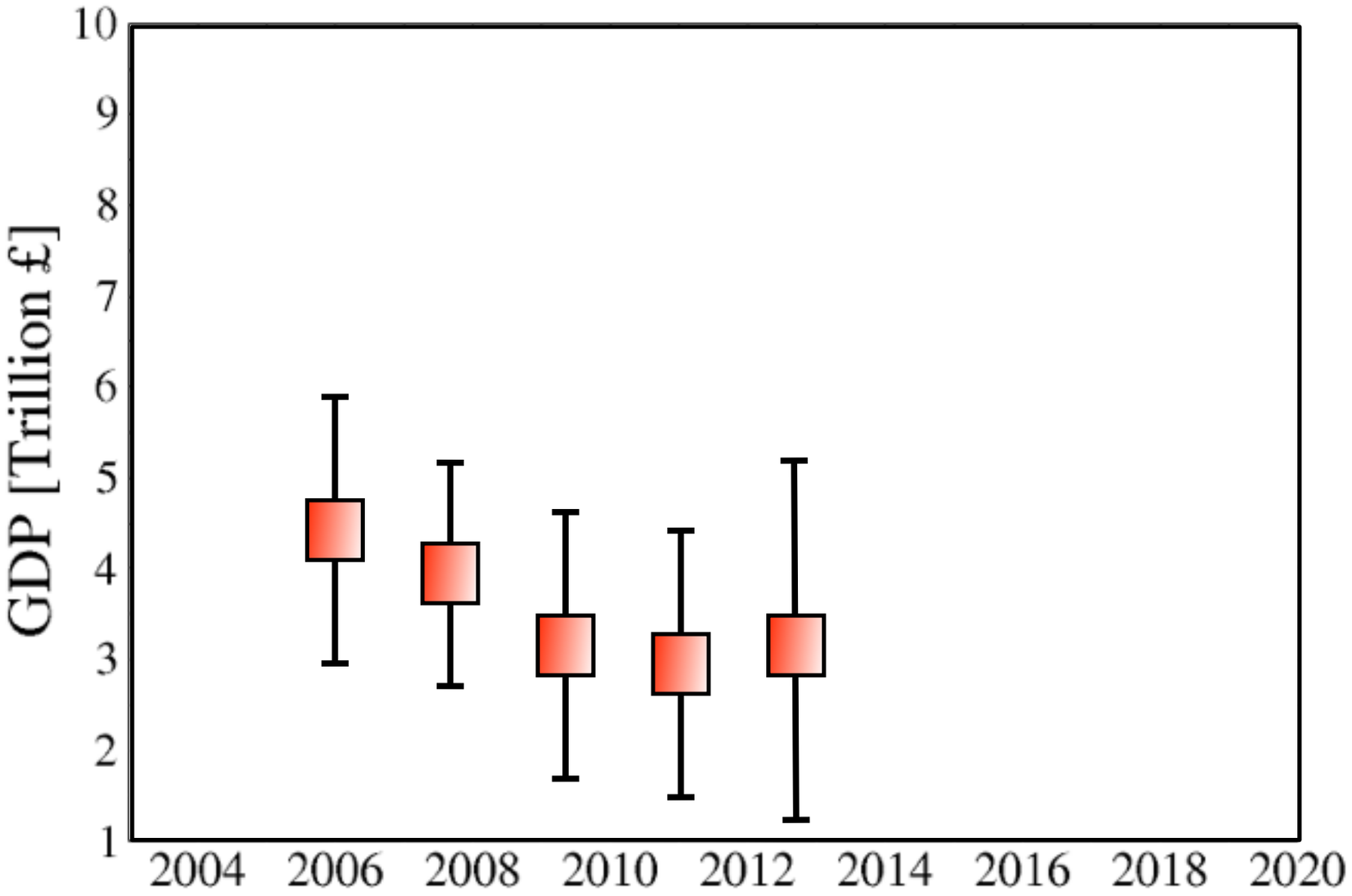


CO2+N2 data

Uncertainty quantification



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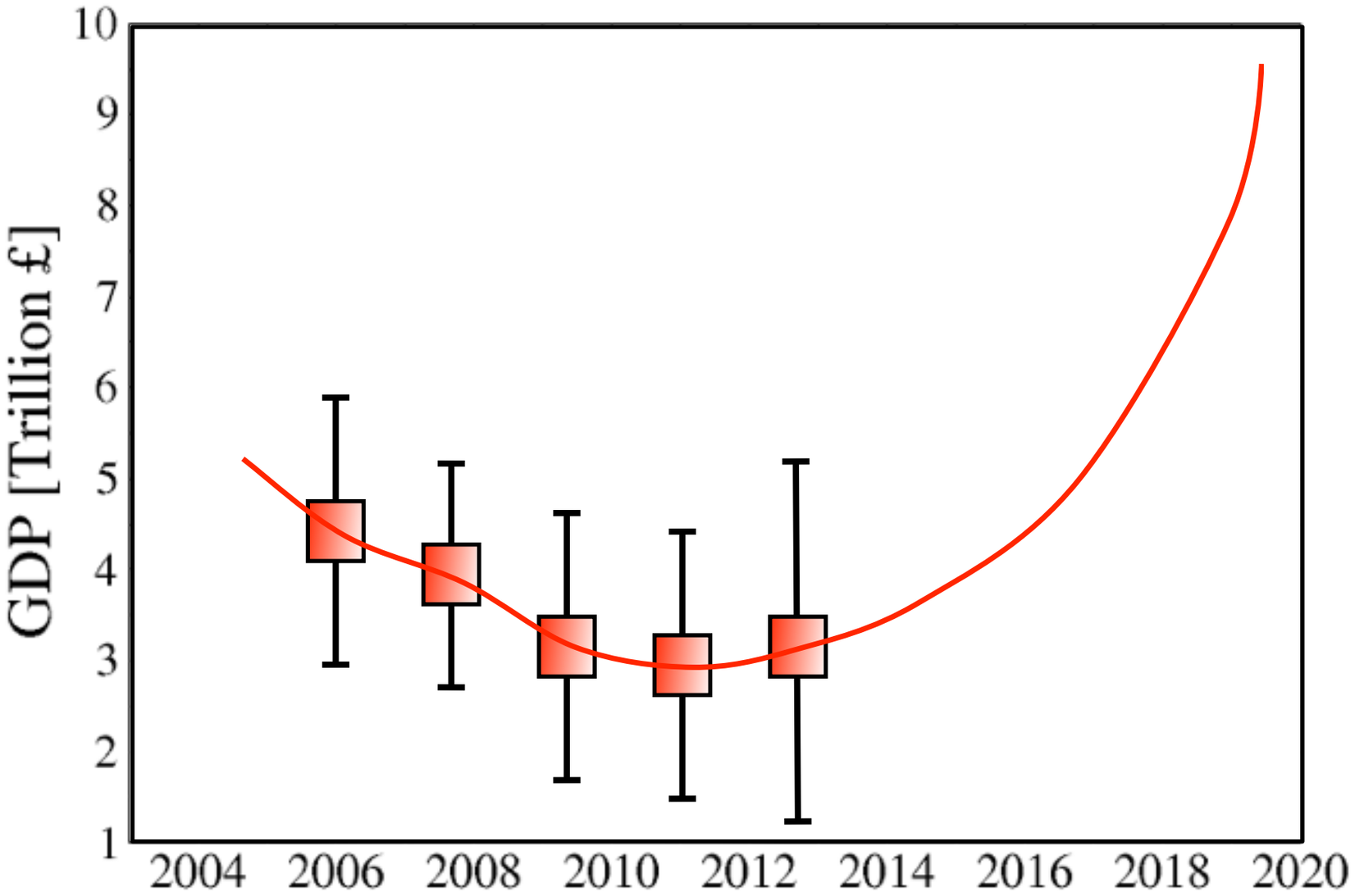

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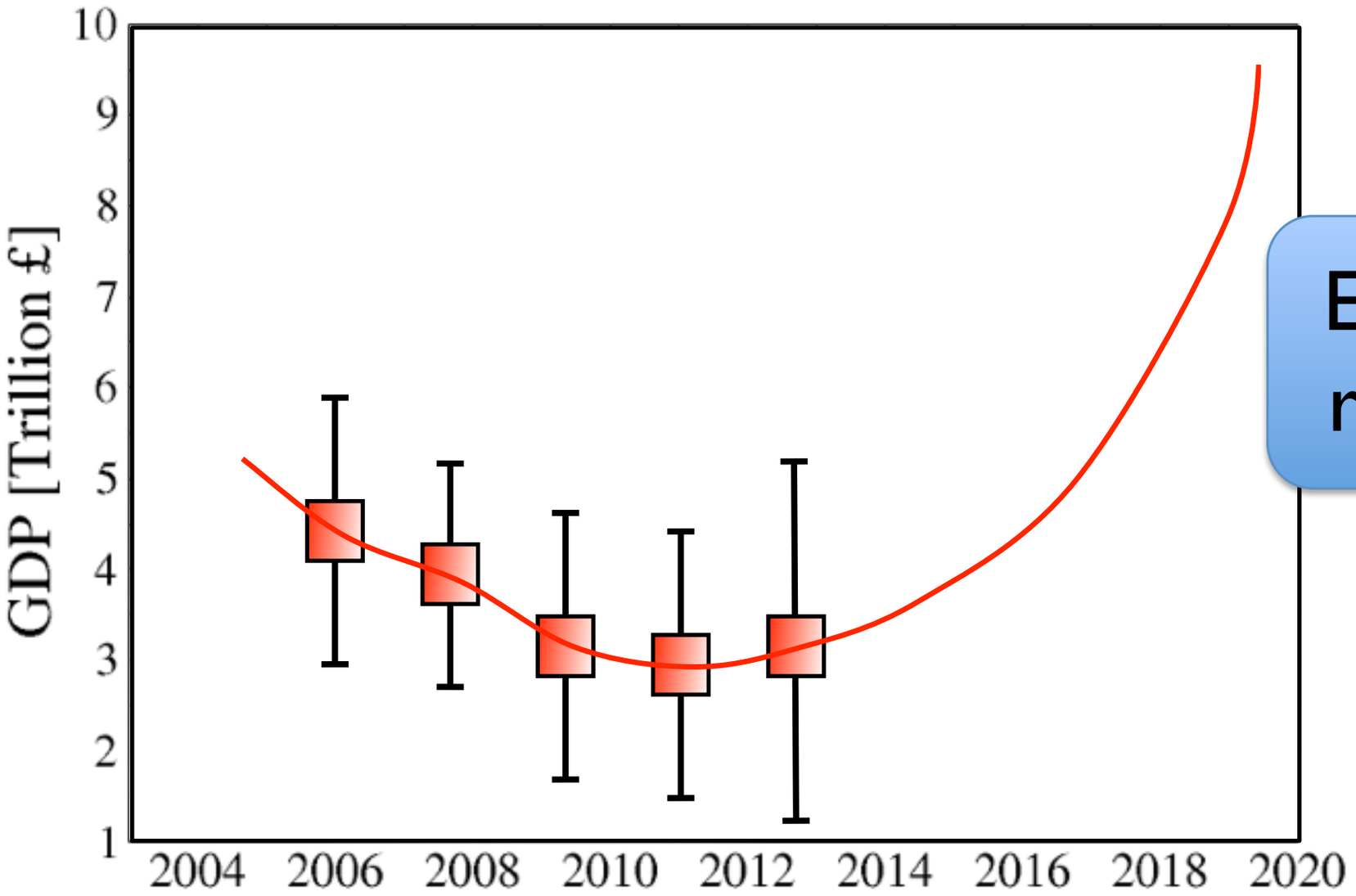

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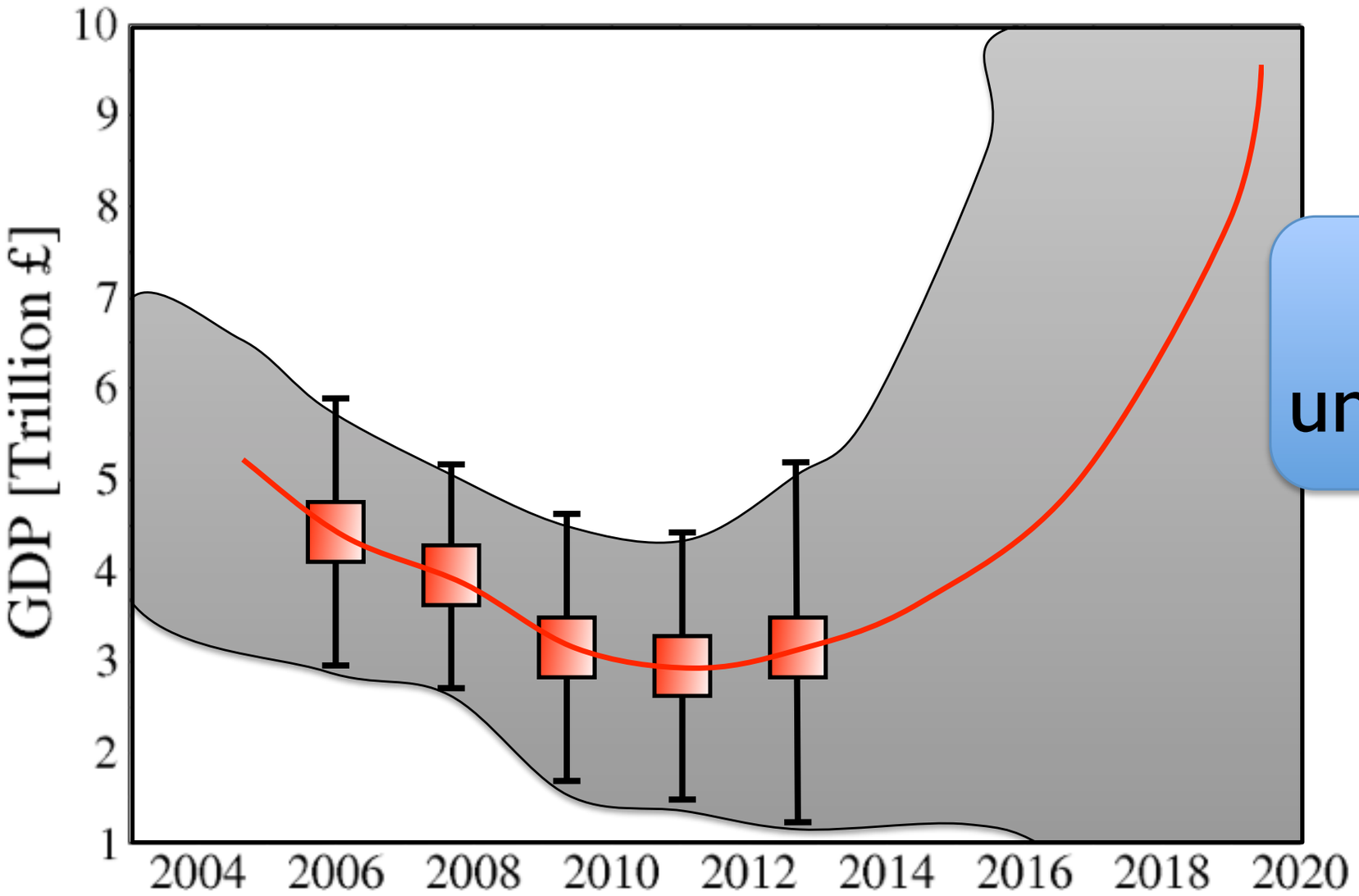

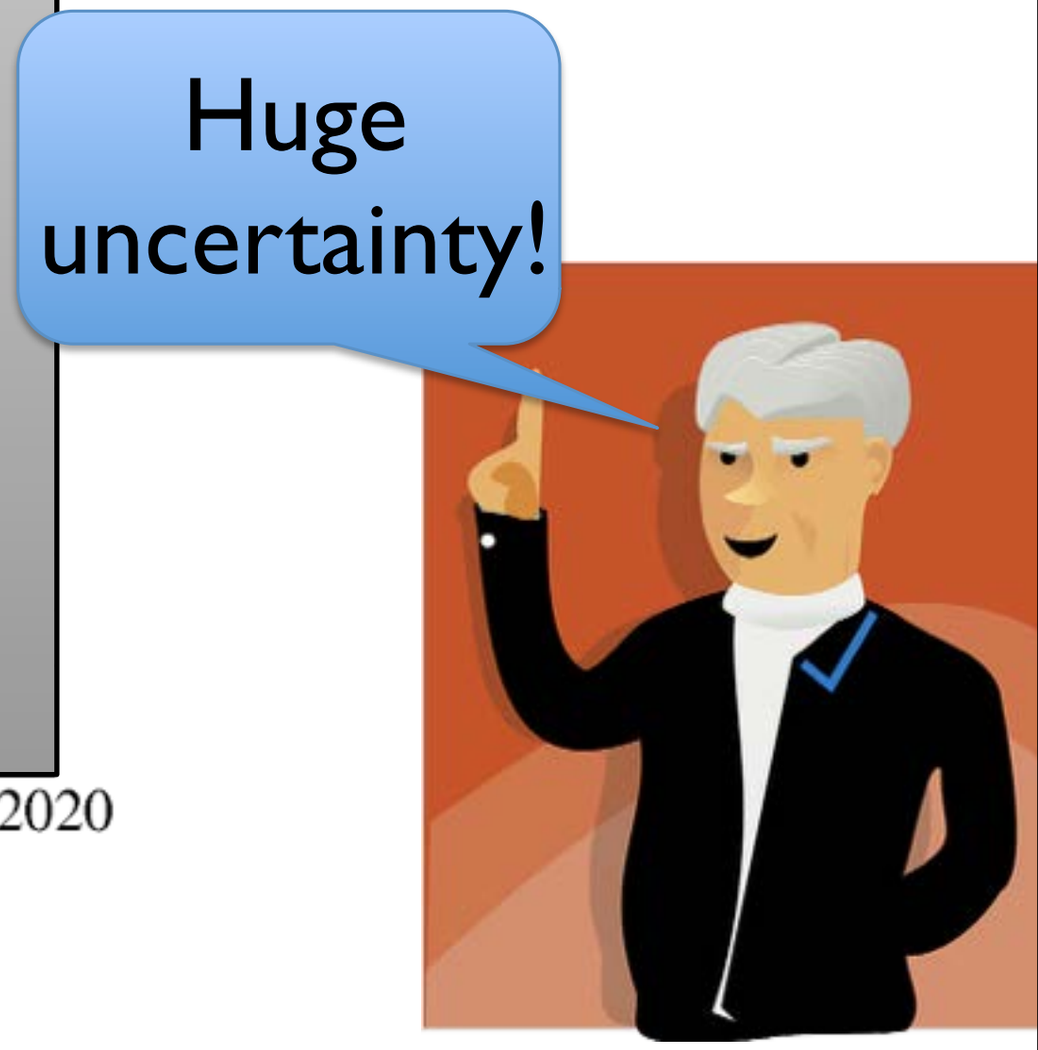

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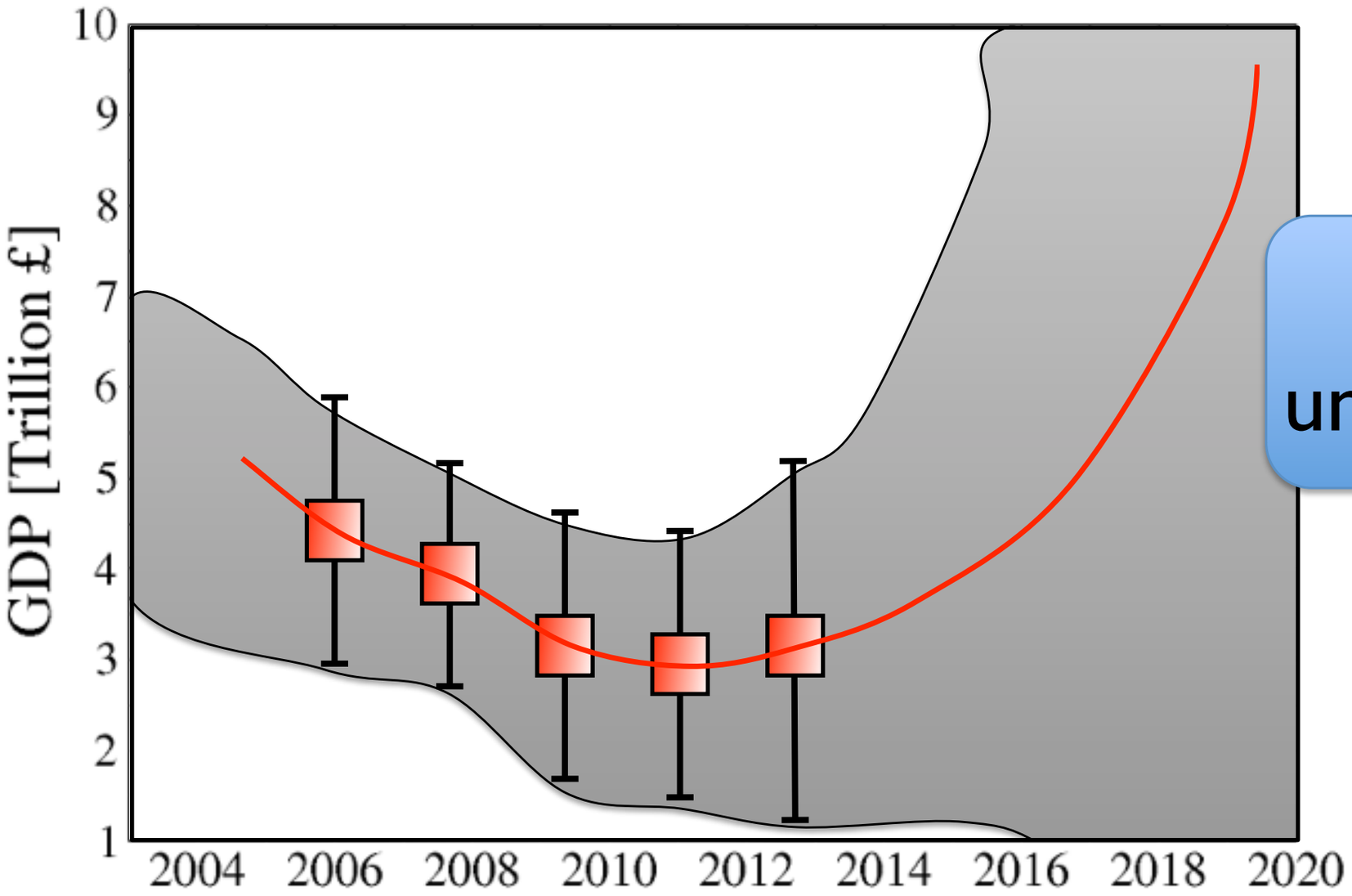

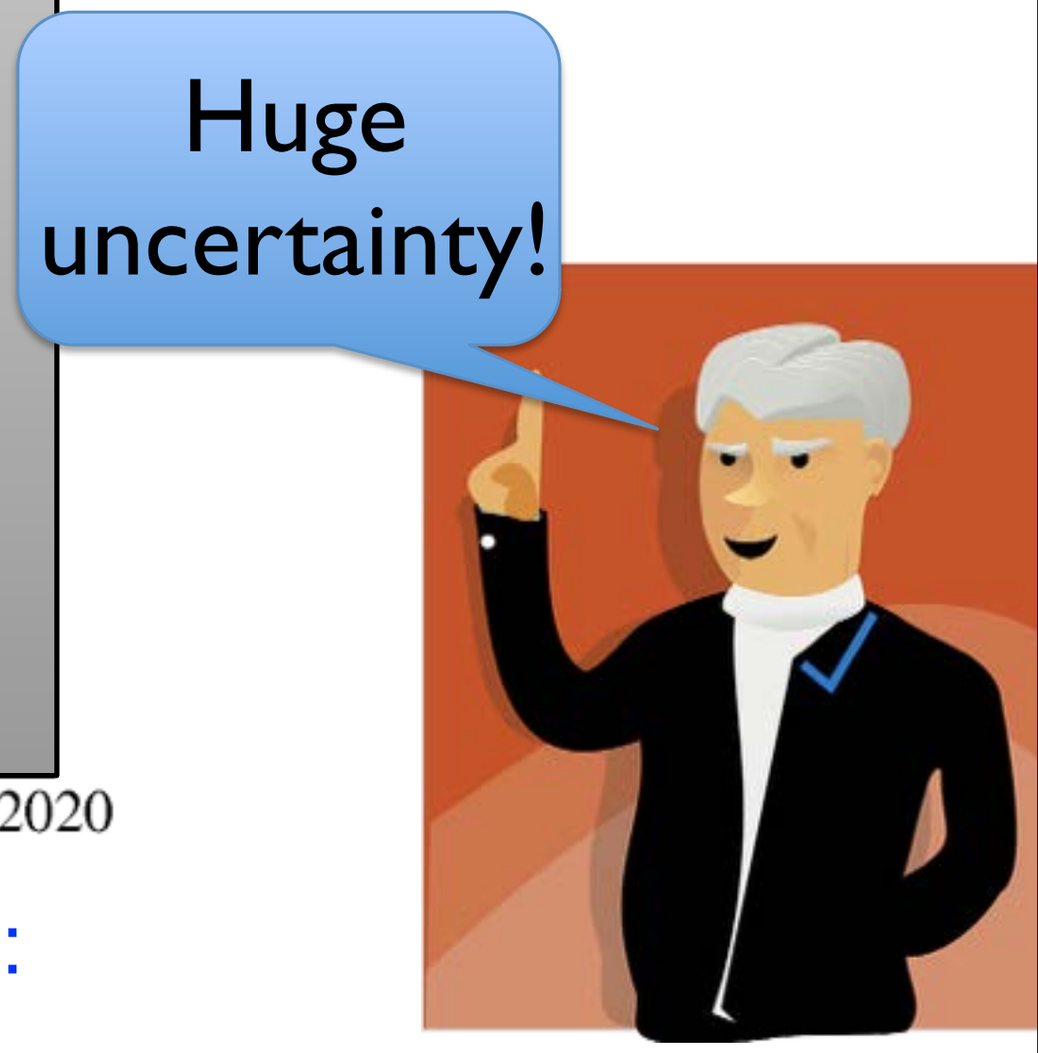

Must account for uncertainty due to:

- Incomplete data
- Measurements errors
- Model imperfection

A generalised equation of state

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)}$$

Peng-Robinson

$$P(v,T) := \frac{RT}{v + a} - \frac{b}{v^2 + c} - \frac{d}{v^3 + e} + \left(\frac{f}{v - g}\right)^6$$

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This work

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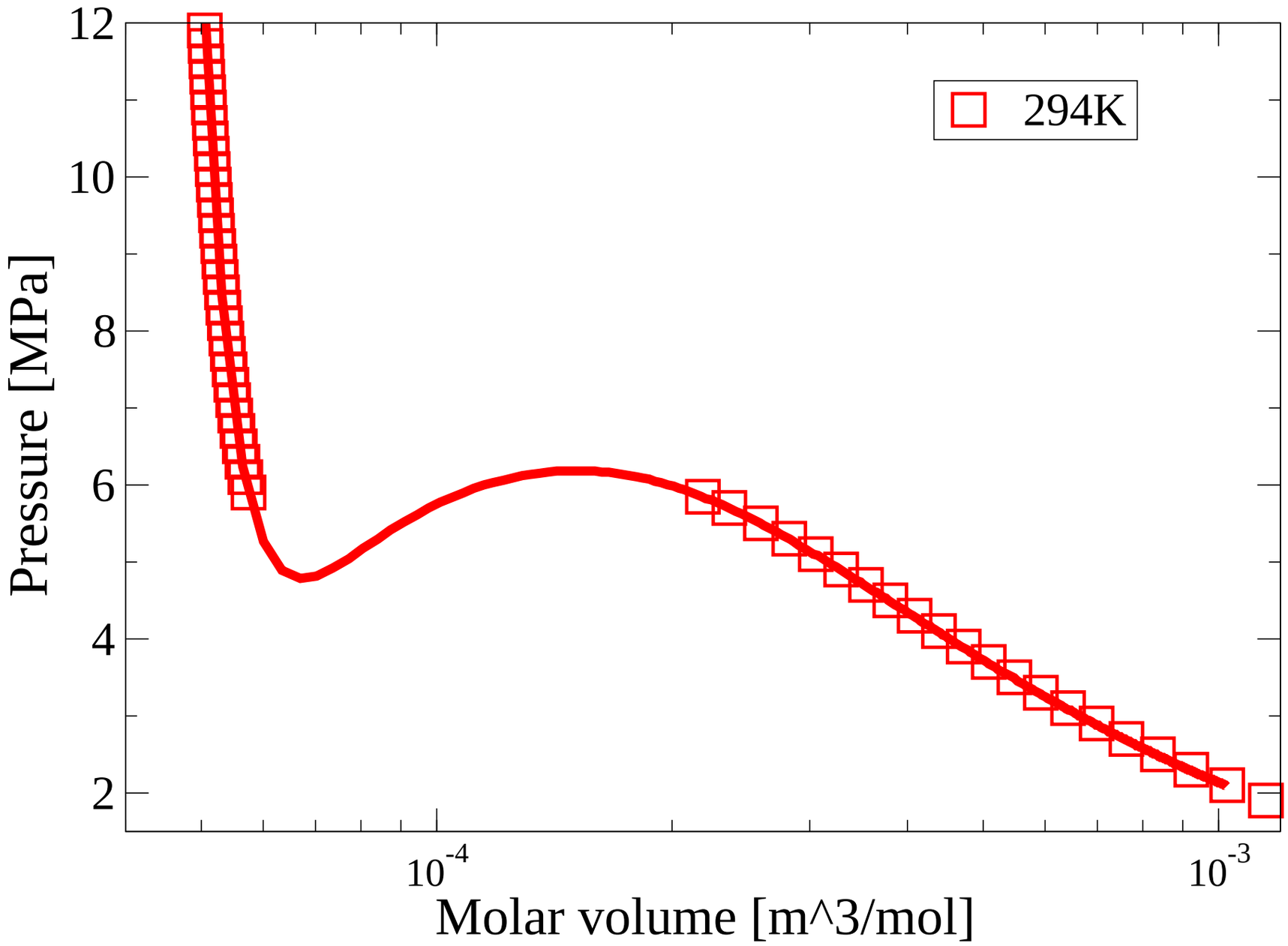
Higher order singularity provides a sharper ‘liquid’ region

Fitting method

Fitting criterion



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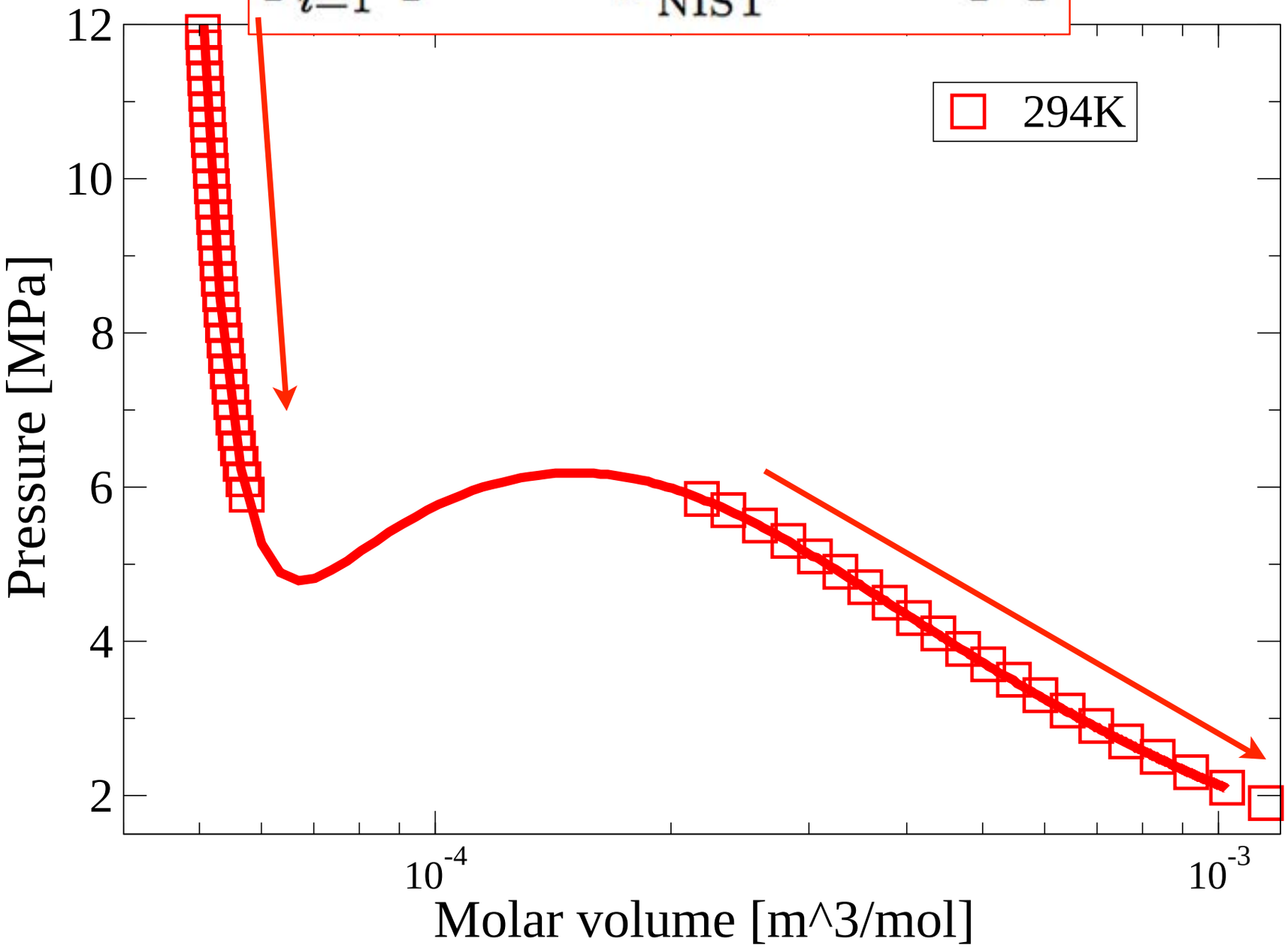

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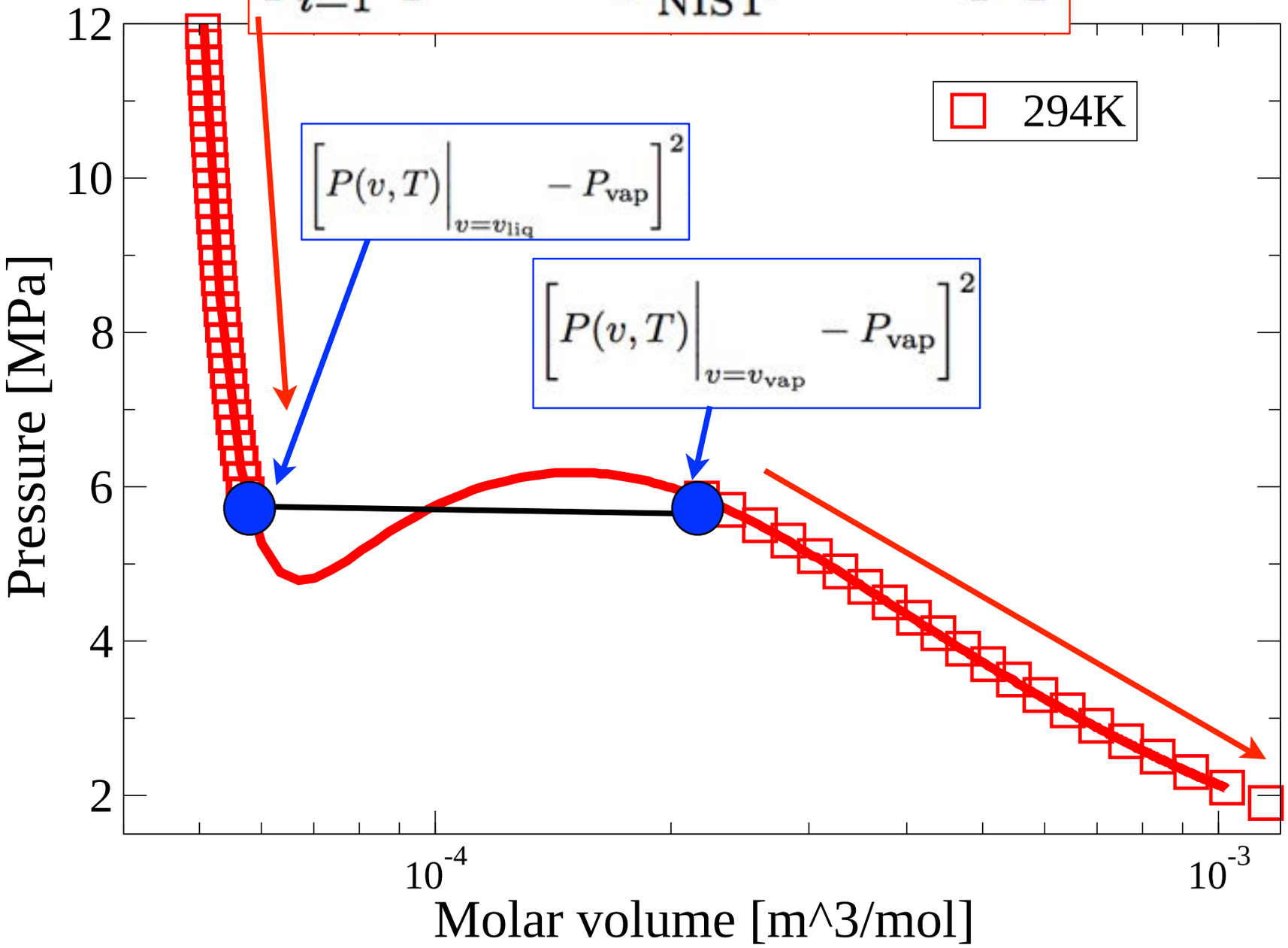

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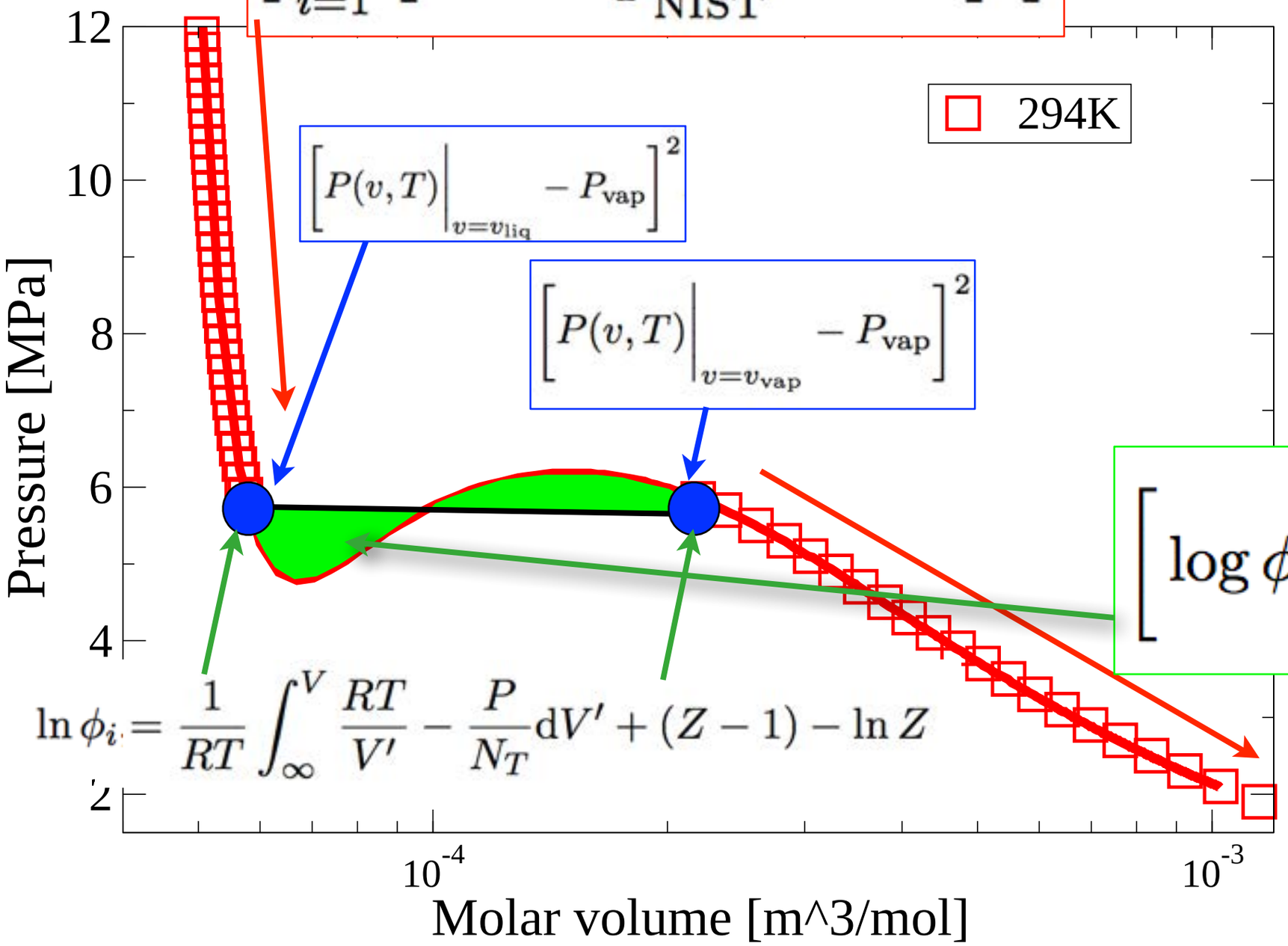

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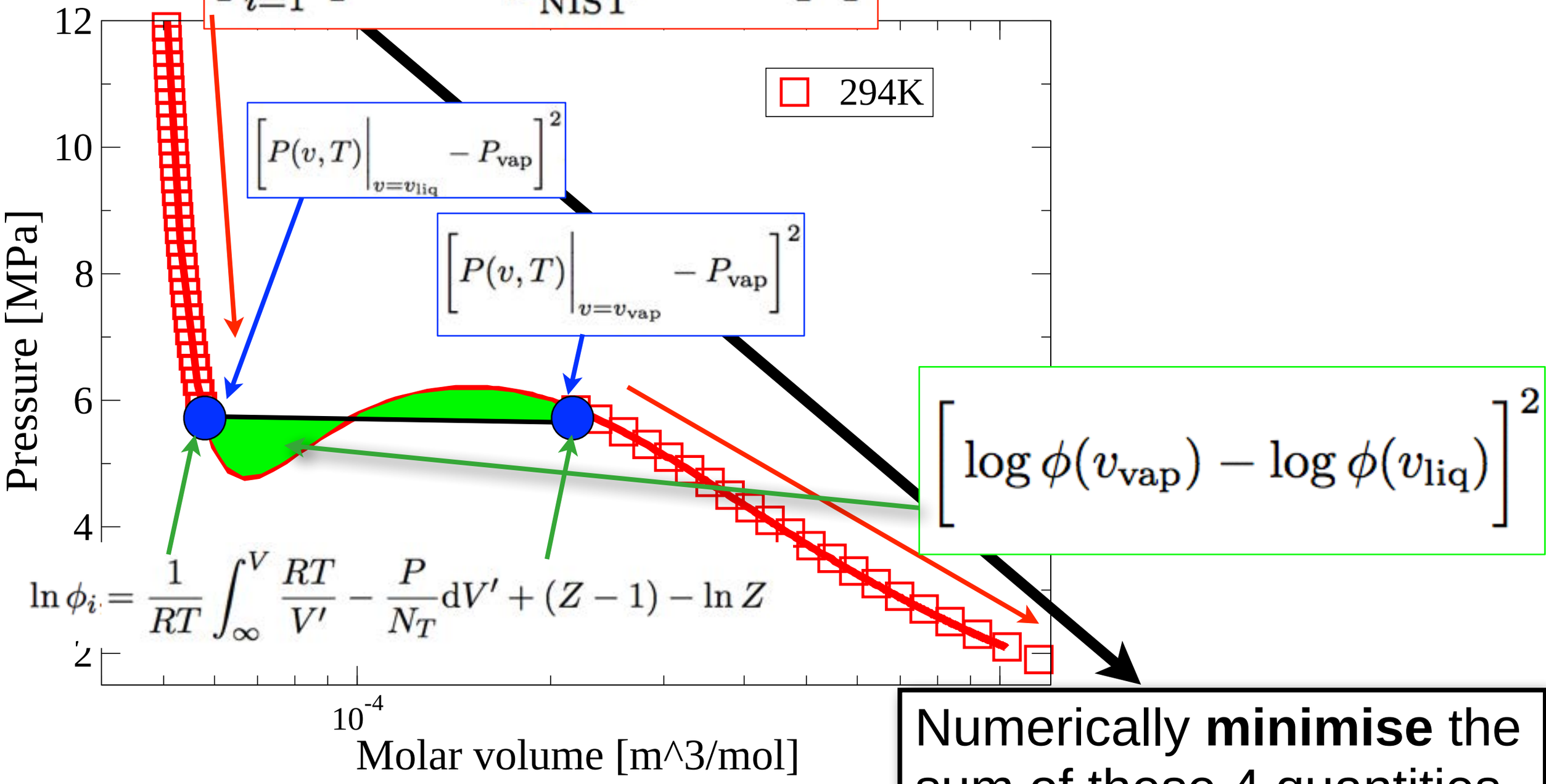
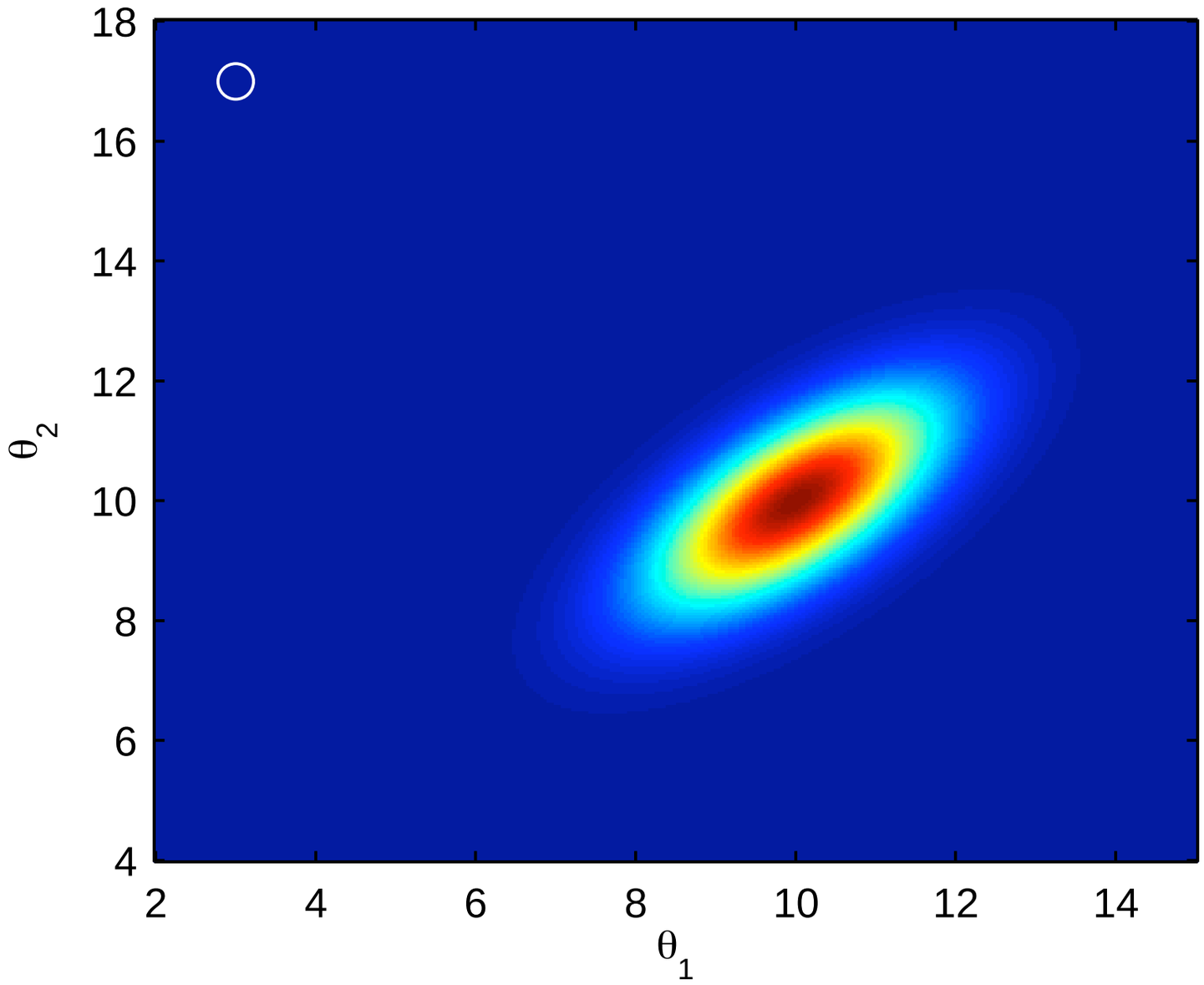


Numerically **minimise** the sum of these 4 quantities over the **parameters** a...g

Markov-Chain Monte-Carlo: an example



The search algorithm explores the fitting criterion, spending more time in regions of good fit.

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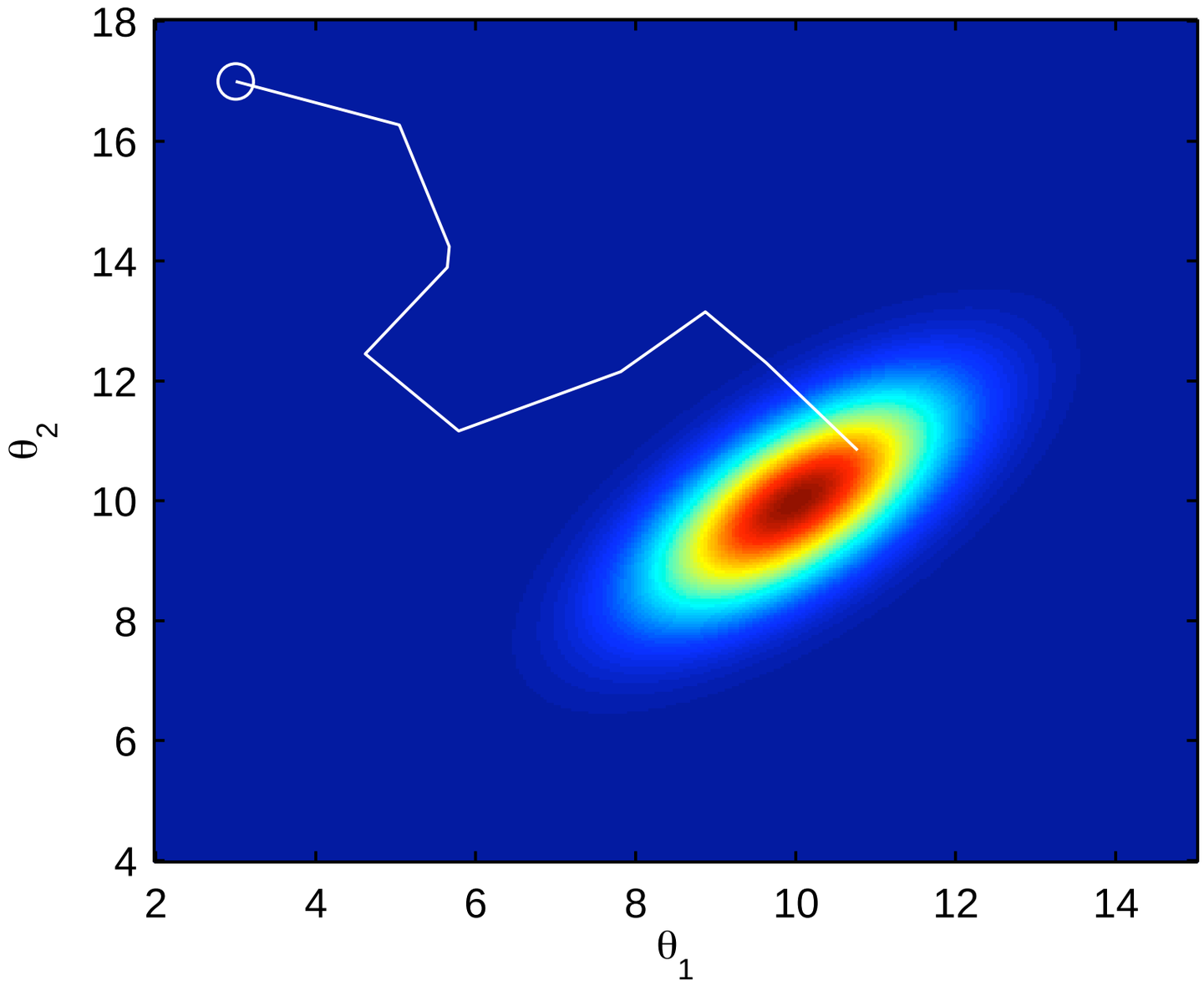

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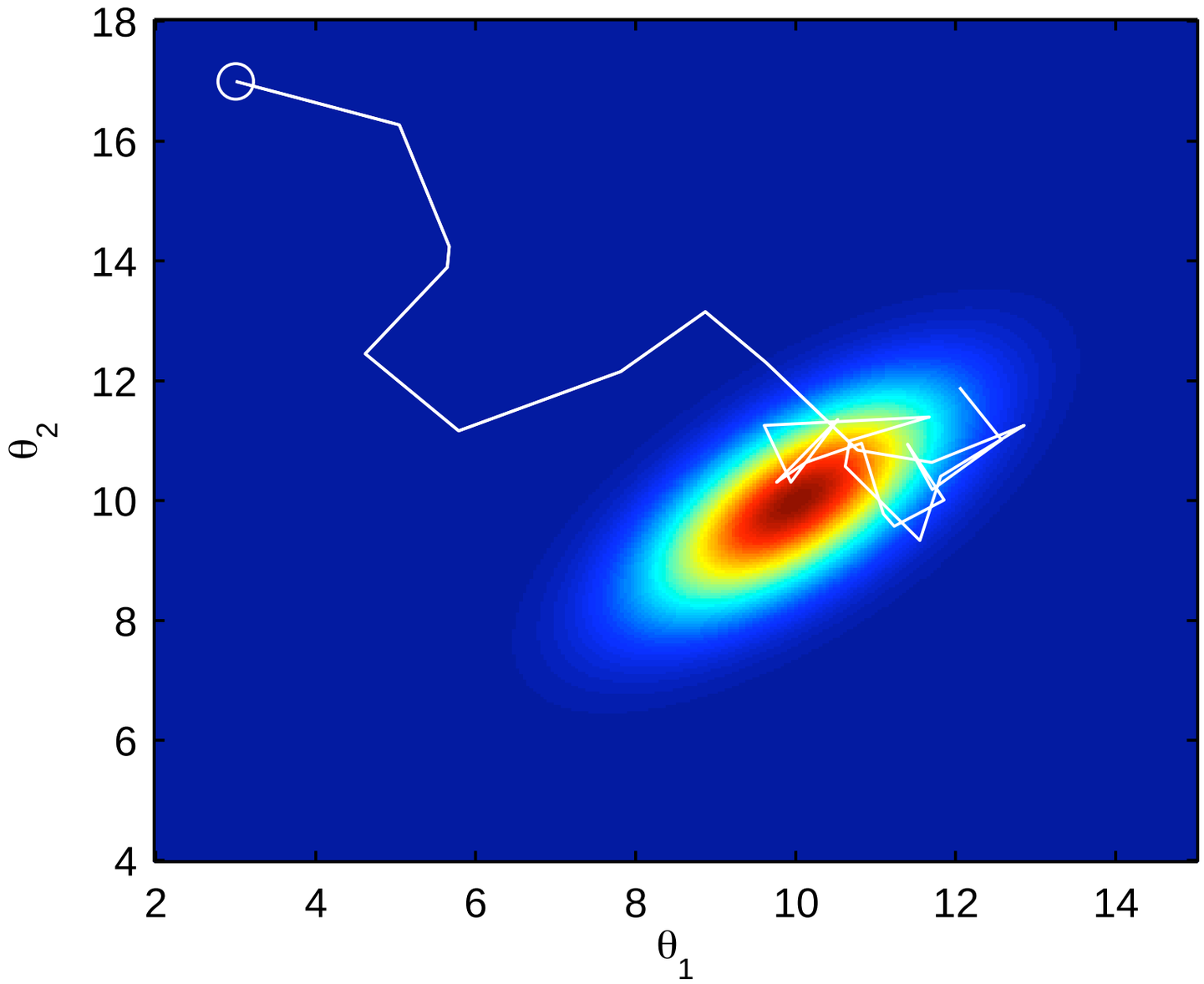

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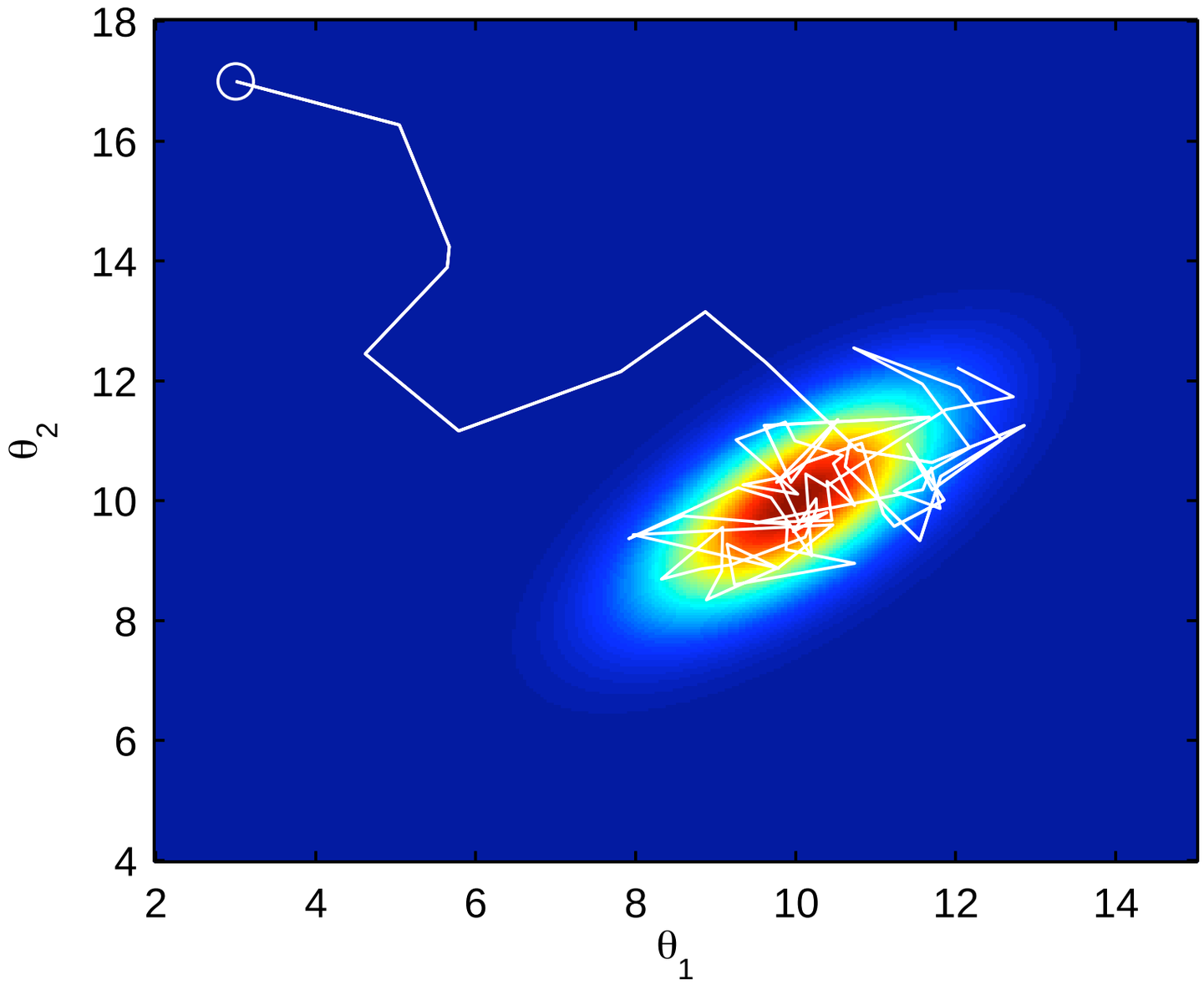

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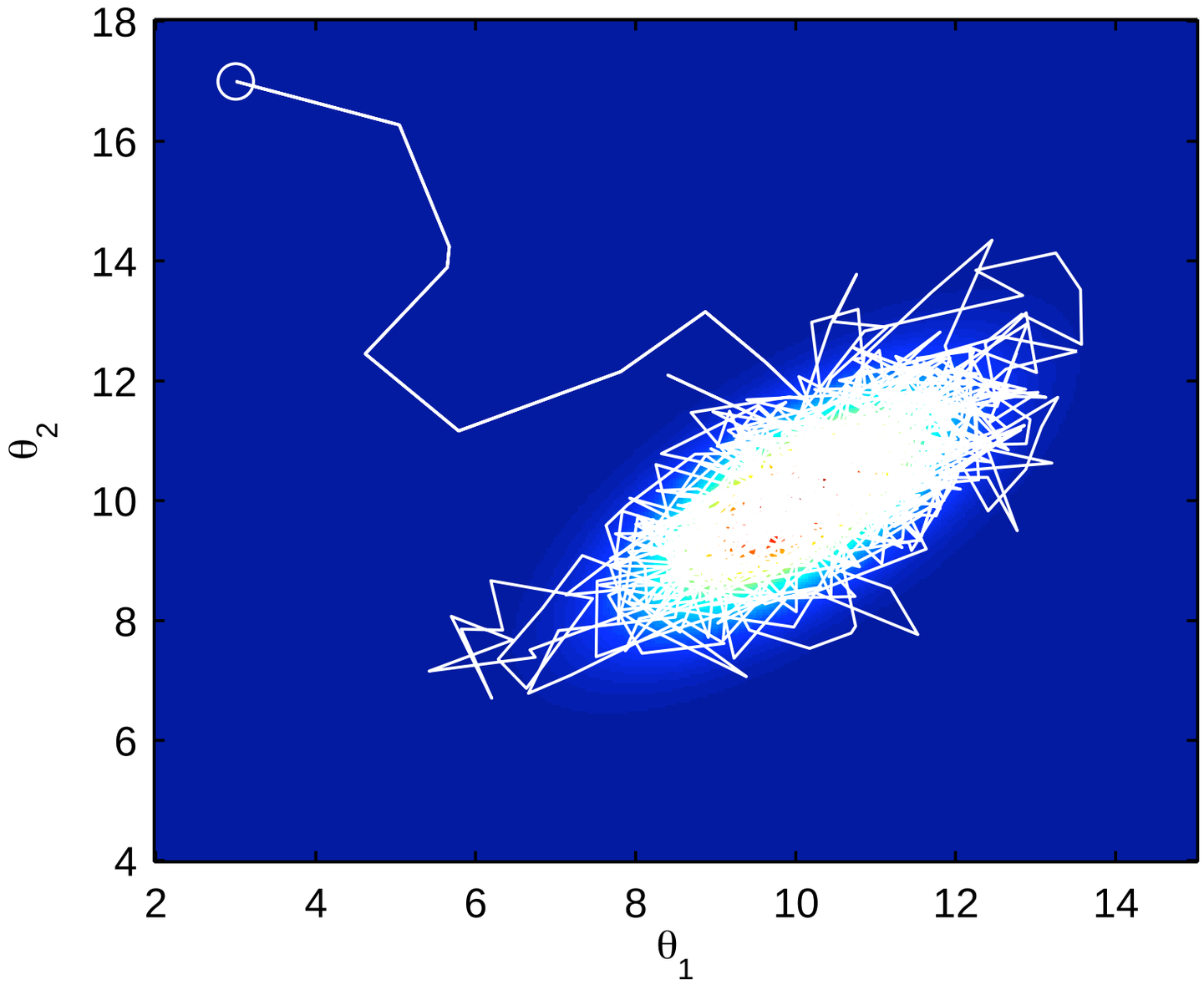

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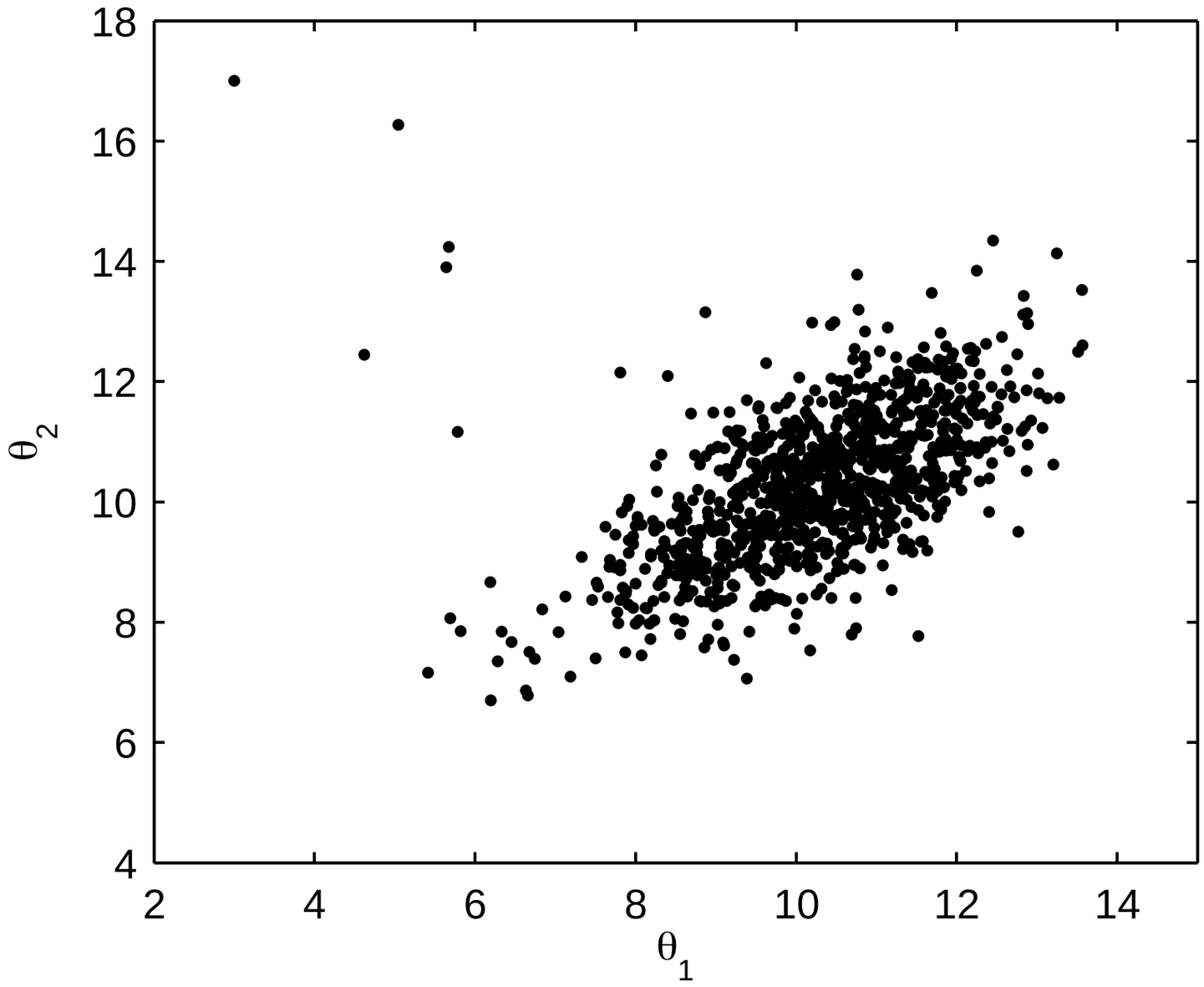

The result is samples of the probability distribution of the parameters

Predictions (pure CO2)

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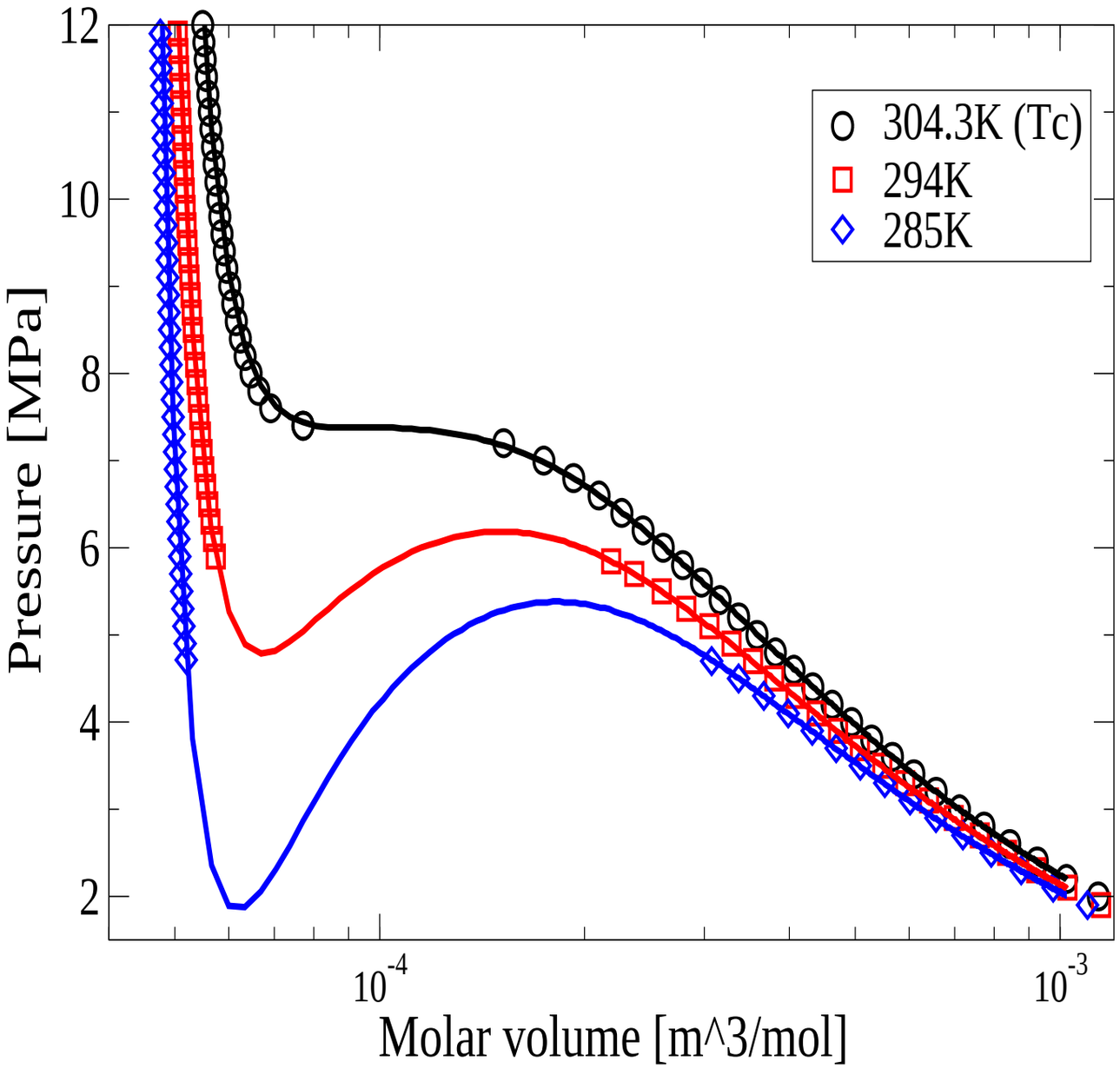

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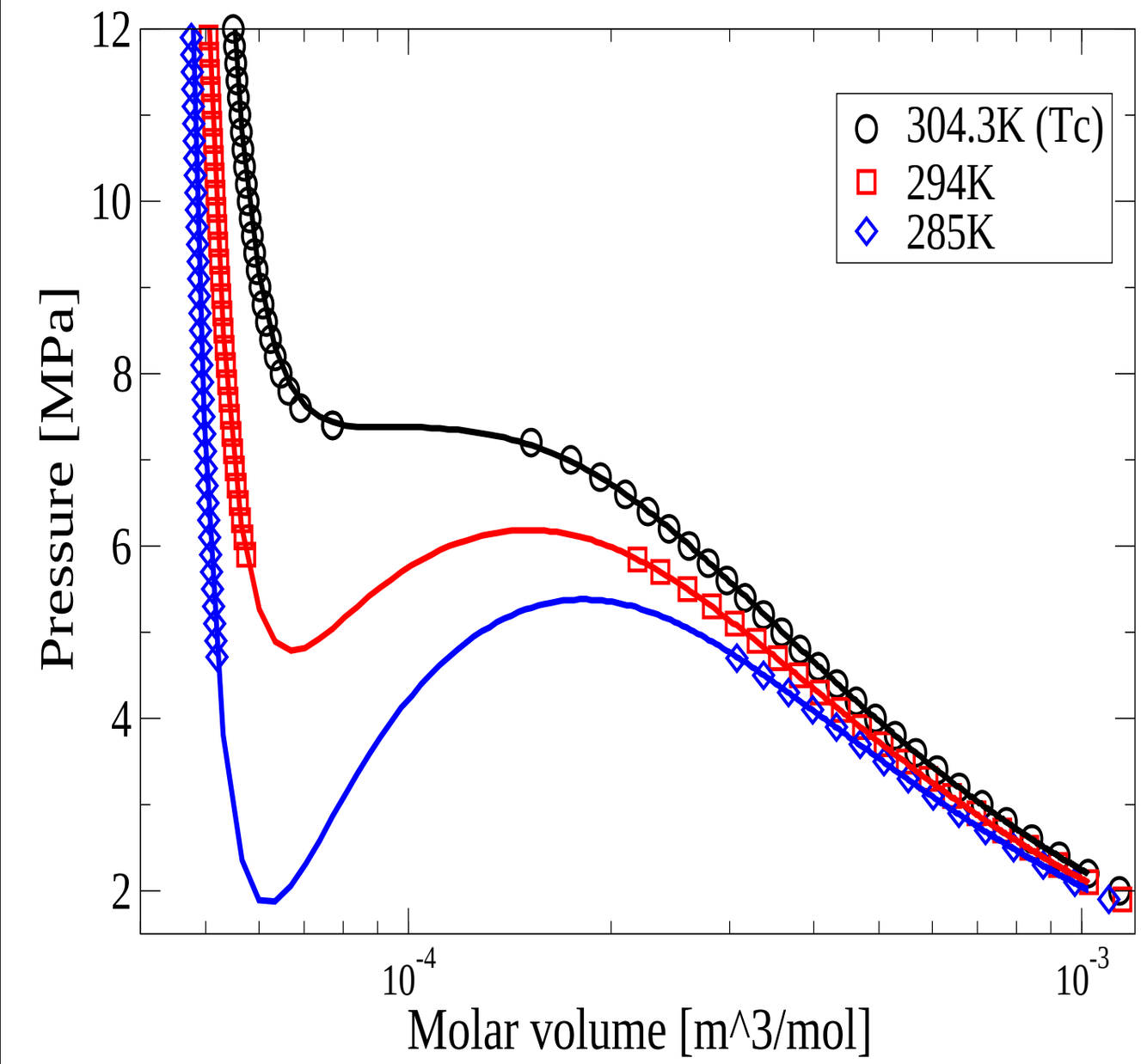
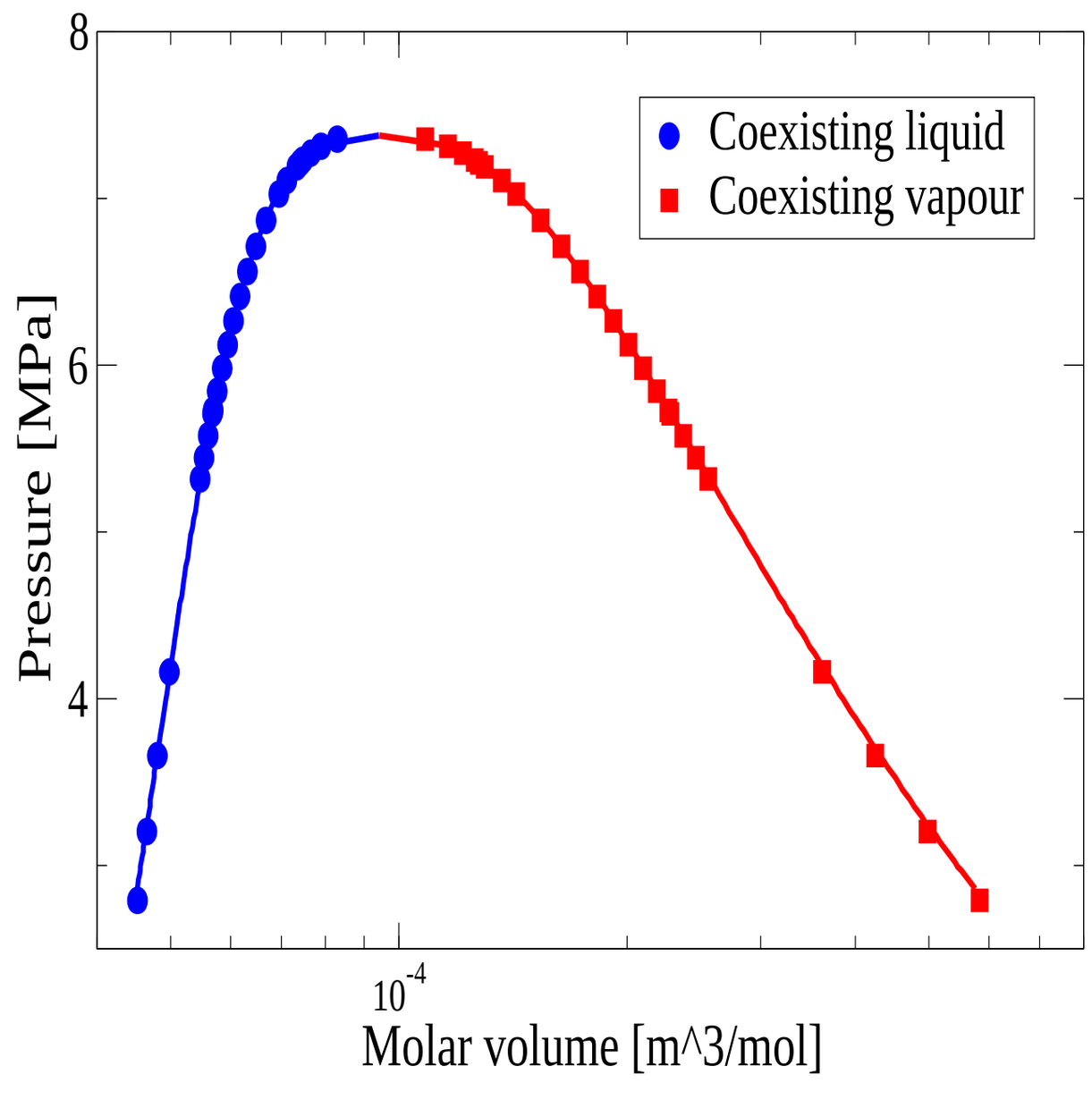
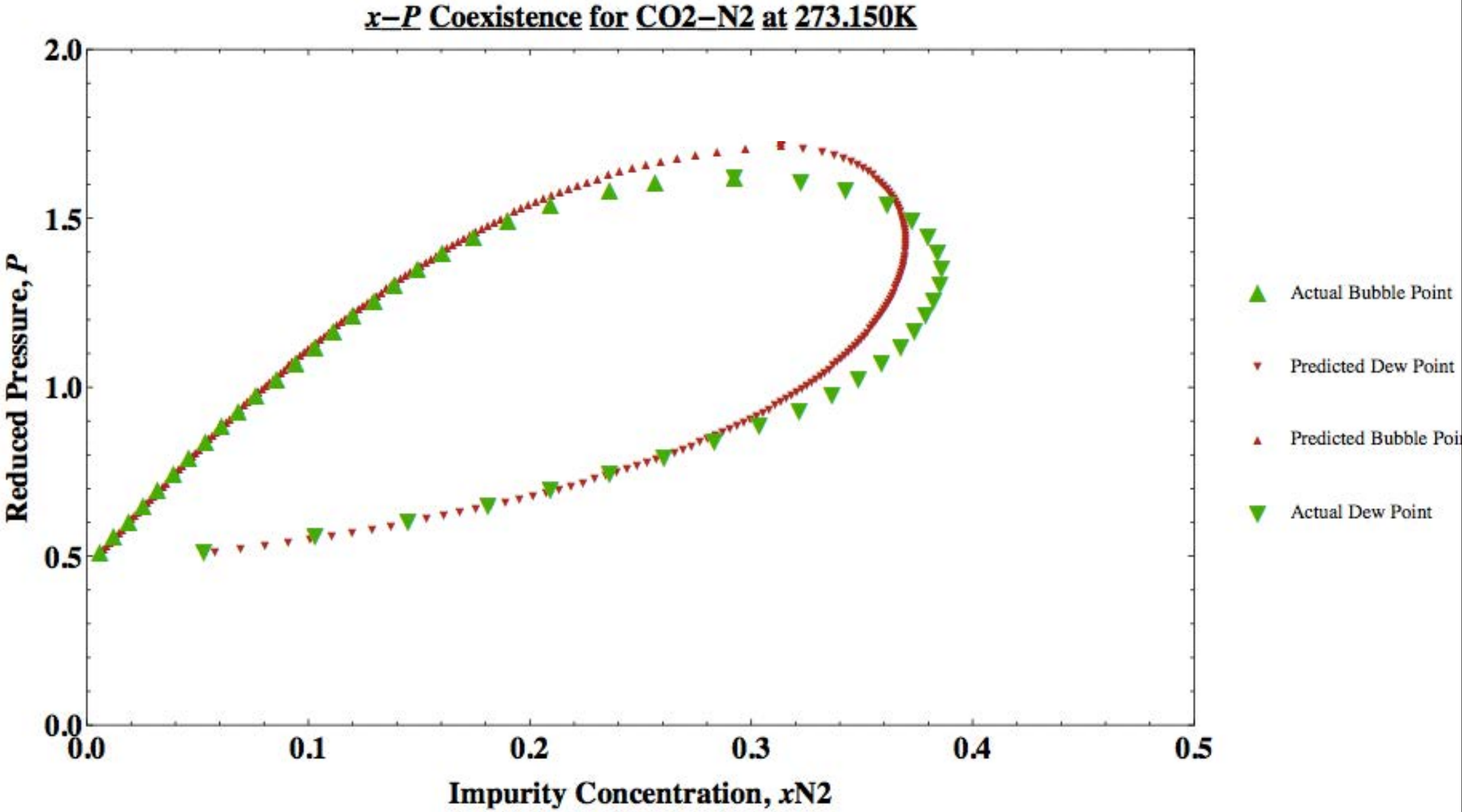


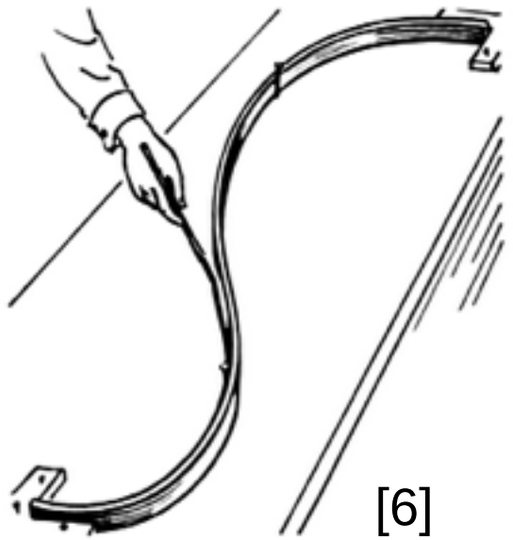


Mixture modelling

CO2+N2



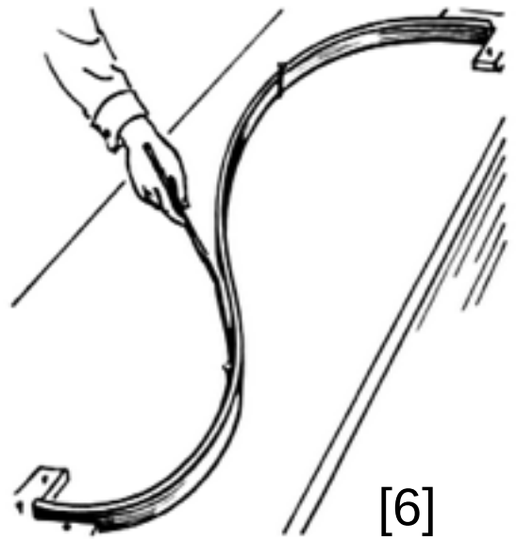
Introduction to non-parametric methods



[6]

Introduction to non-parametric methods

- Model for **pressure against volume,** as with an equation of state.
- However, no need to specify **terms** or **parameters**
- Model '**learns**' the P(v) functional form **from the measurements**



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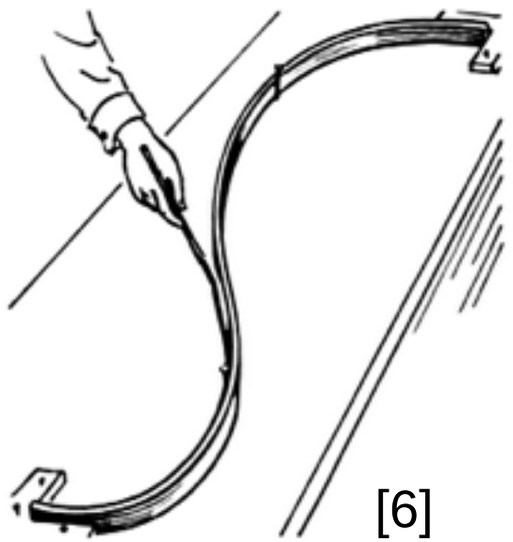

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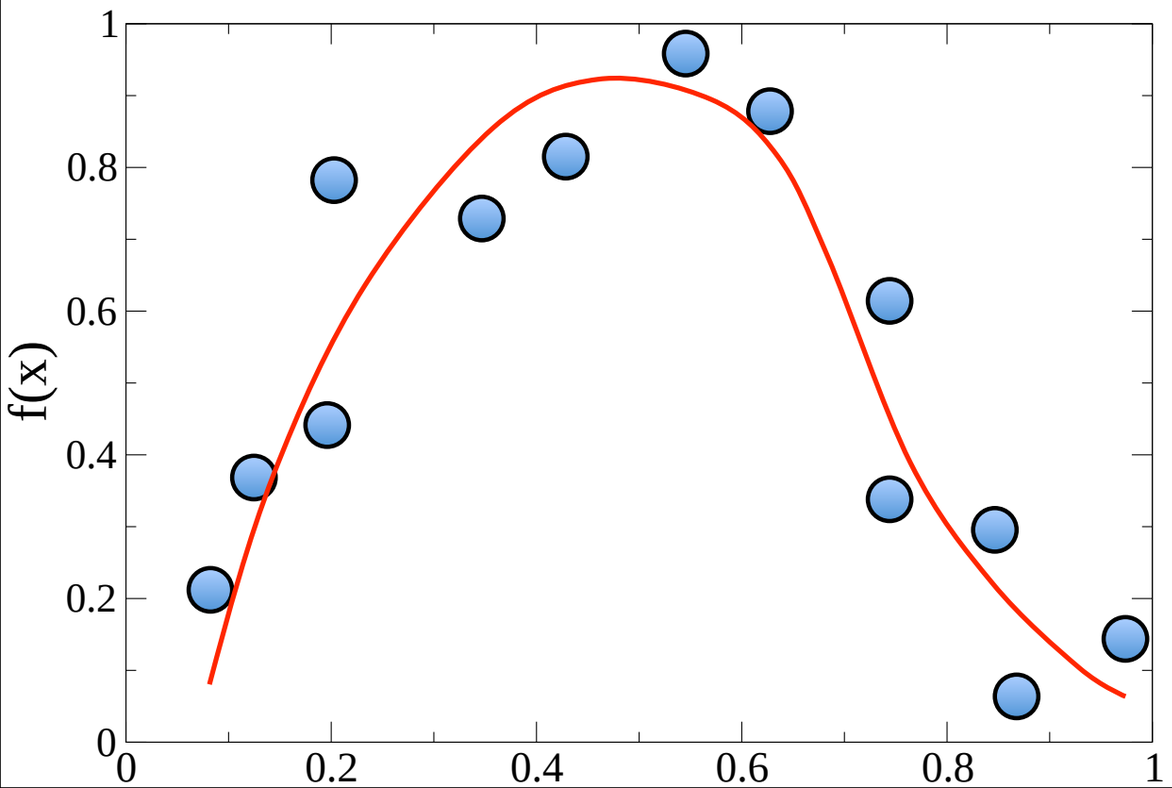
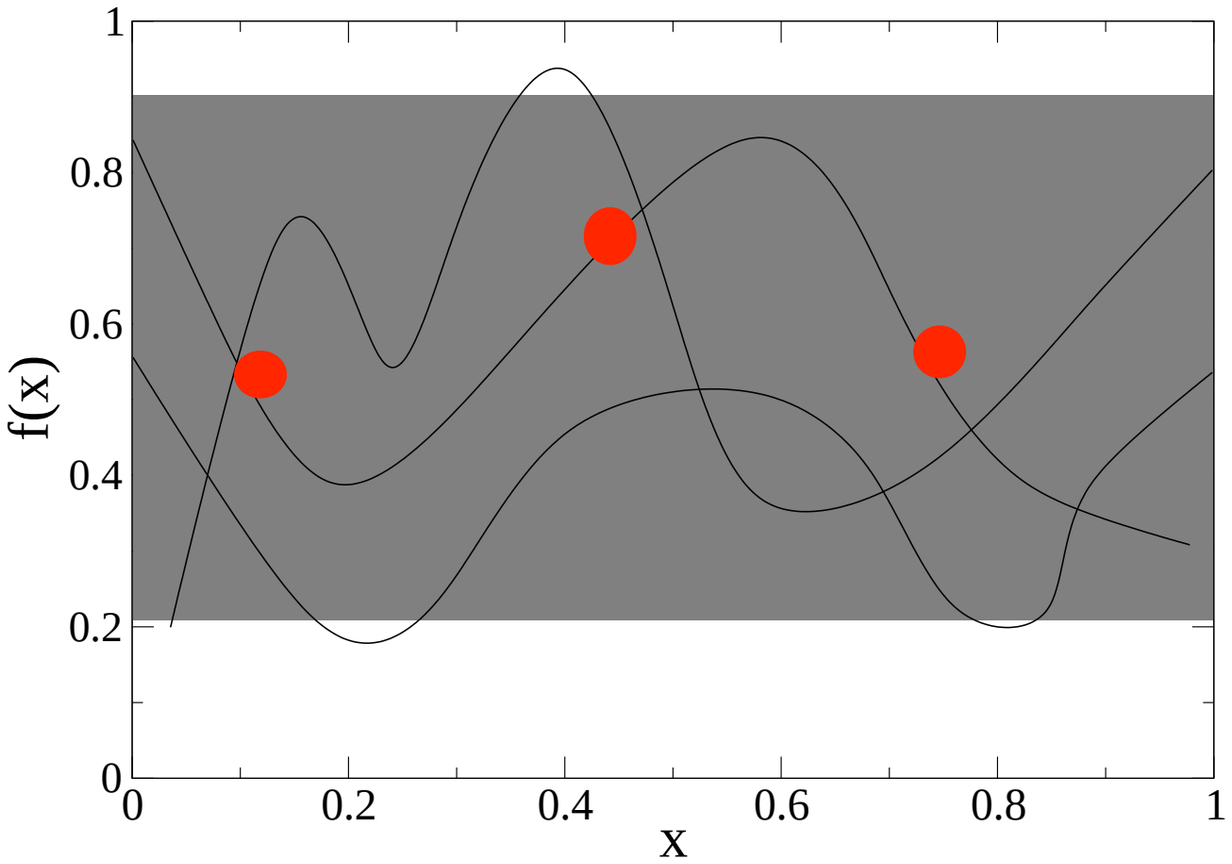


- Basic examples include **splines** and other **interpolation** techniques
- **Modern** implementations are significantly more **sophisticated**

Gaussian processes



a) Generate random functions from a distribution that favours smooth functions

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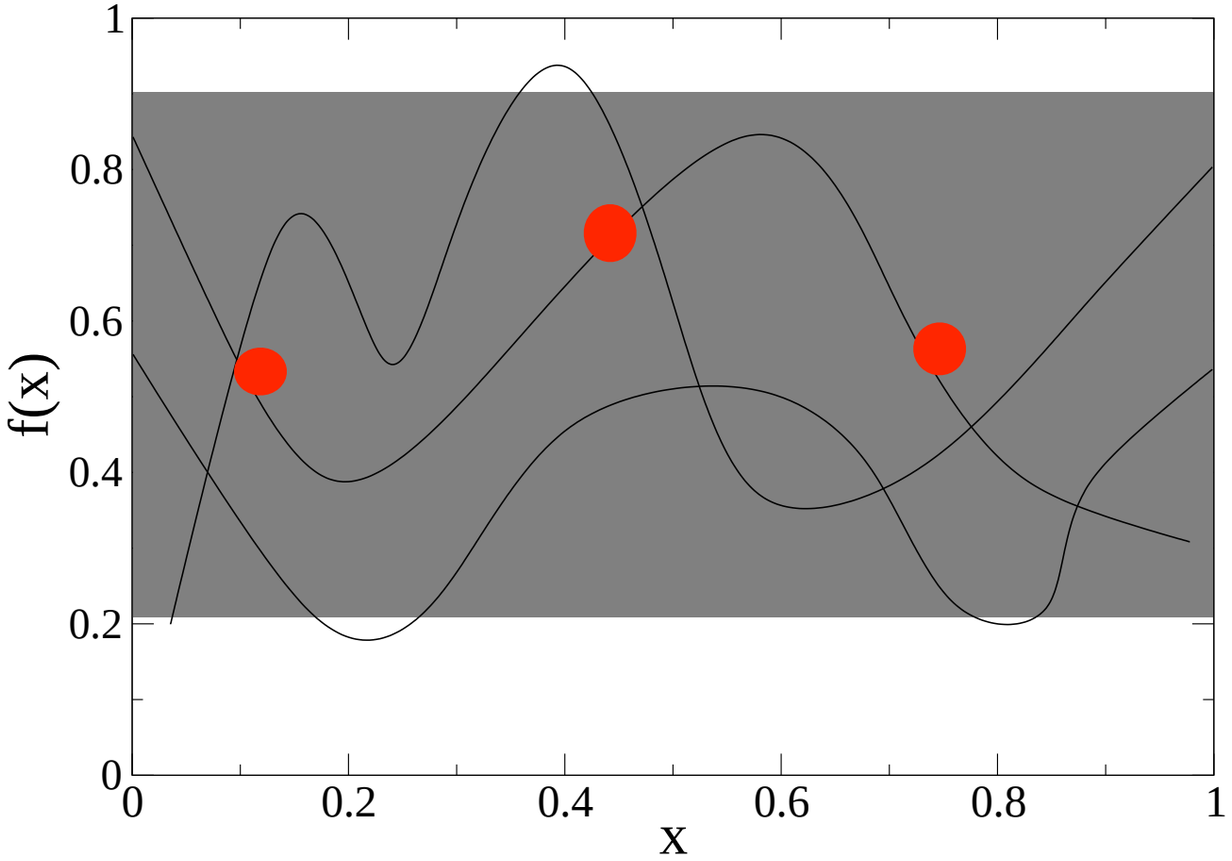

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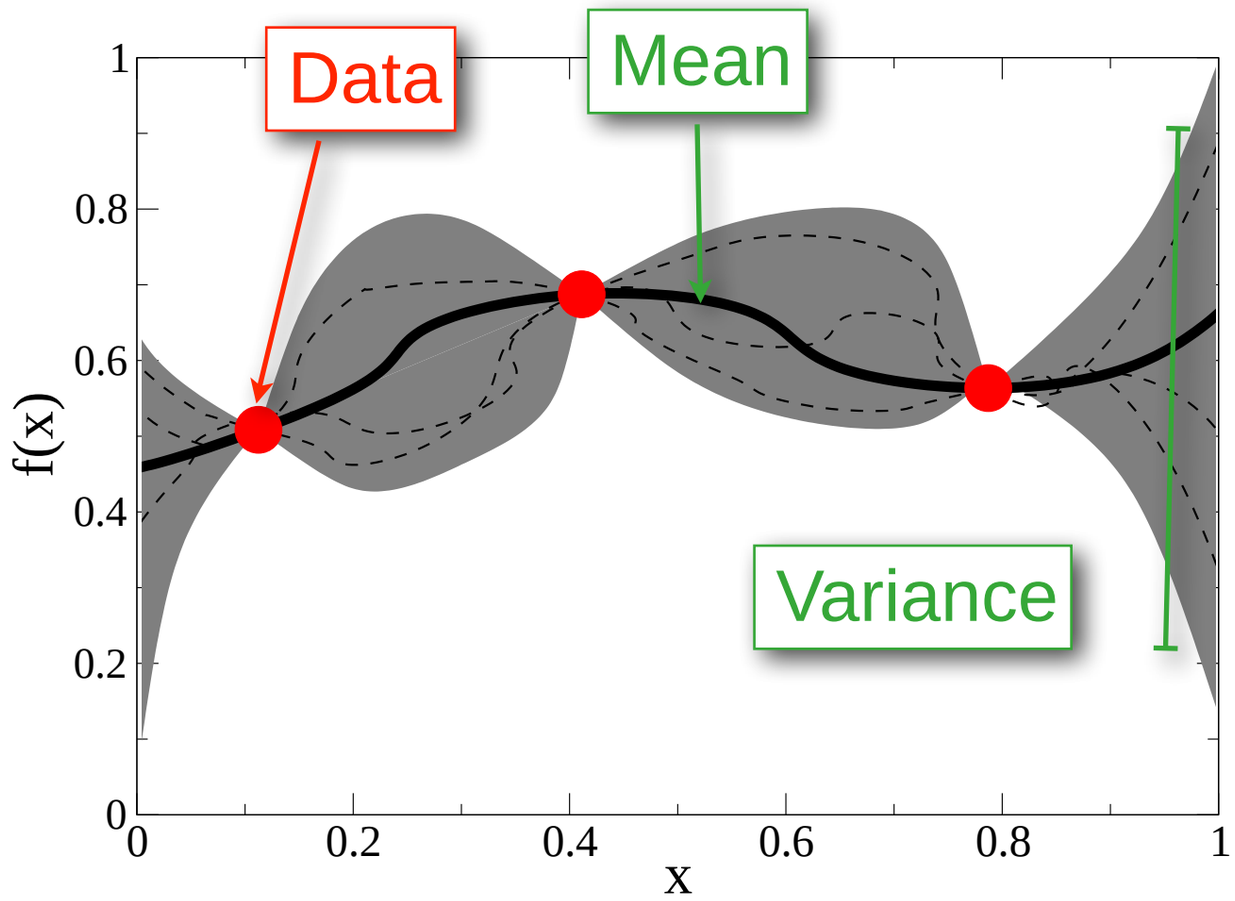
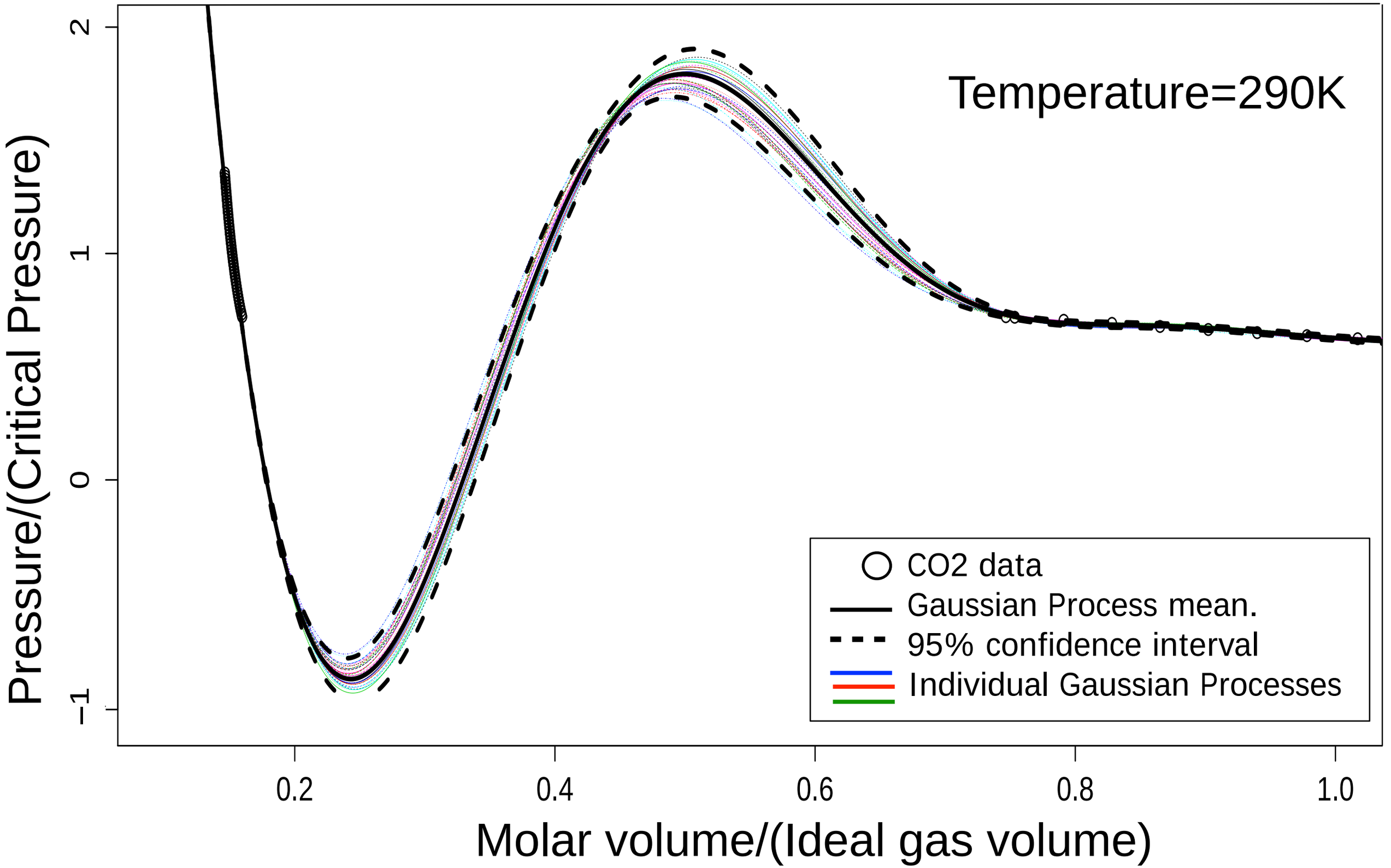


b) Keep only the functions that pass through the data points

Mean of accepted functions = Model
Variance of accepted functions = Uncertainty quantification

A Gaussian process for pure CO2



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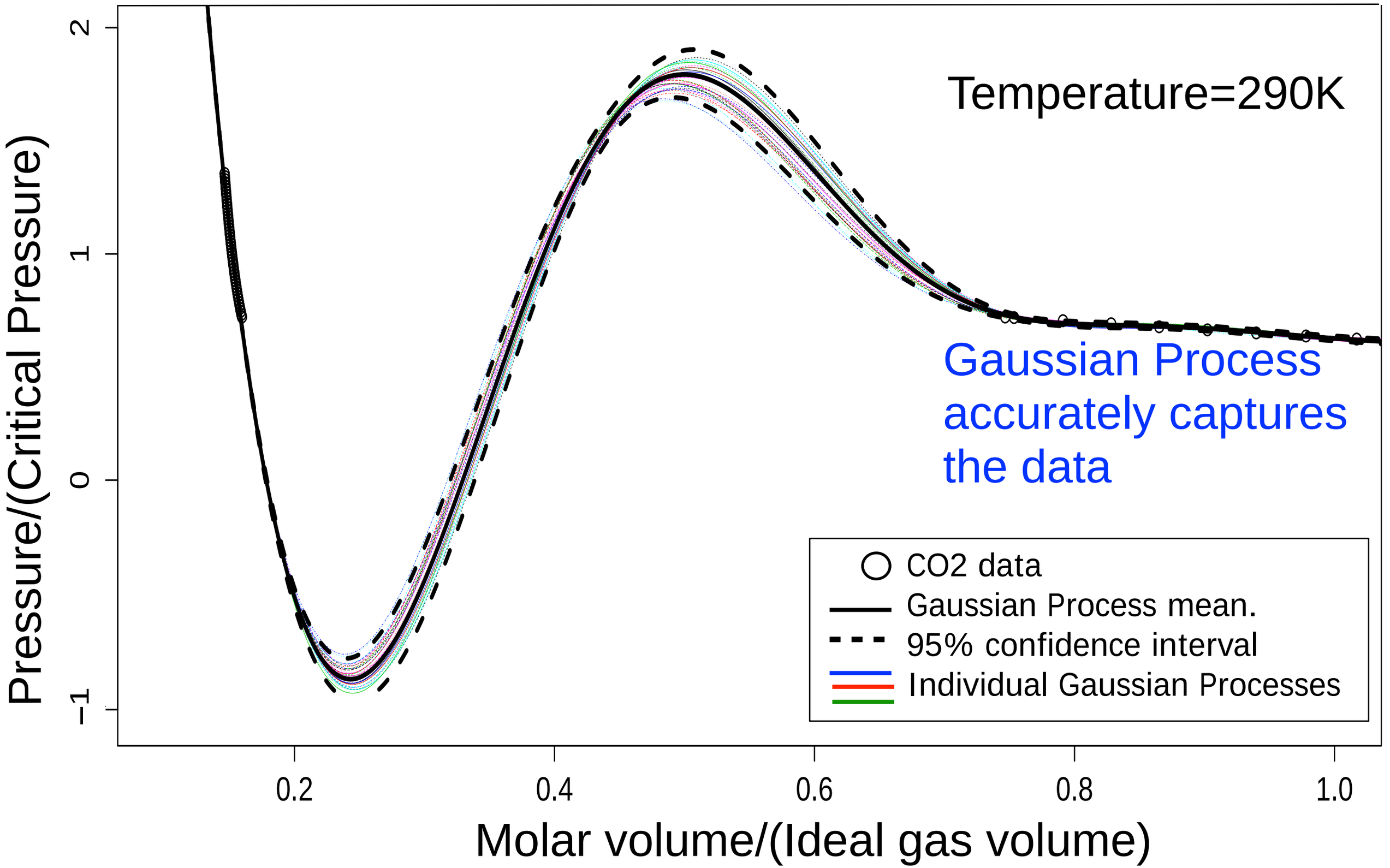

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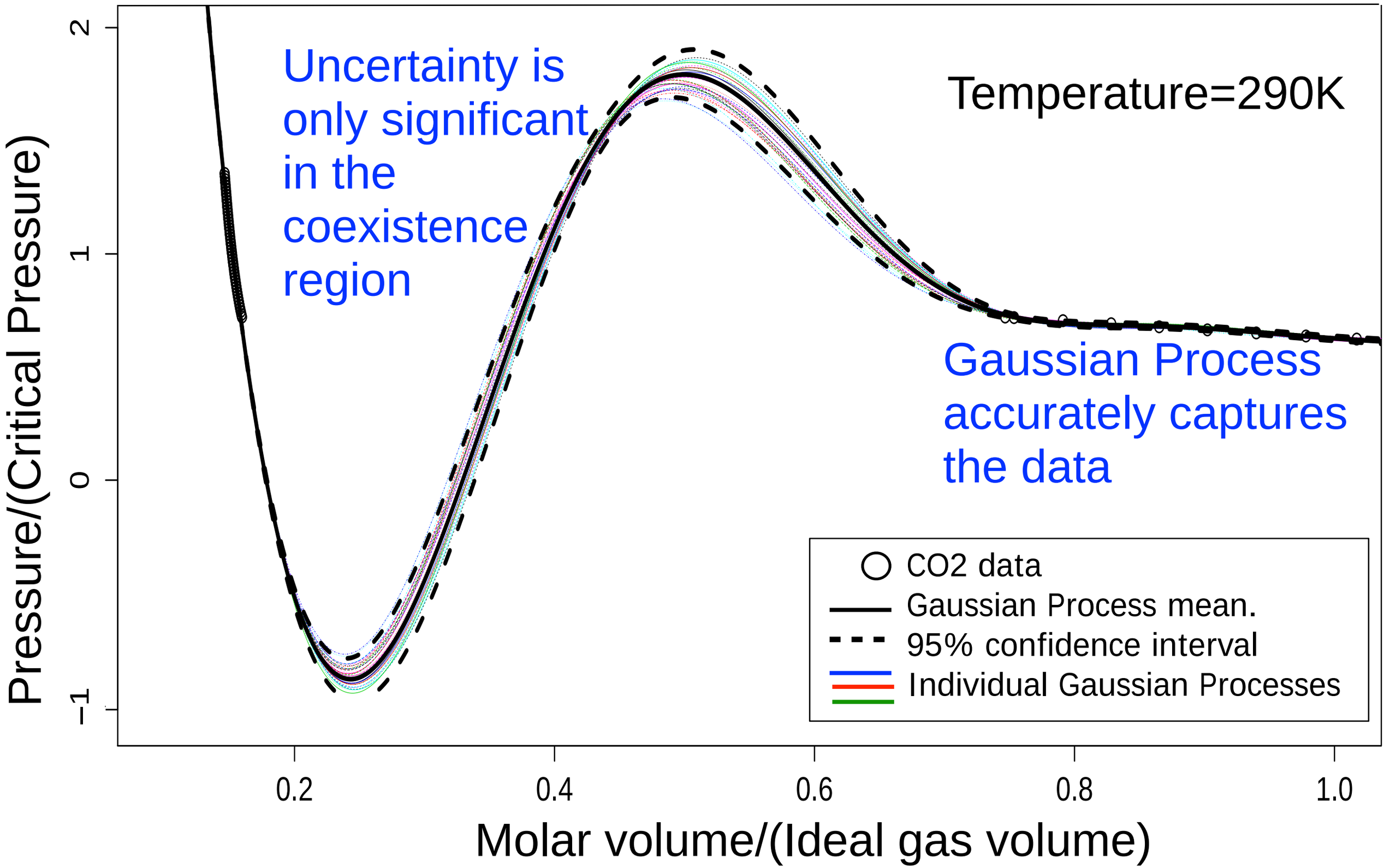

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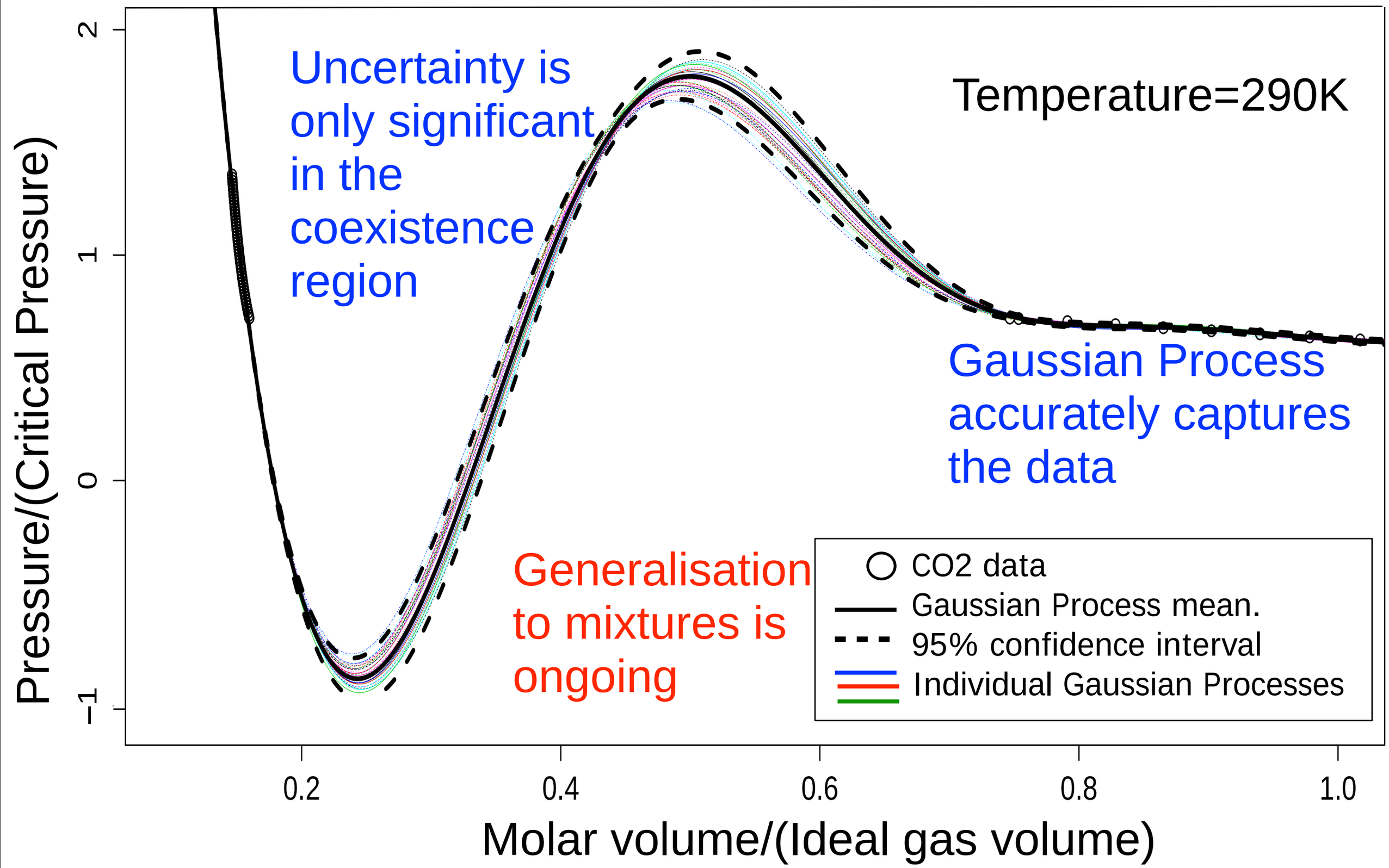
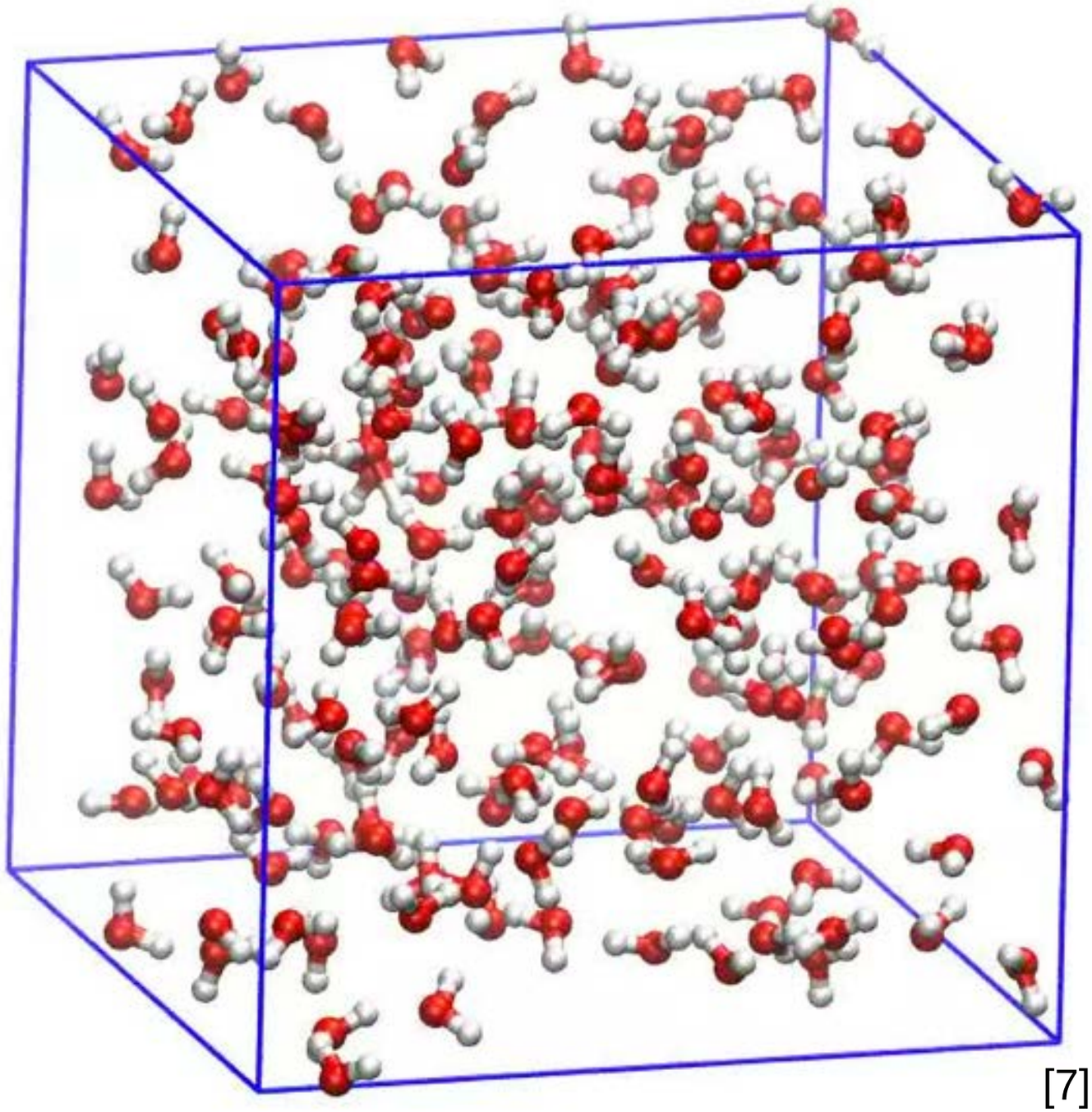


Molecular simulation



[7]

Computer model of individual molecules within a small box of fluid.

Can predict:

- Pressure-volume
- Coexistence
- Effect of impurity
- Most other quantities of interest

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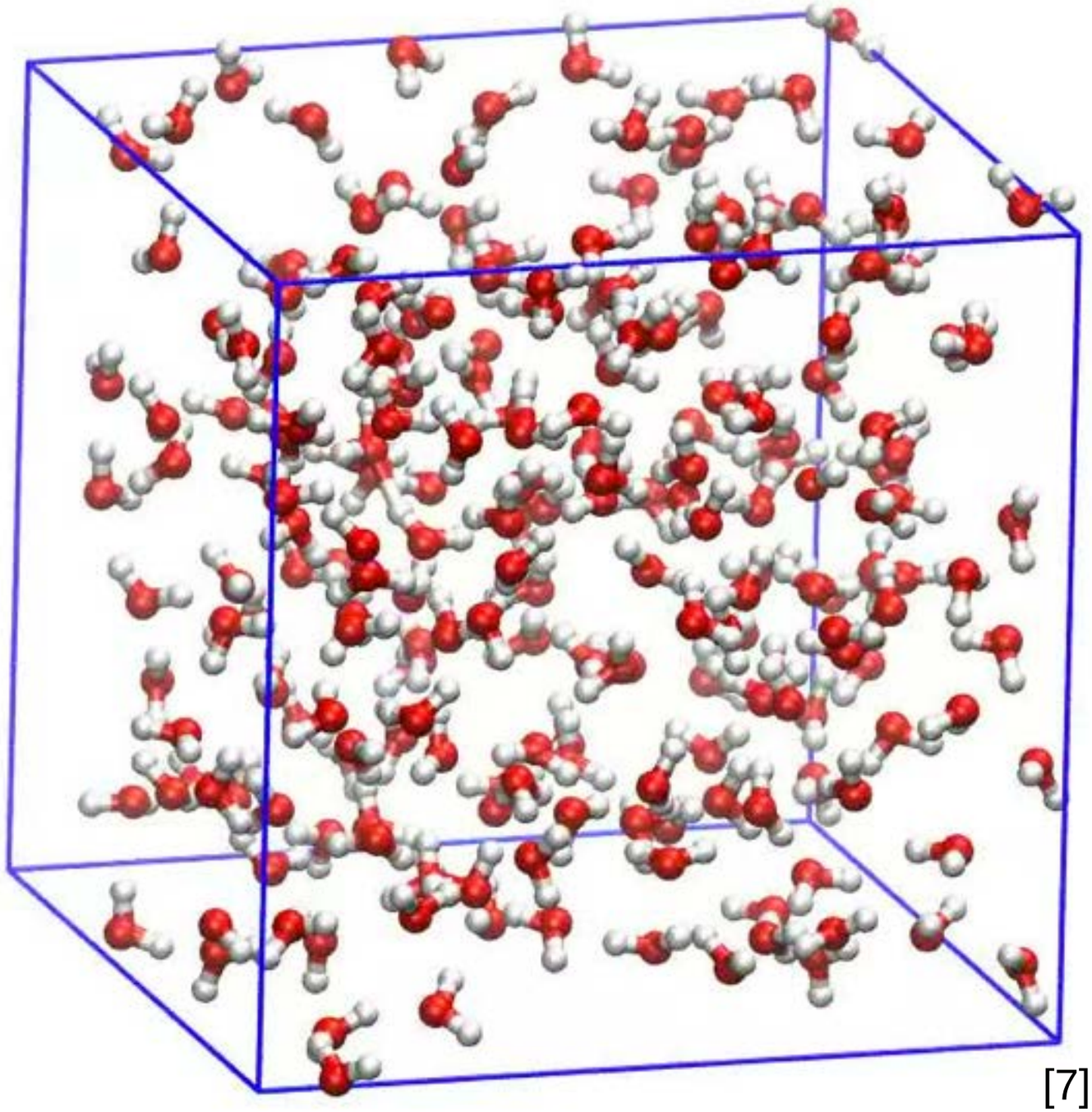

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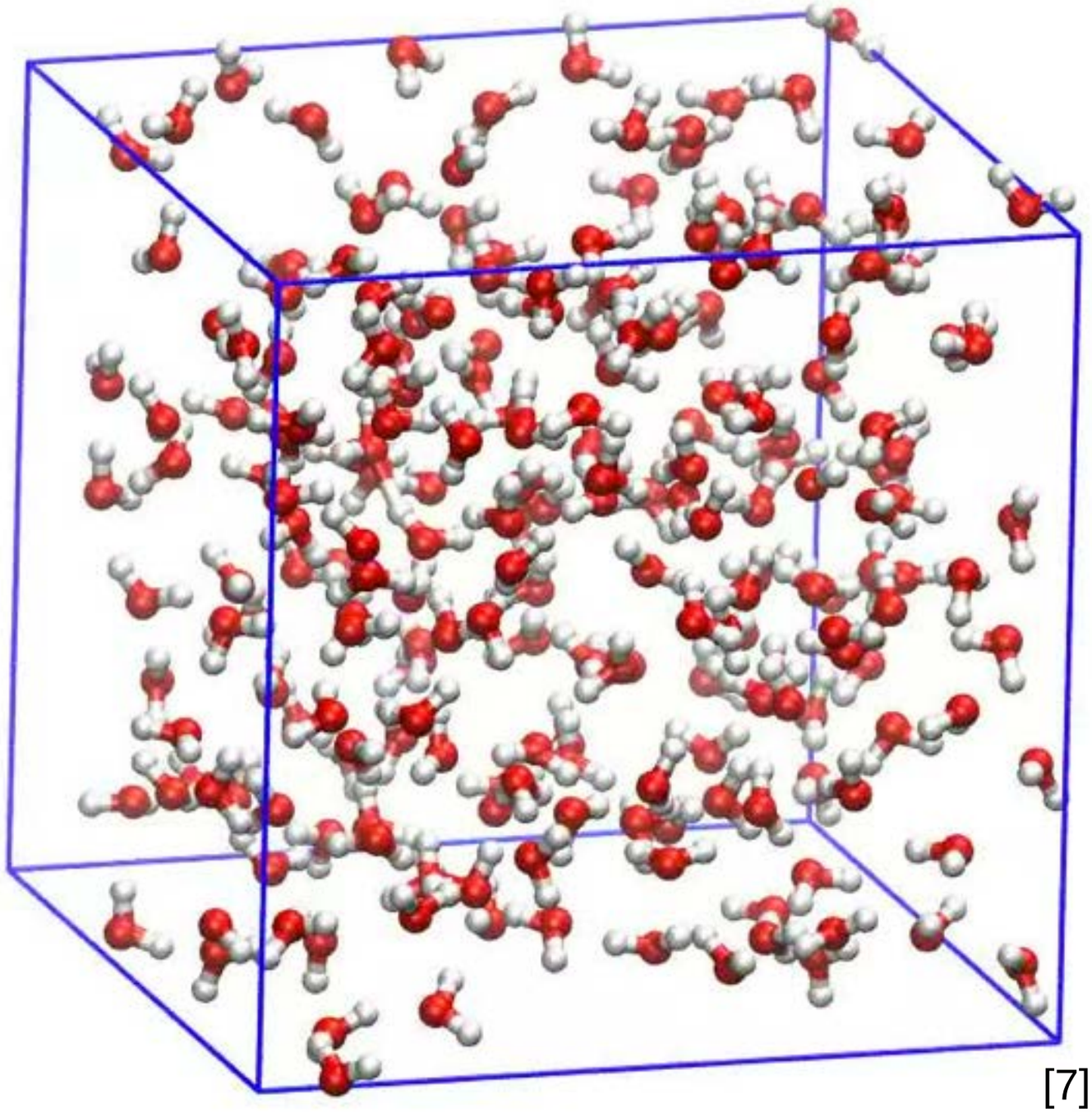

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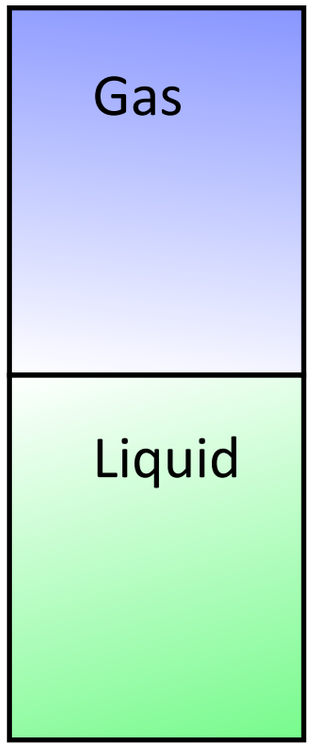
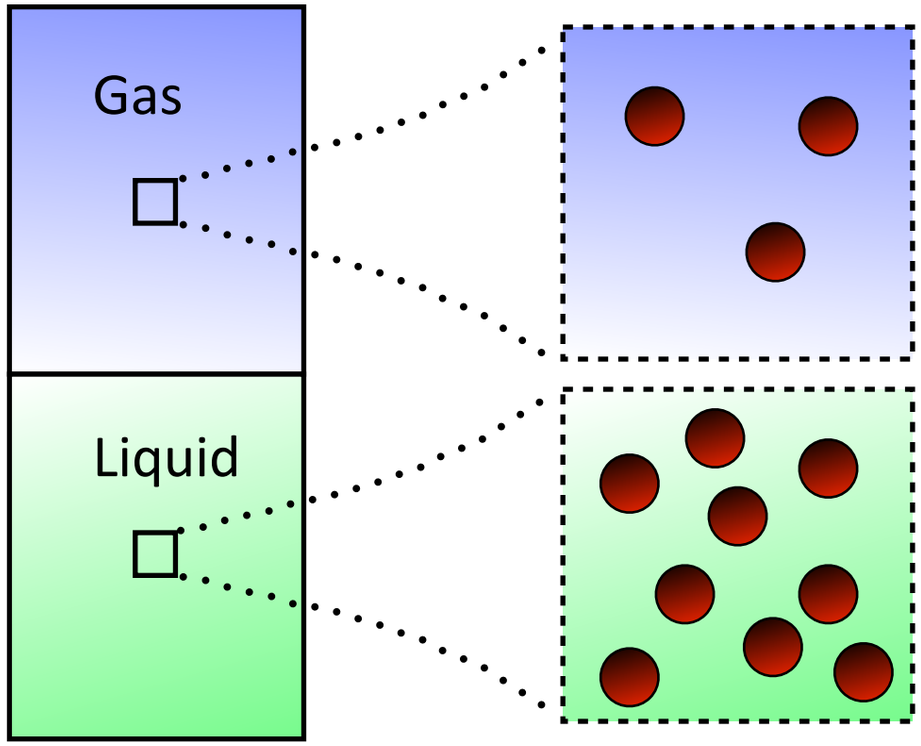
Can be used to derive an Equation of State?

Gibbs ensemble simulations



Gibbs ensemble simulations

Two simulation boxes, representing coexisting phases



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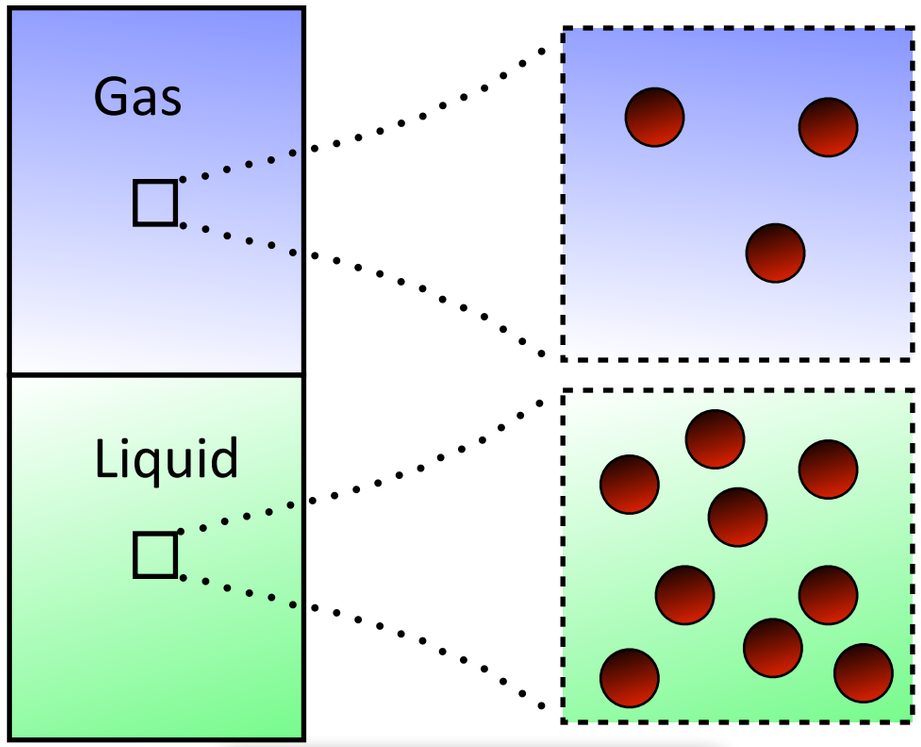
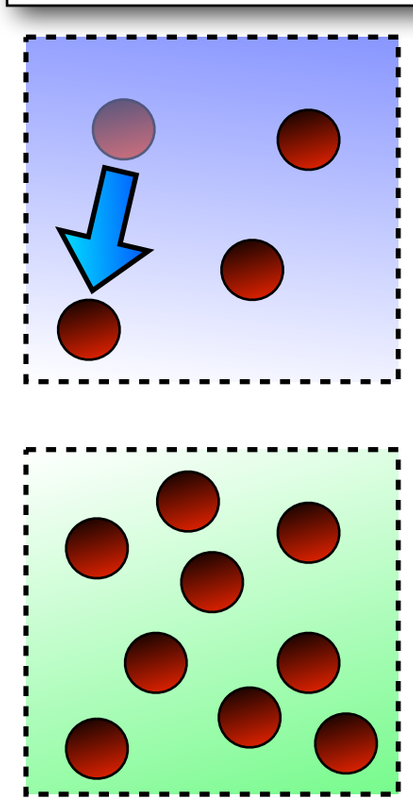
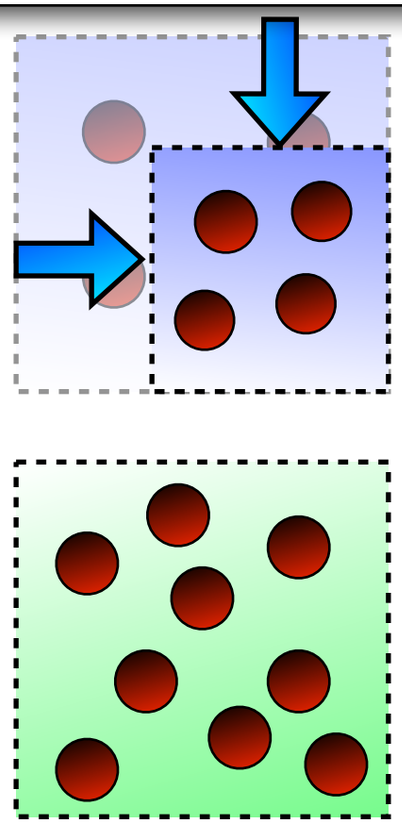


The system approaches equilibrium by making a series of moves, consistent with statistical mechanics

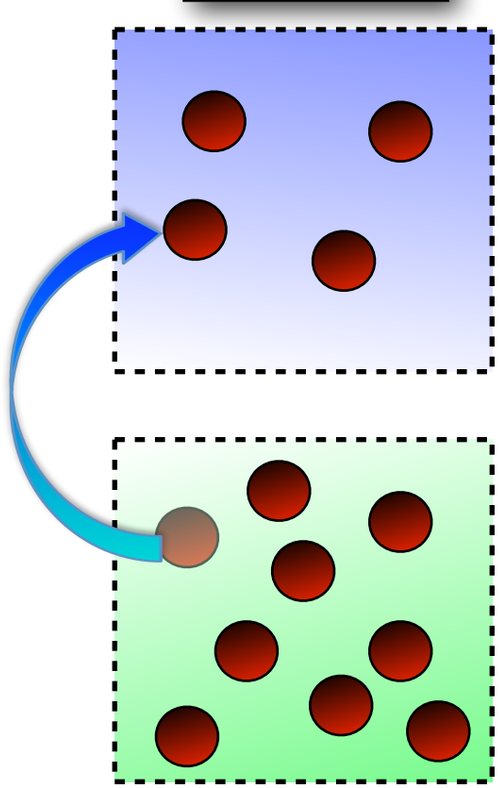
Particle displacement



Volume change

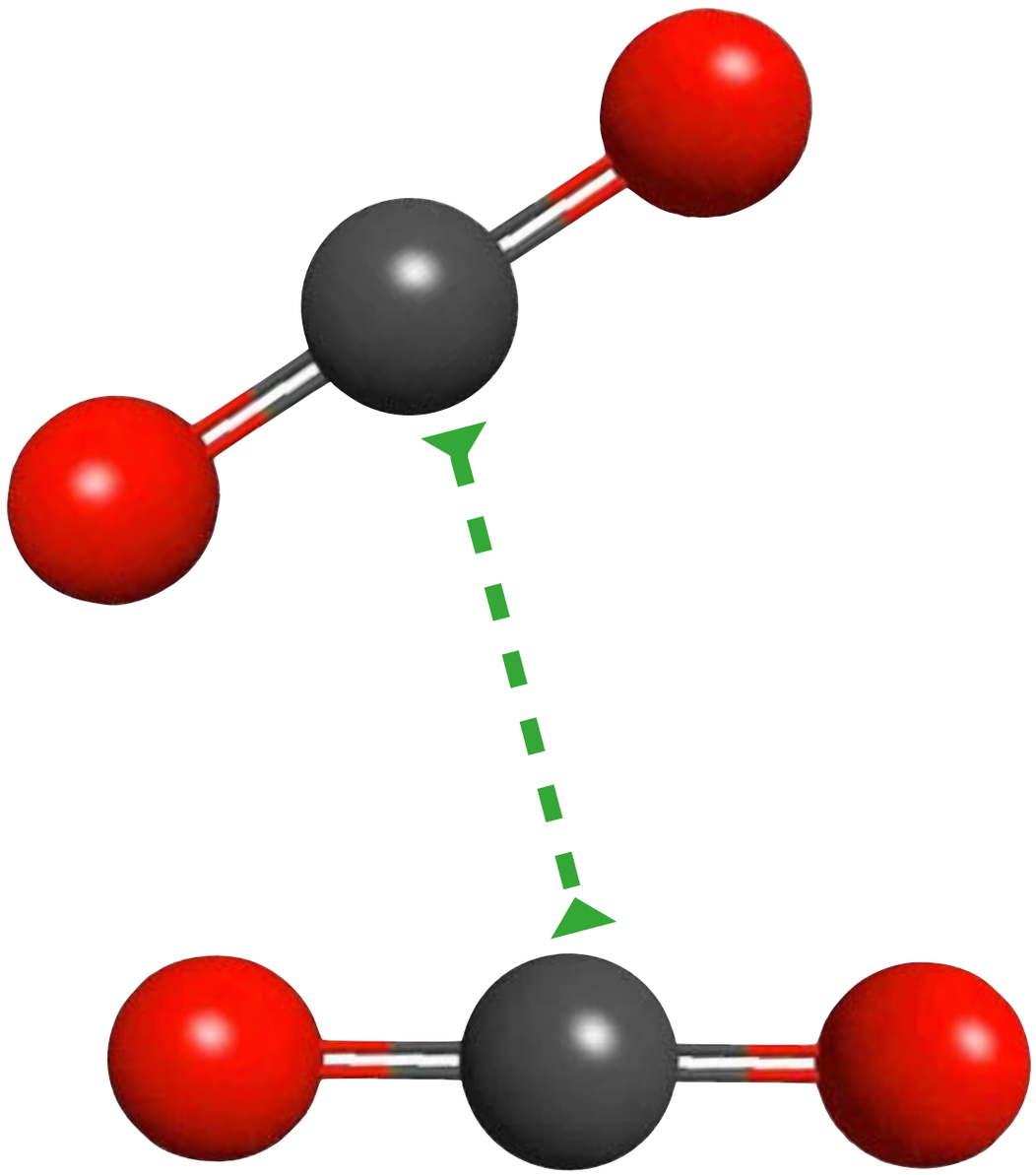


Particle transfer



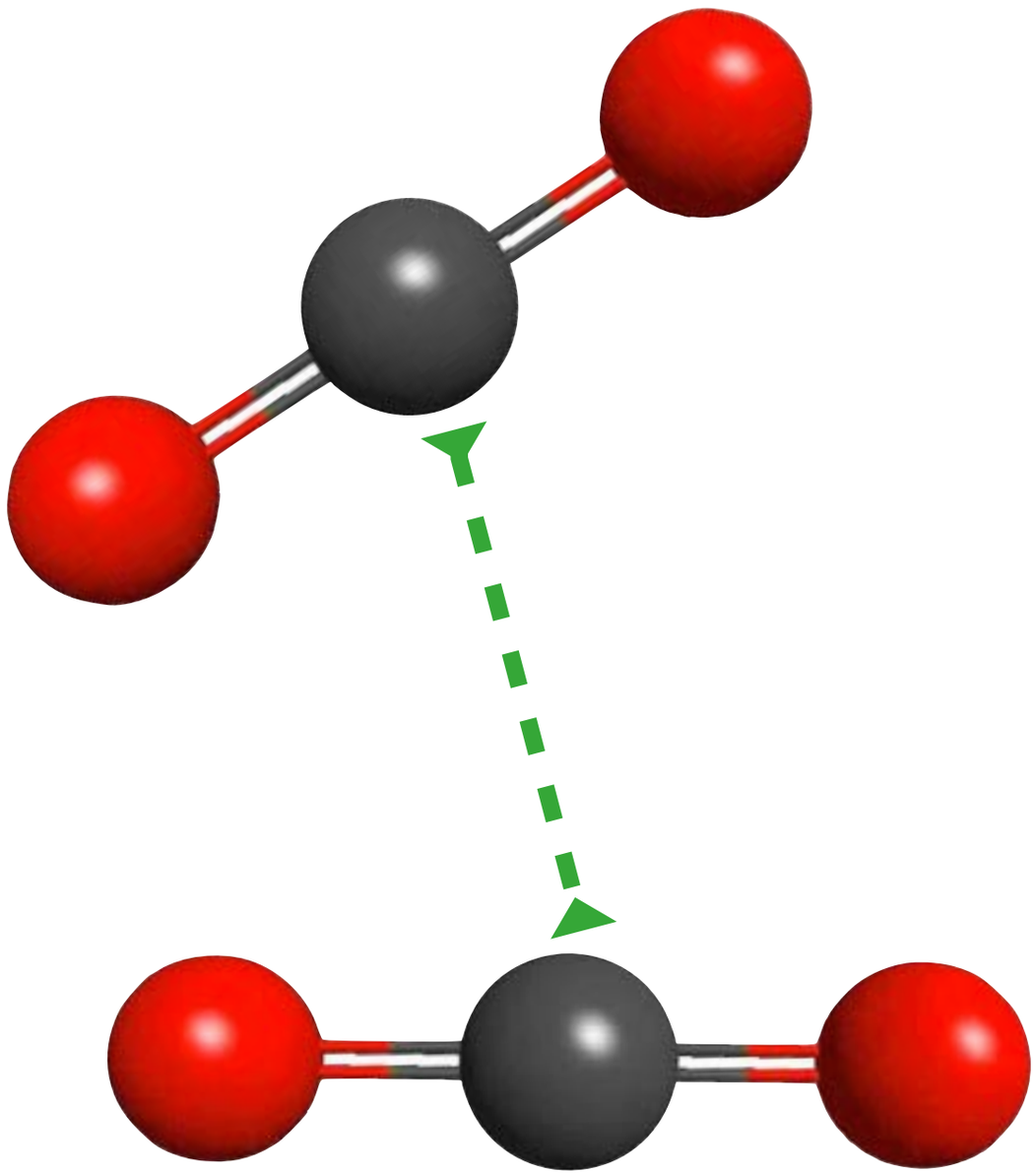
Once in equilibrium, the system predicts the coexistence properties

Molecular force-fields



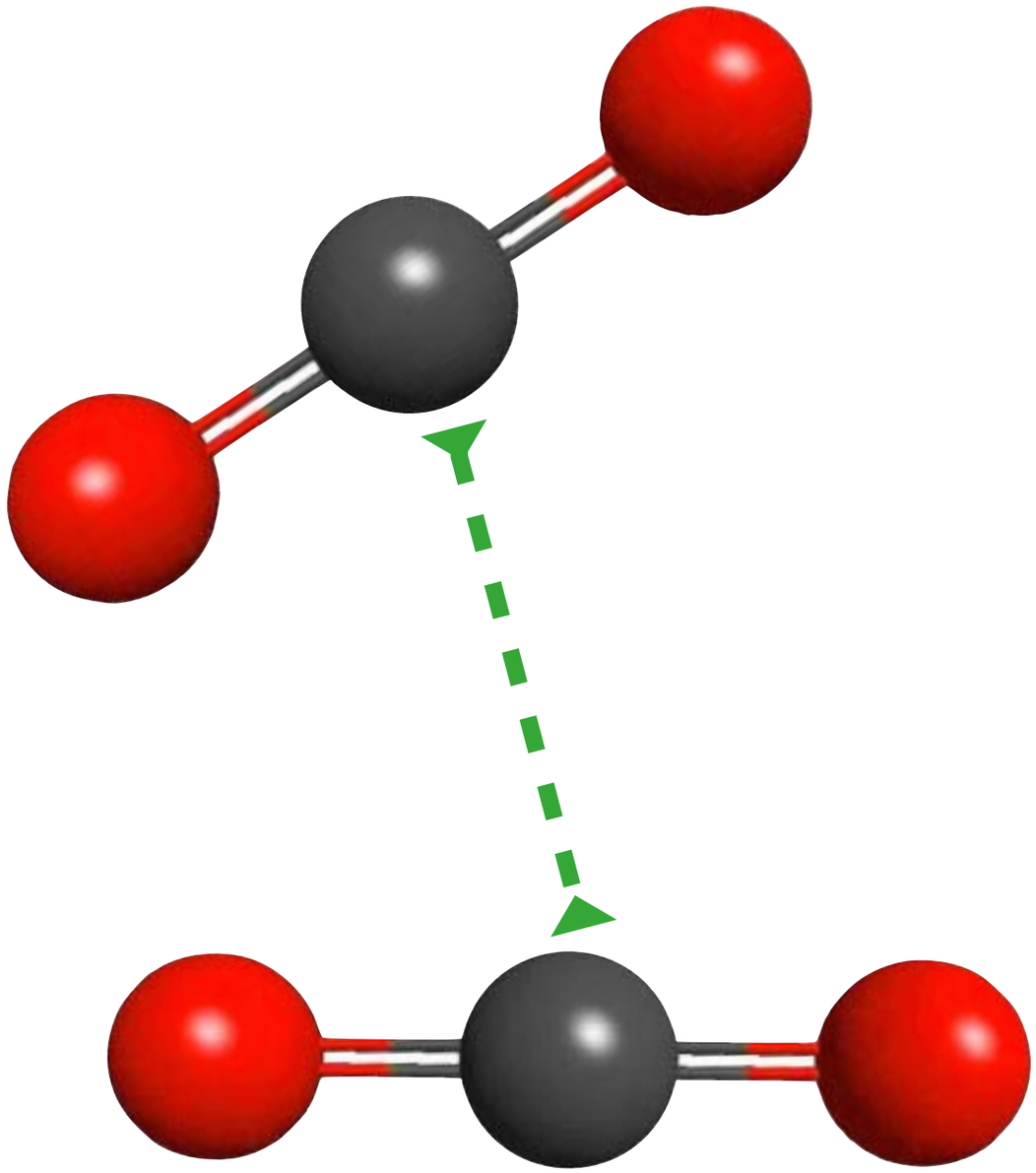
Molecular force-fields

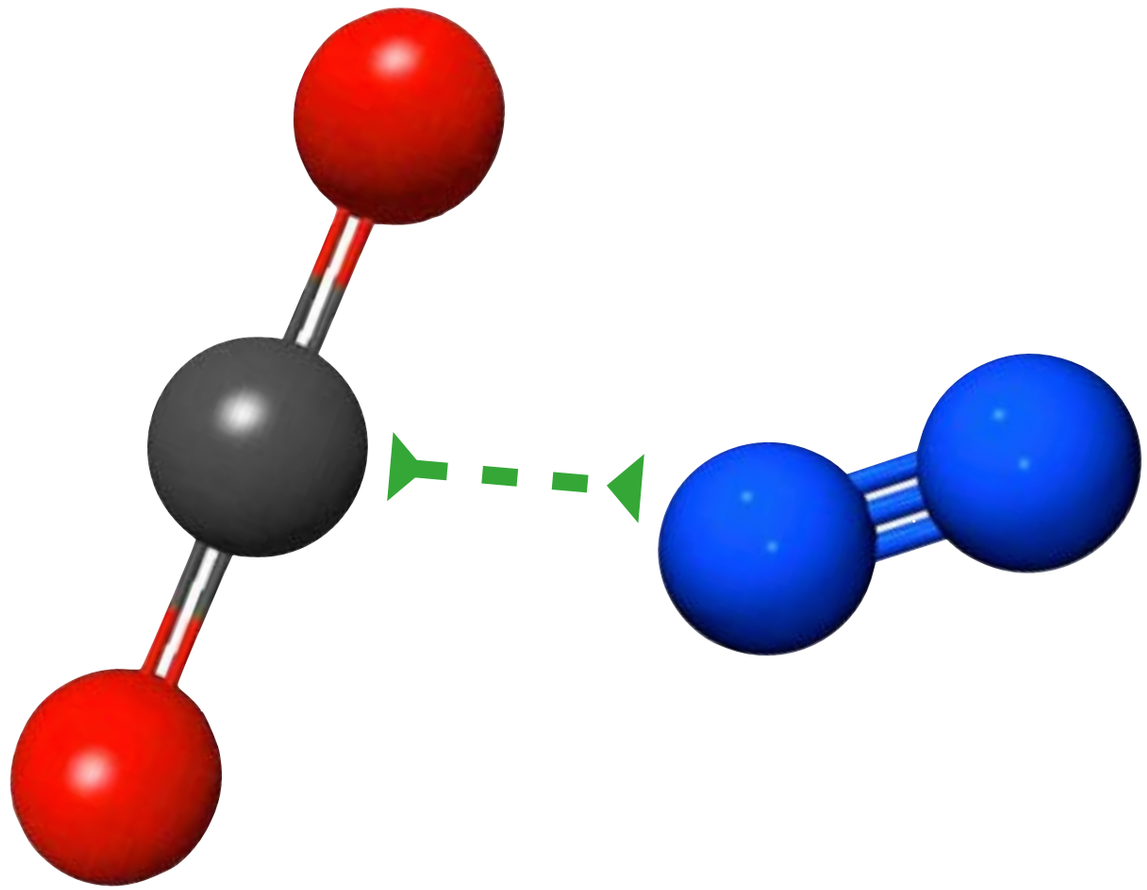
- All **physical properties** are ultimately determined by **interactions** between **molecules**
- Force-fields that describe these interactions are a **key input** to **simulations**



Molecular force-fields

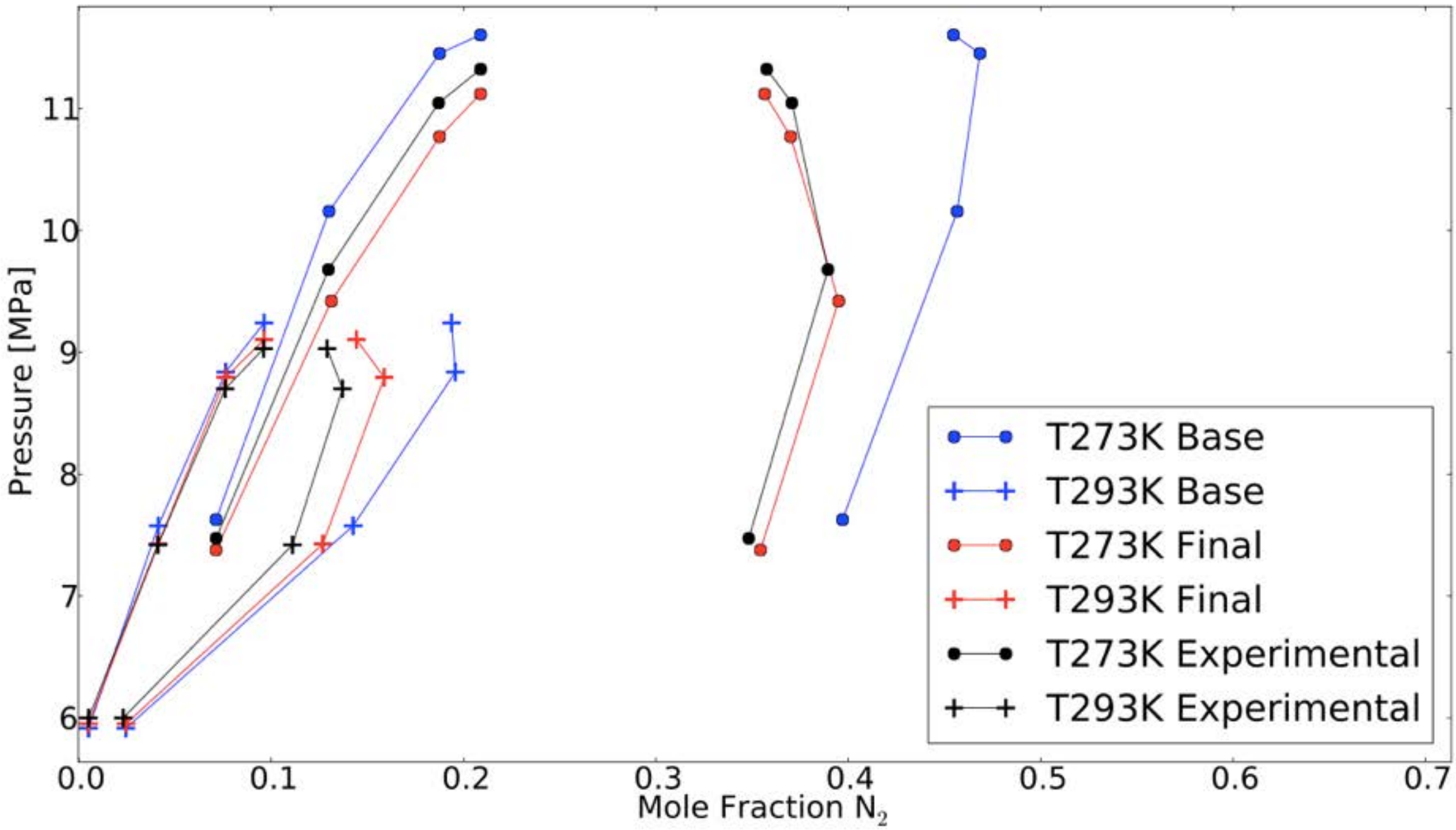
- All **physical properties** are ultimately determined by **interactions** between **molecules**
- Force-fields that describe these interactions are a **key input** to **simulations**
- Interactions of **CO2** with **itself** and with **impurities** must be specified





Semi-empirical forcefields

CO2+N2



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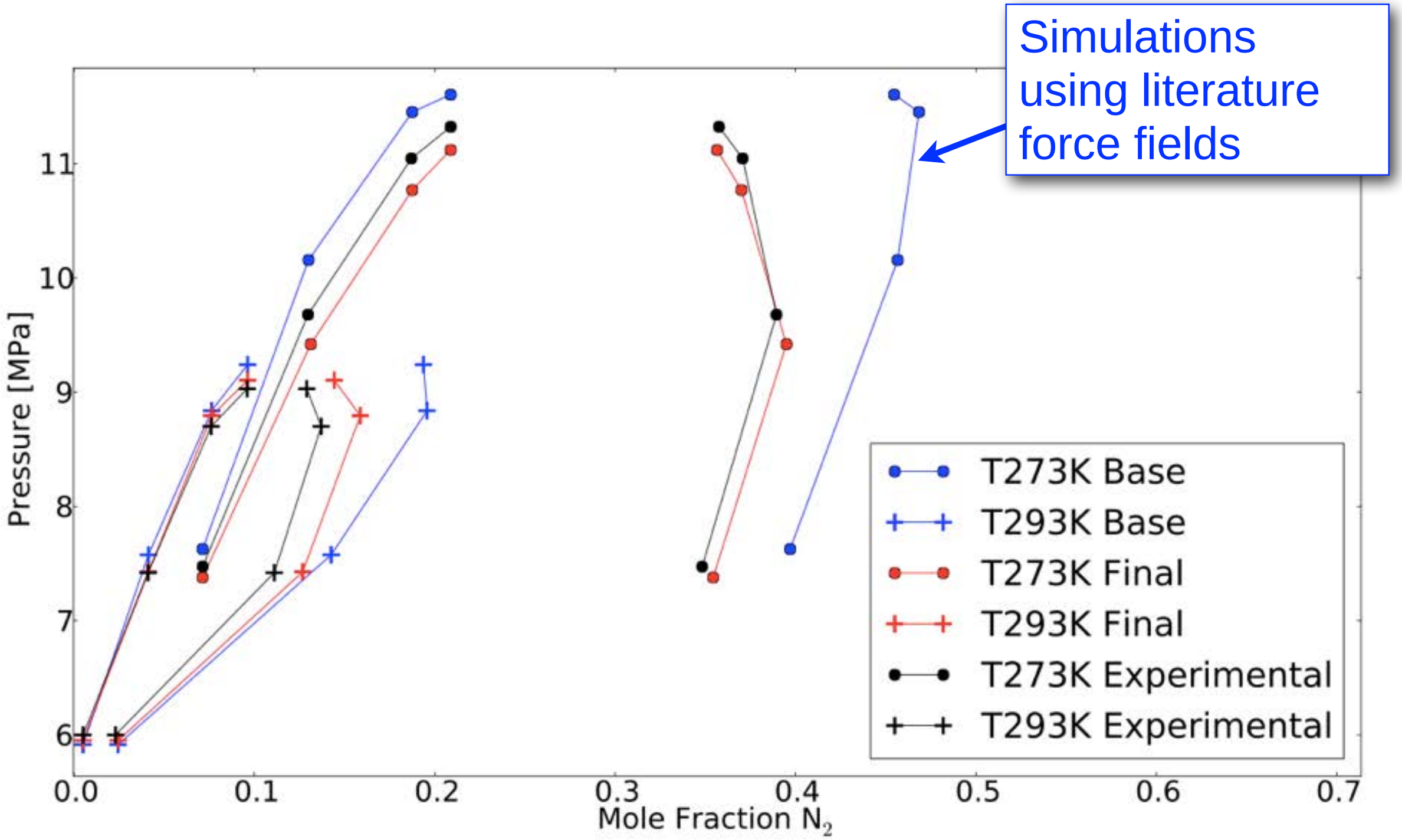

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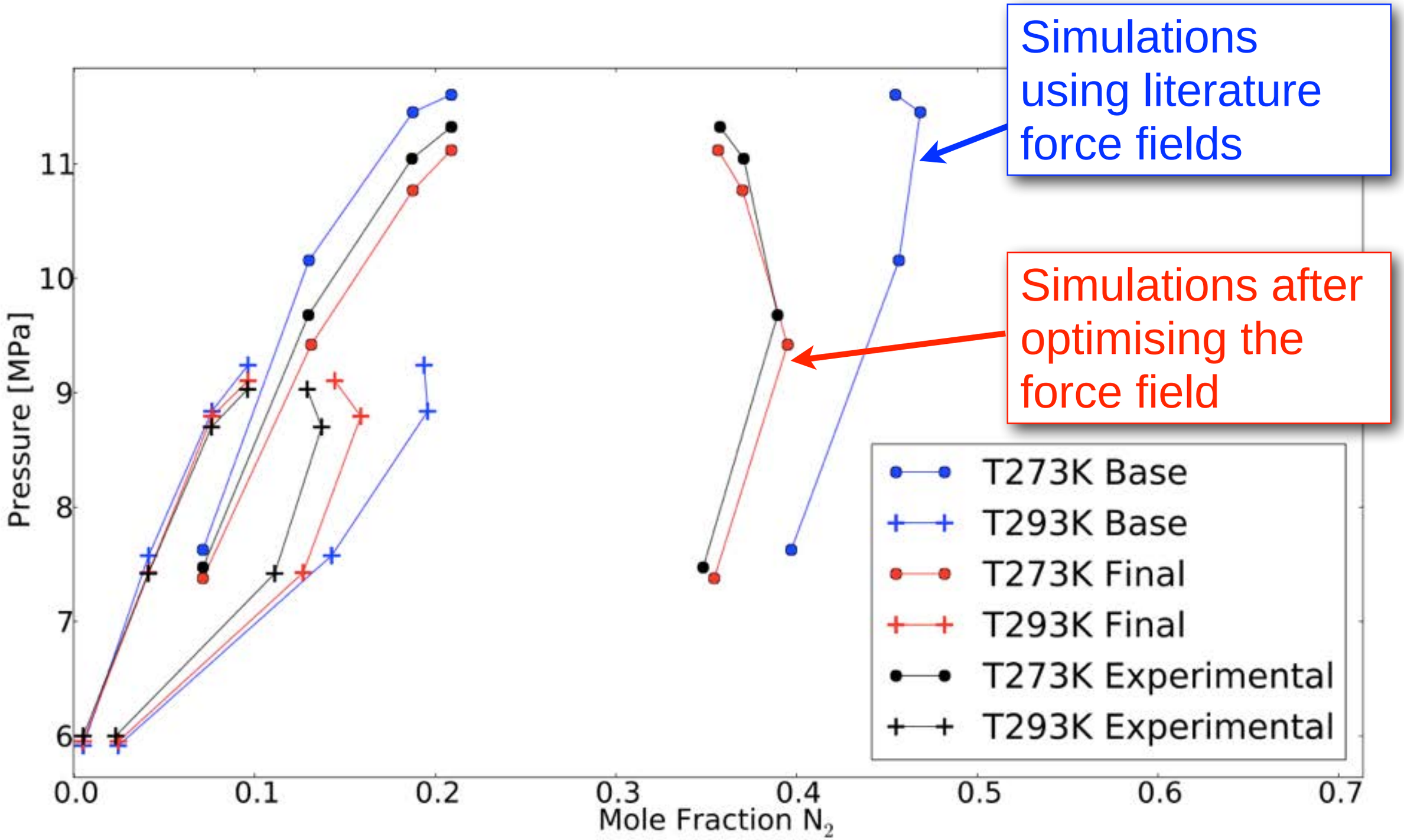
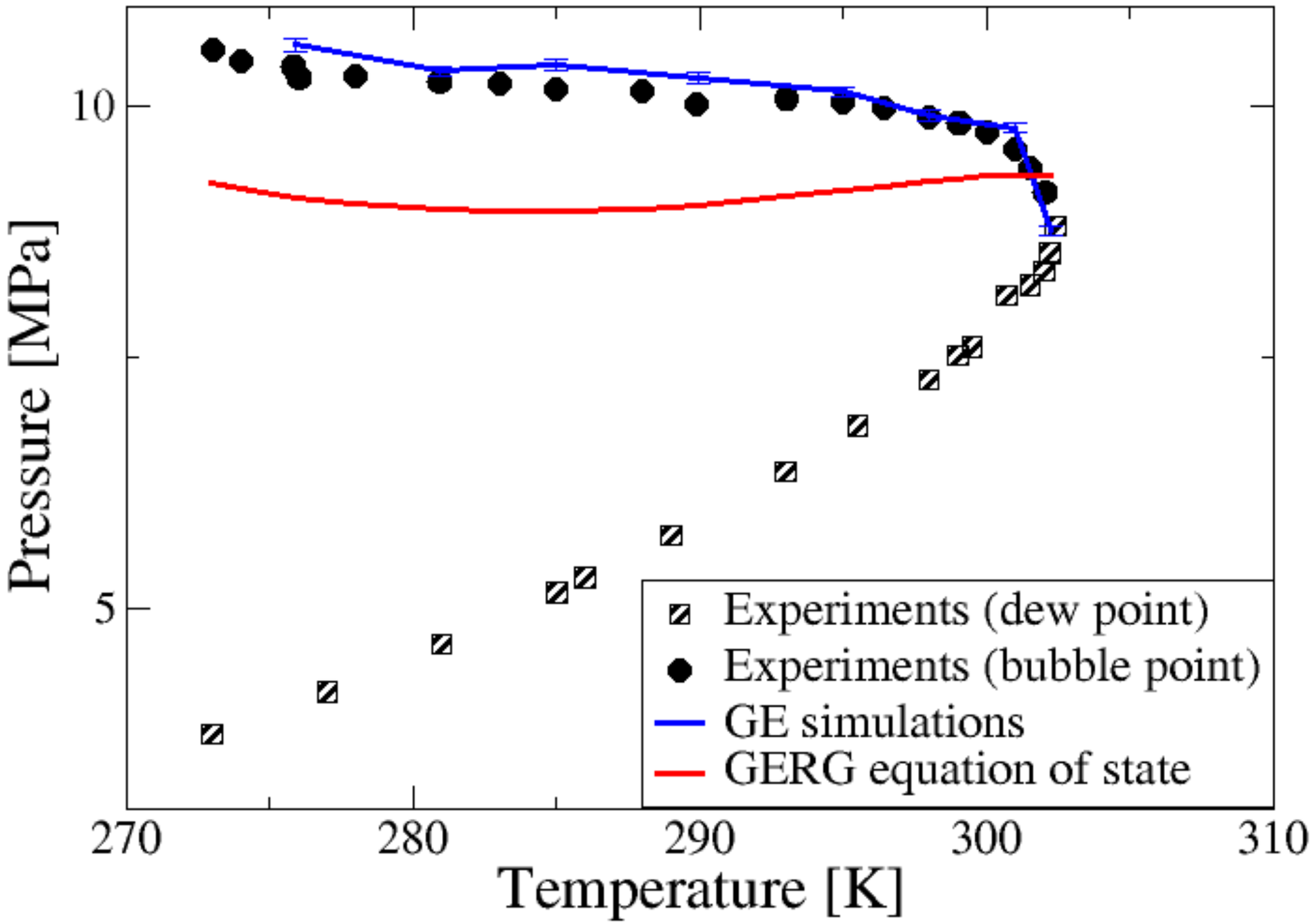


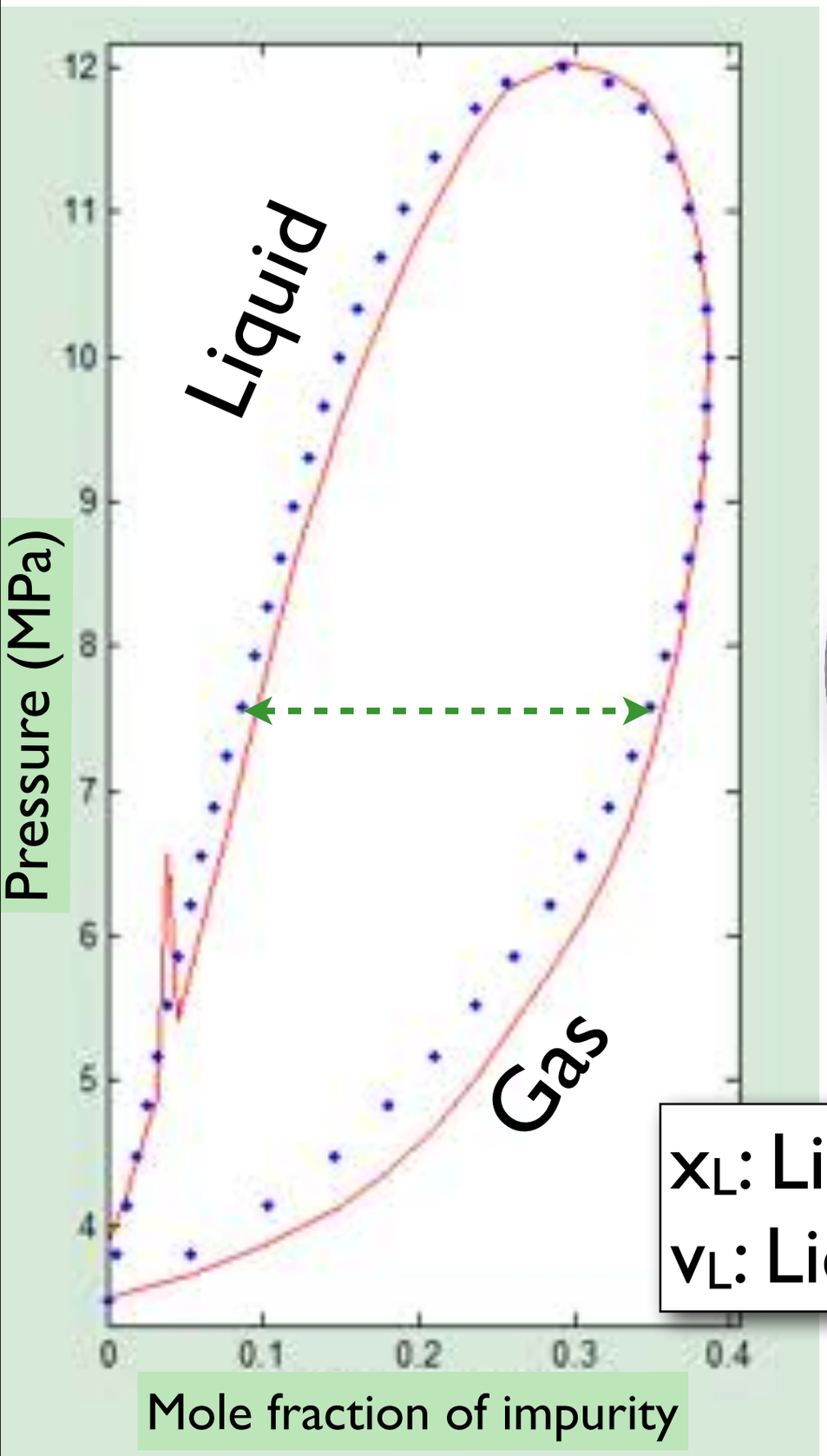
Bubble point comparison

CO2 + 5%H2

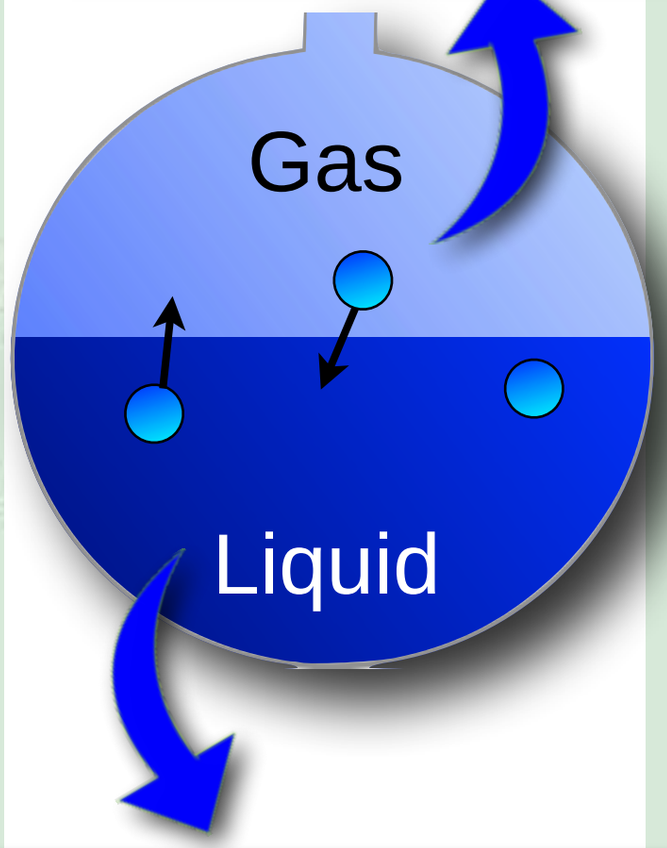


Phase boundary measurements by Jie Ke, Mike George et al

Simulation aids EoS development



x_G: Gas composition
v_G: Gas volume



x_L: Liquid composition
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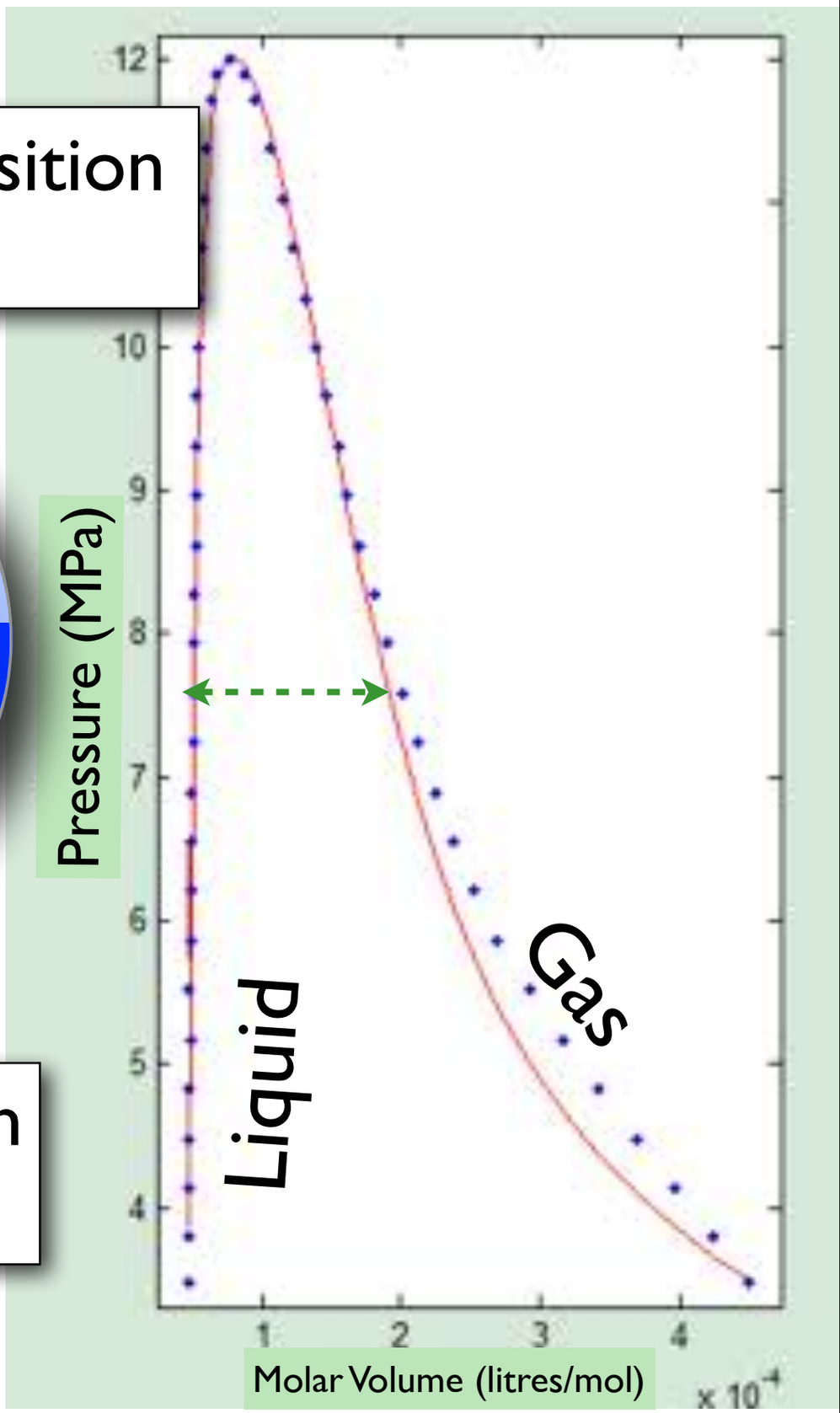

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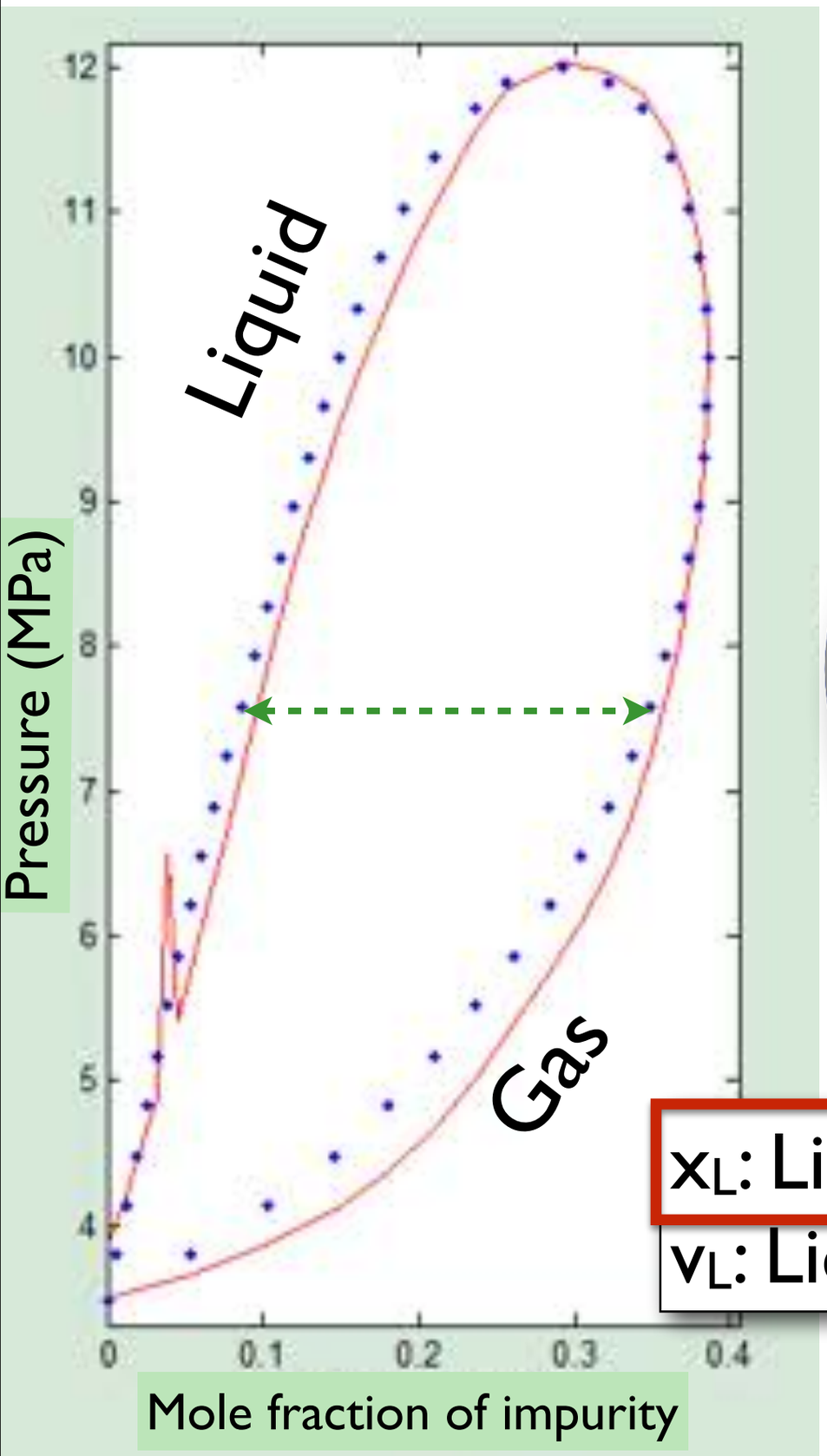

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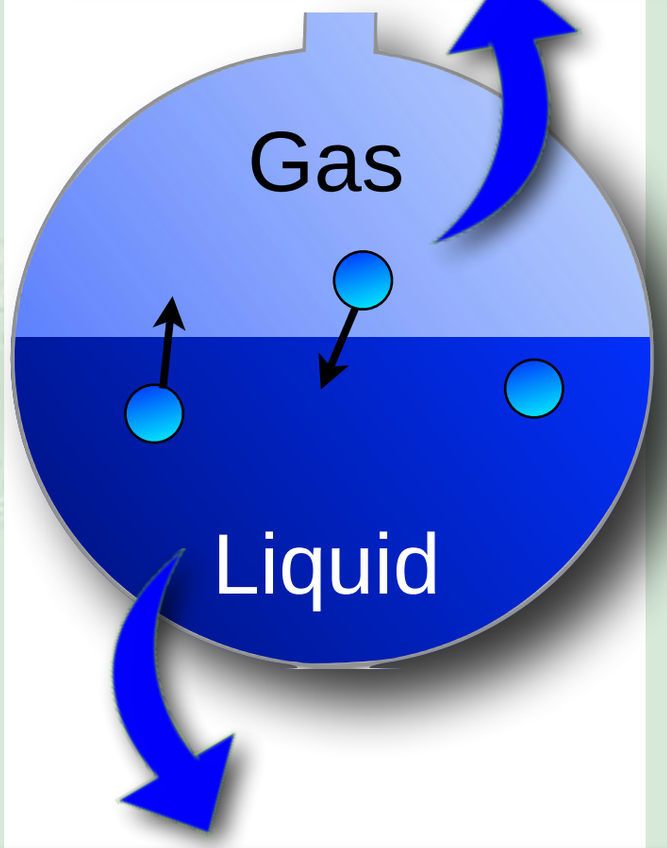

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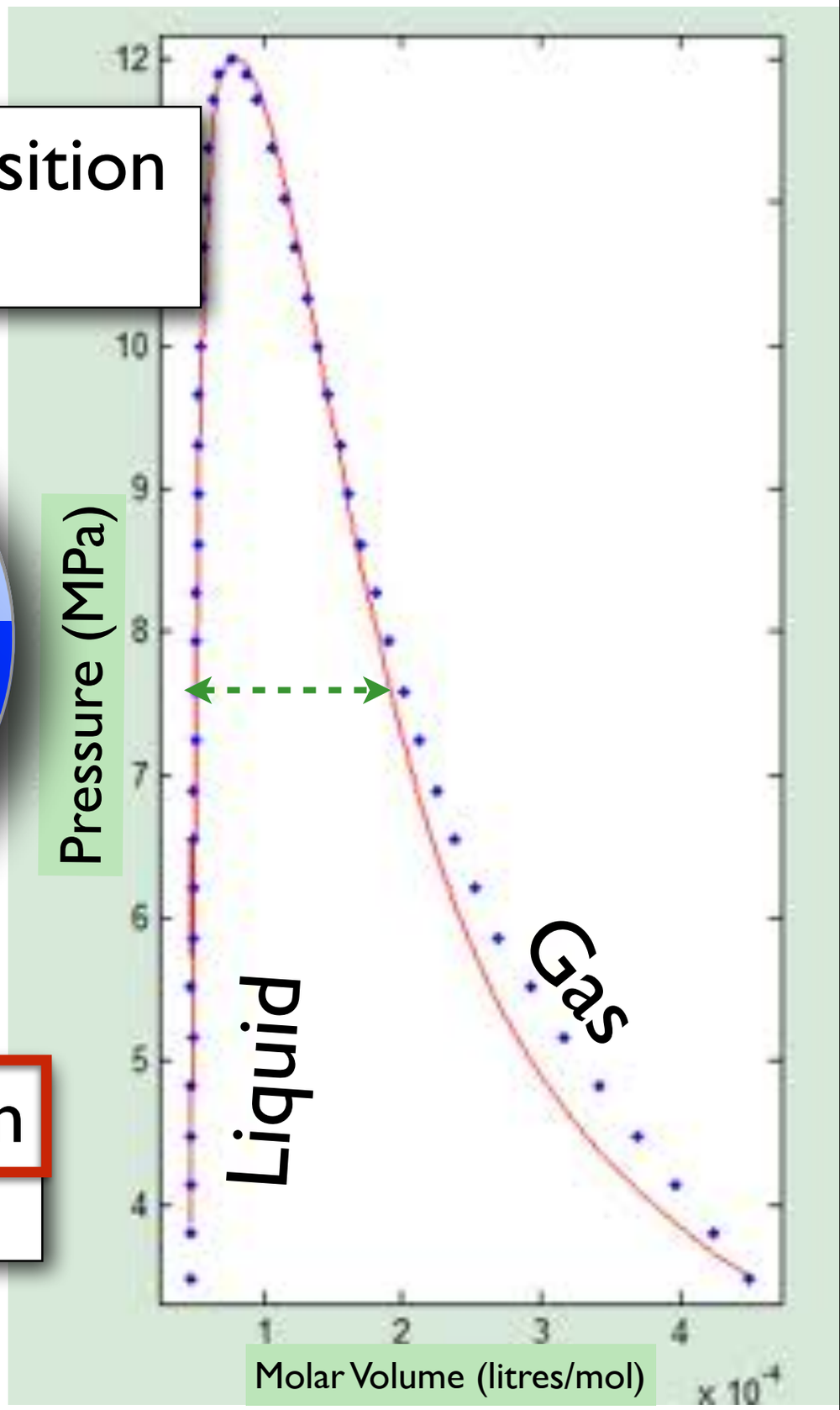

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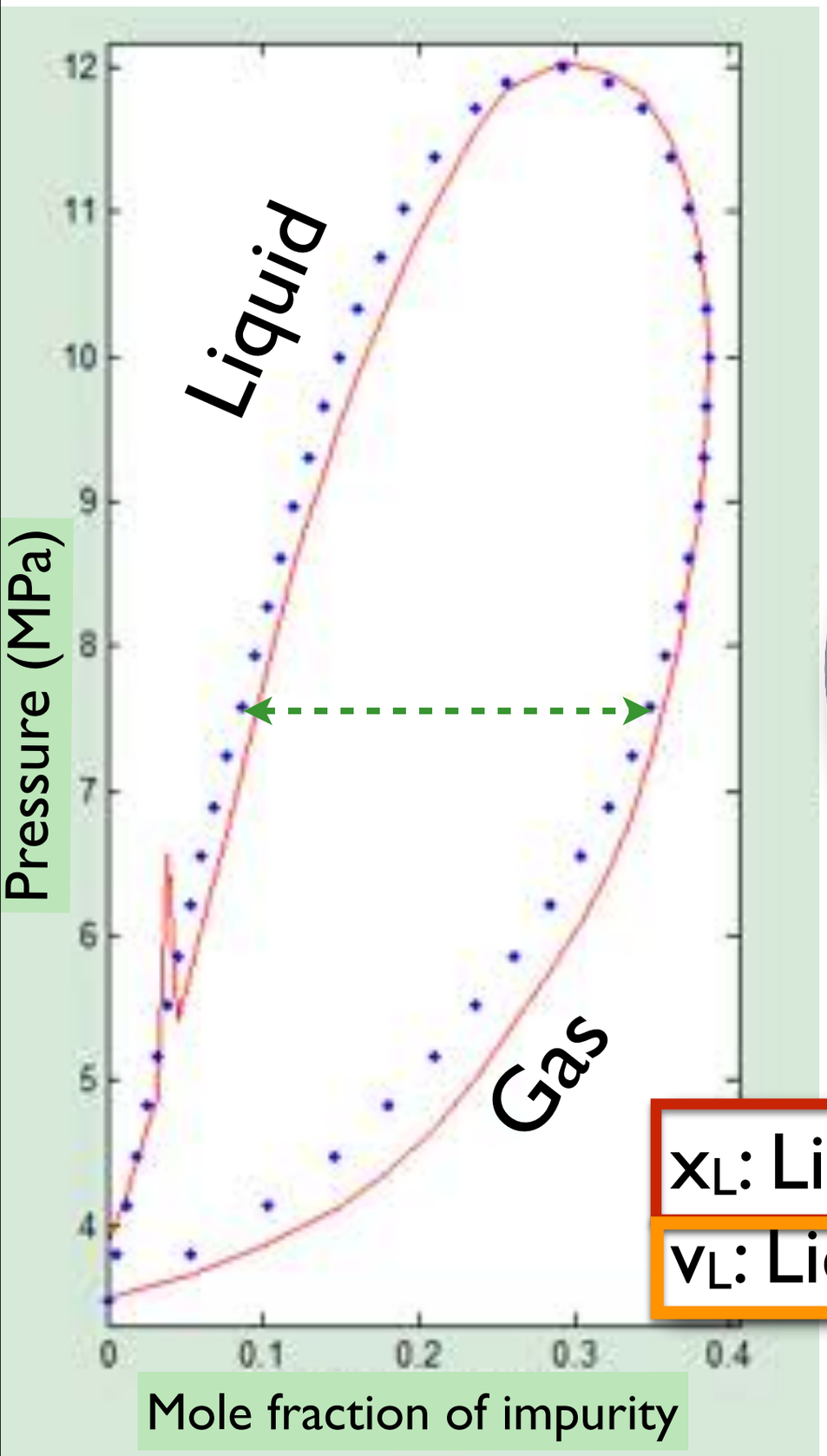

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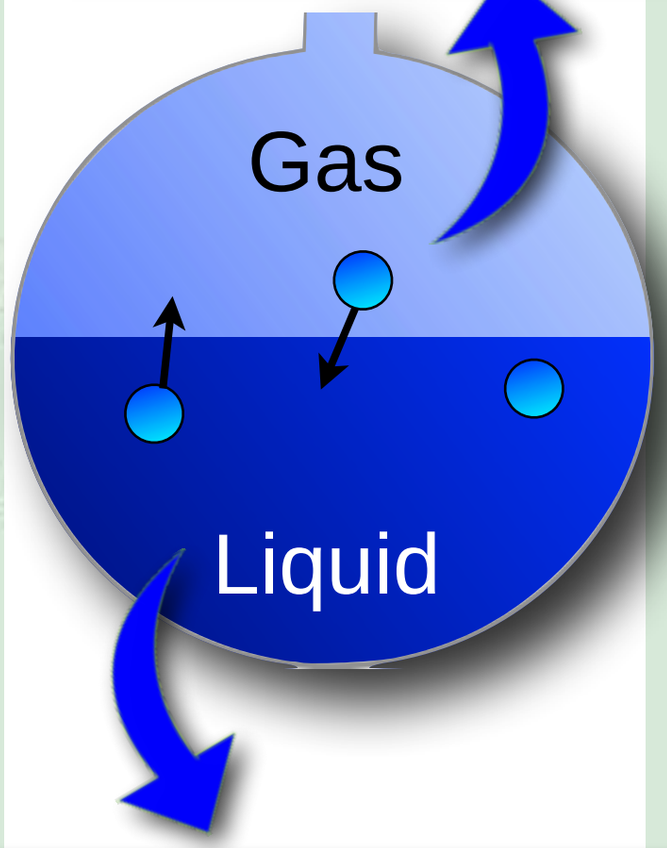

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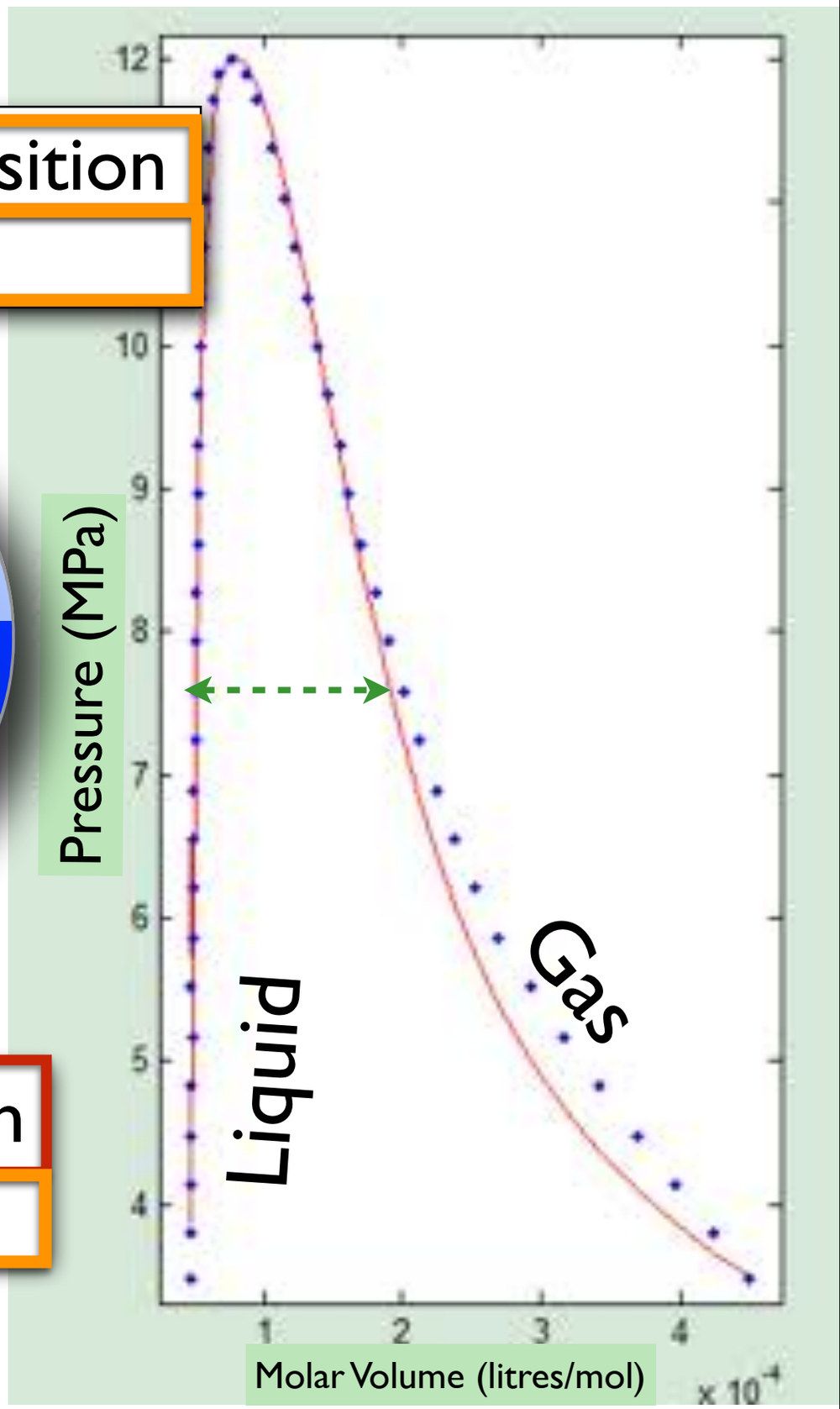
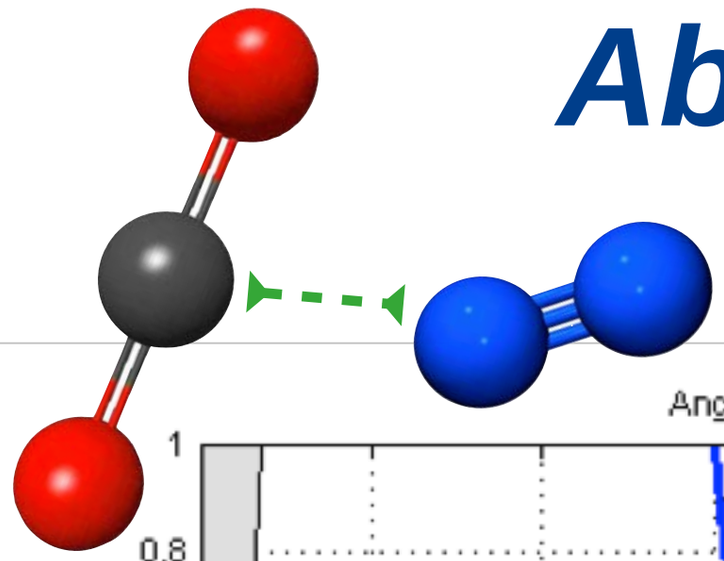
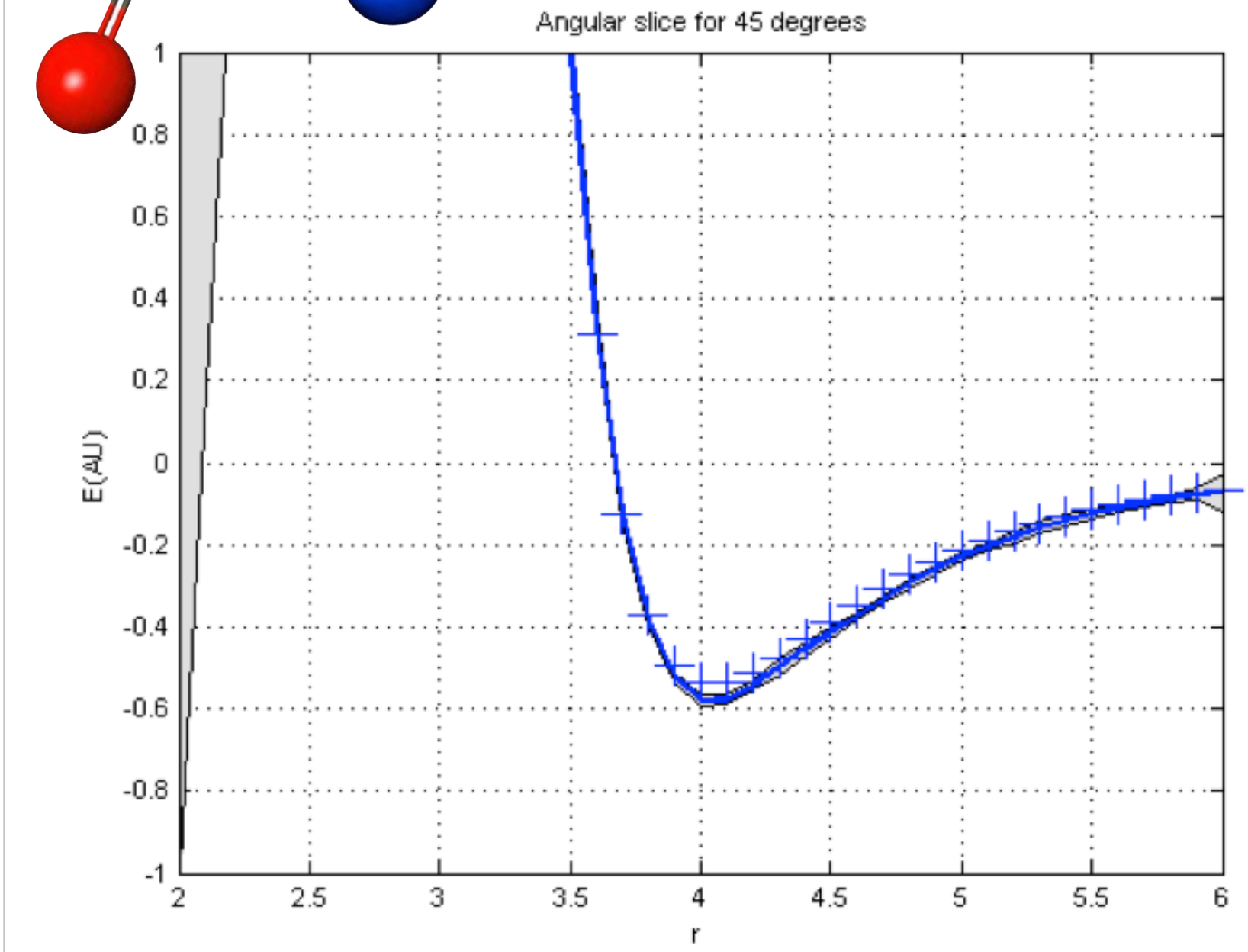


Ab initio force fields

CO2+H2





\+ Quantum Chemistry calculations of CO2-H2 interaction

— Gaussian Process fit for use in simulations

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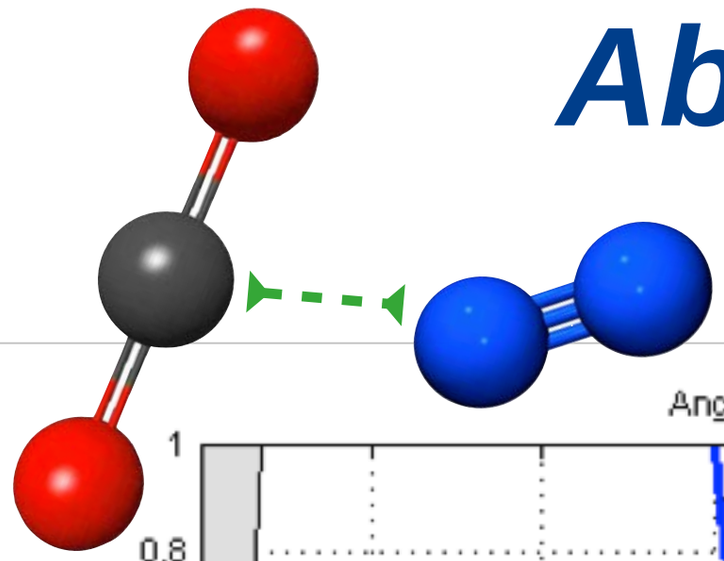

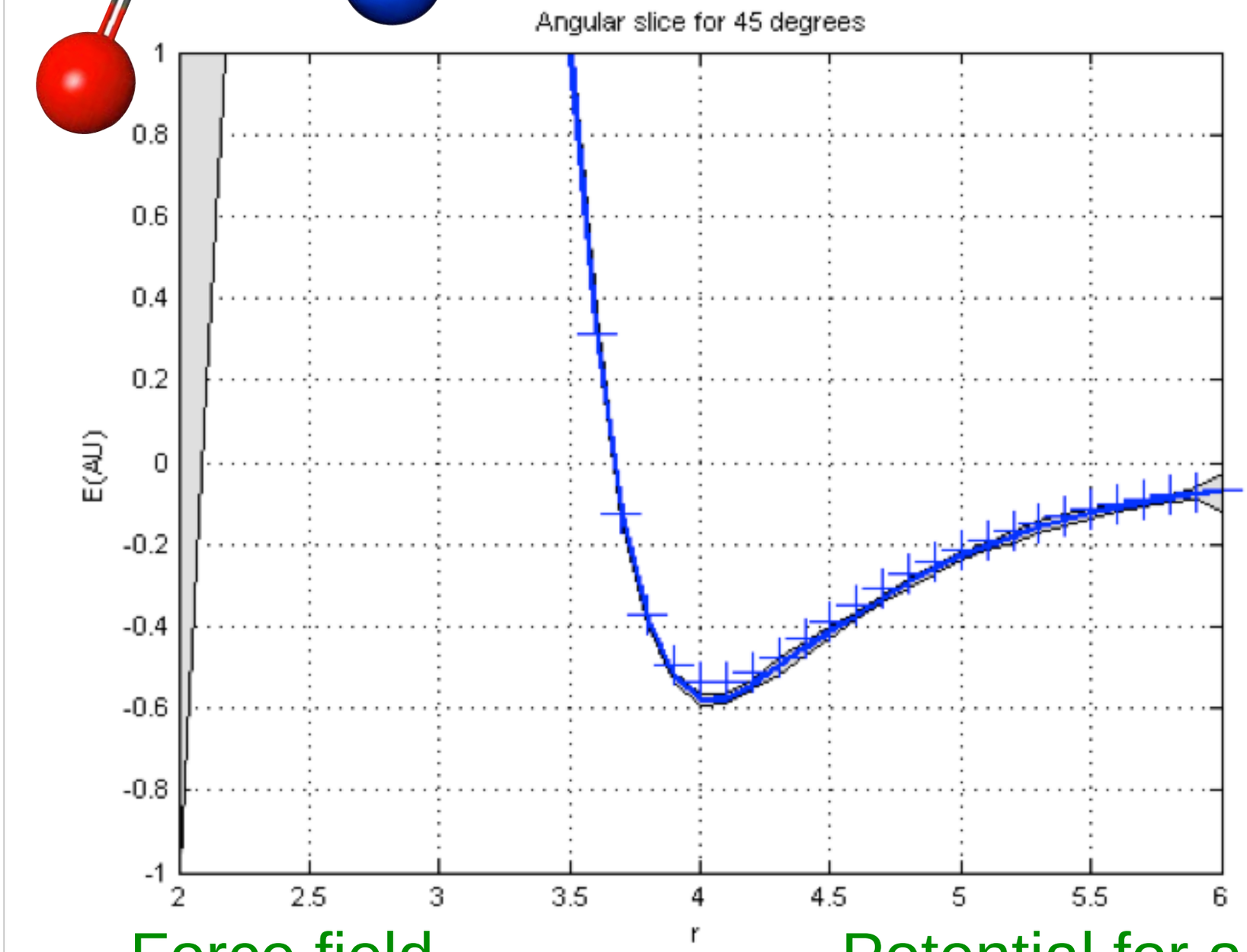

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Force field computed from **first principles**

⇒

Potential for accurate predictions **without data fitting**

Making it all work together

- **Parametric equations of state**
- **Non-parametric EoS**
- **Semi-empirical molecular simulation**
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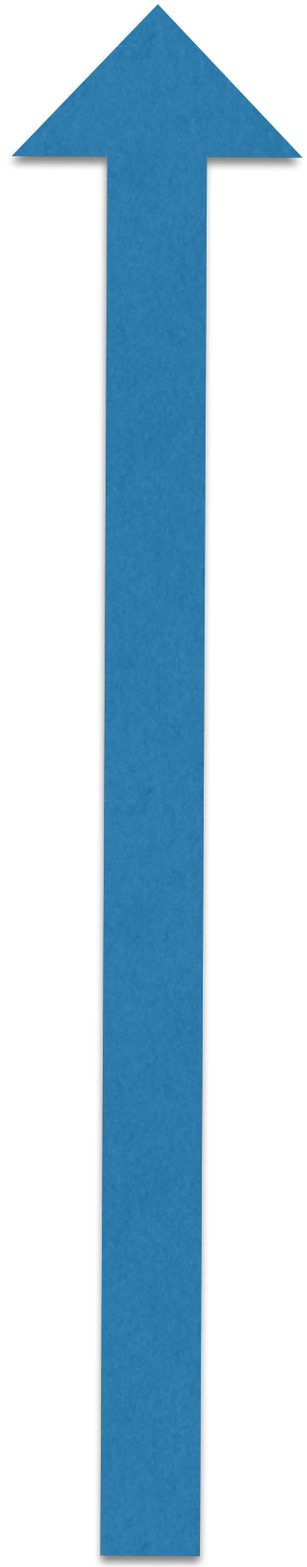

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  - Fit to experiments, simulation data more advanced EoS

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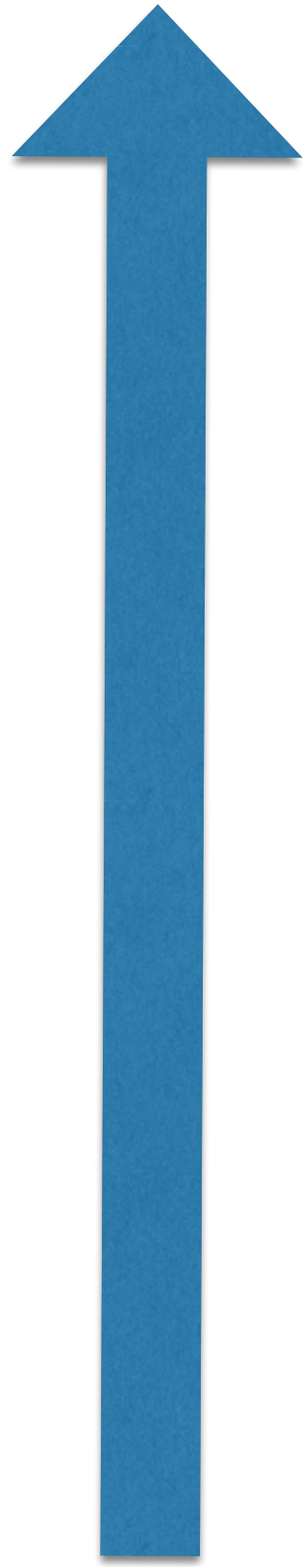

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- Most physically realistic but also most expensive.
- Can augment or replace experiments