Modelling the Thermophysical Properties of Impure CO_2

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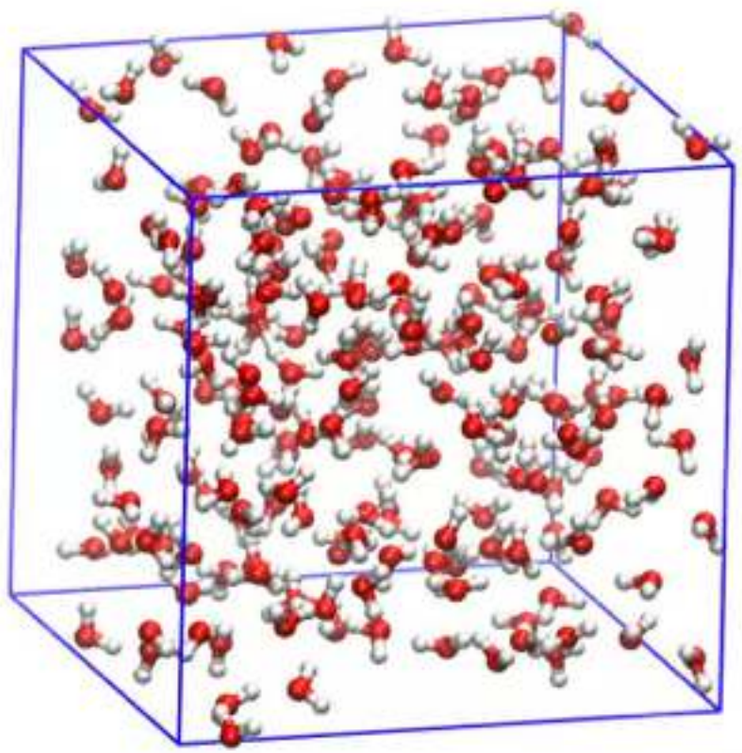
2 School of Chemistry, University of Nottingham

3 School of Mathematics and Statistics, University of Sheffield

The University of Nottingham

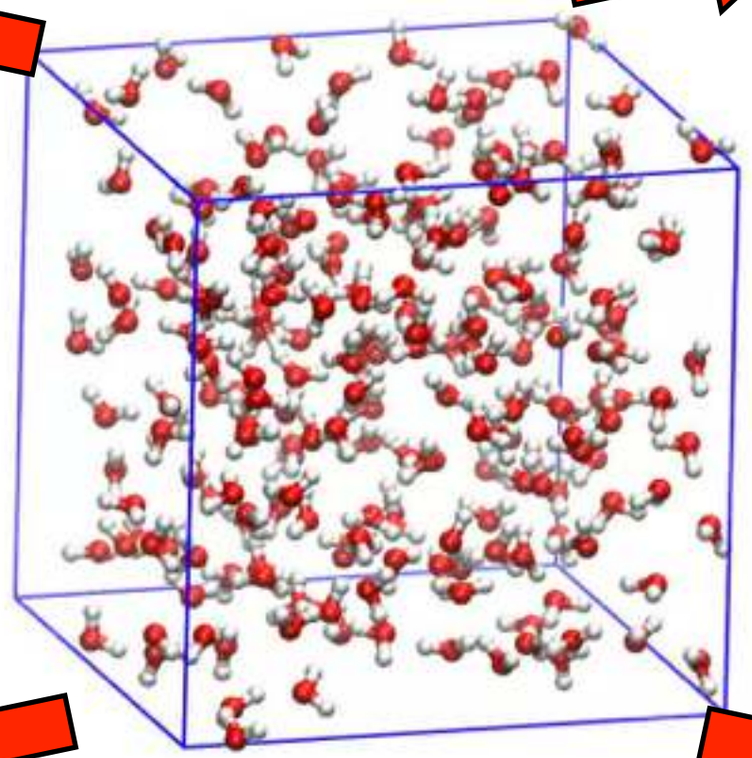
The University Of Sheffield.

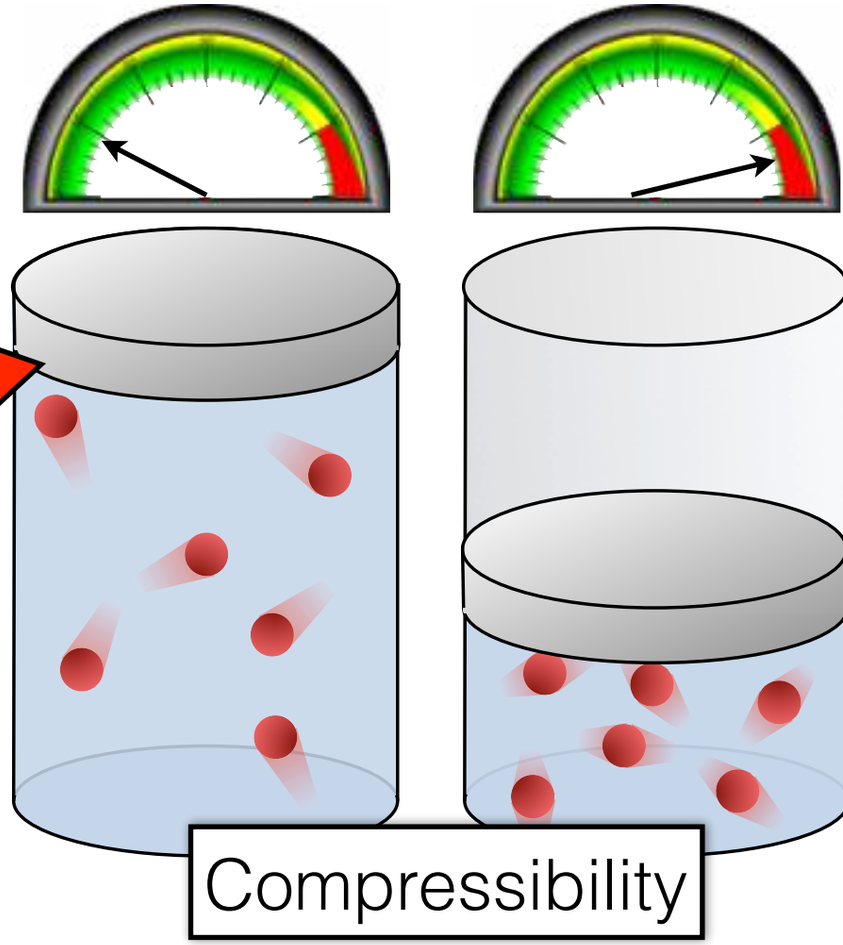
Physical properties



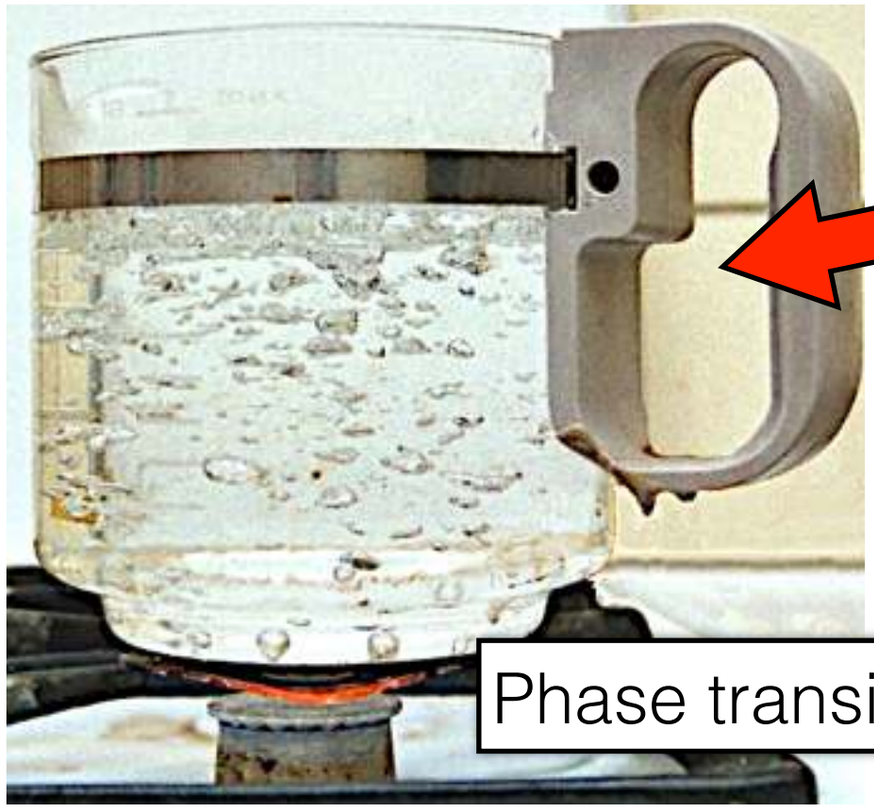
Physical properties

Miscibility





Compressibility



Phase transitions

Speed of sound

Three levels of modelling

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1. Empirical equations of state

- Direct expression for the pressure
- Many parameters
- Extensive fitting to data required

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

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- Requires a small number of empirical parameters
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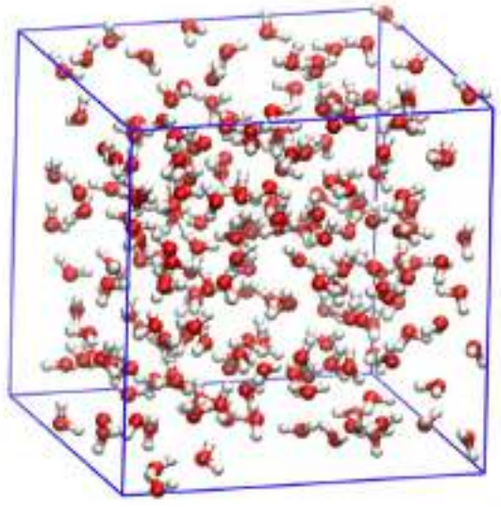

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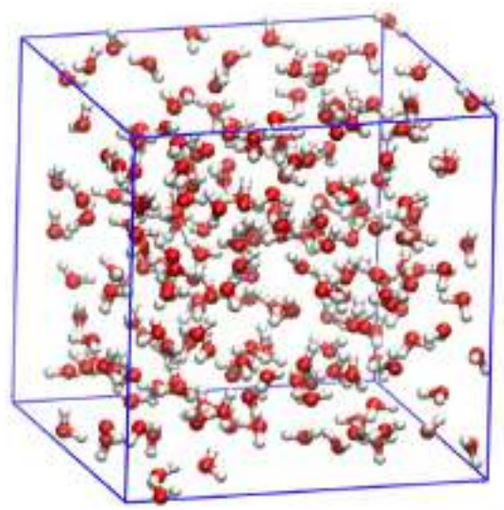
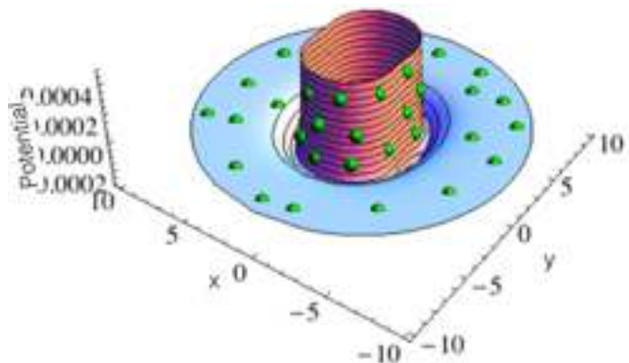


3. First-principles calculation

- Molecular interactions from ab-initio computational chemistry
- First-principals: i.e. **no parameters**
- **Predicts data without fitting**



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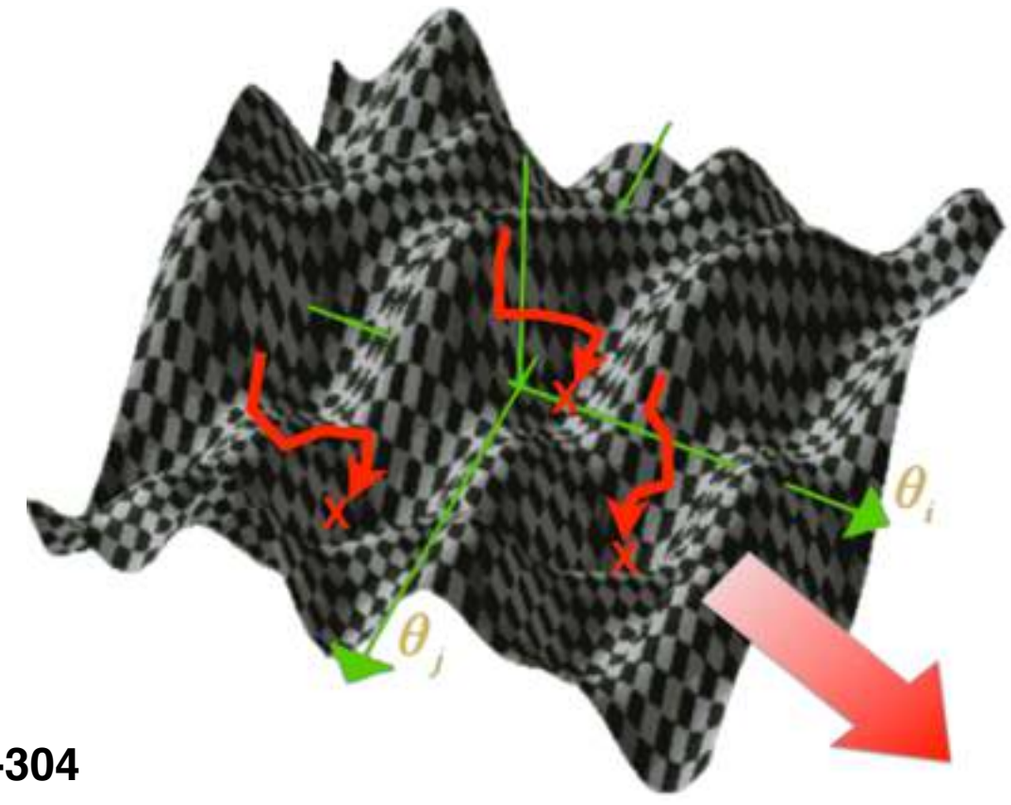

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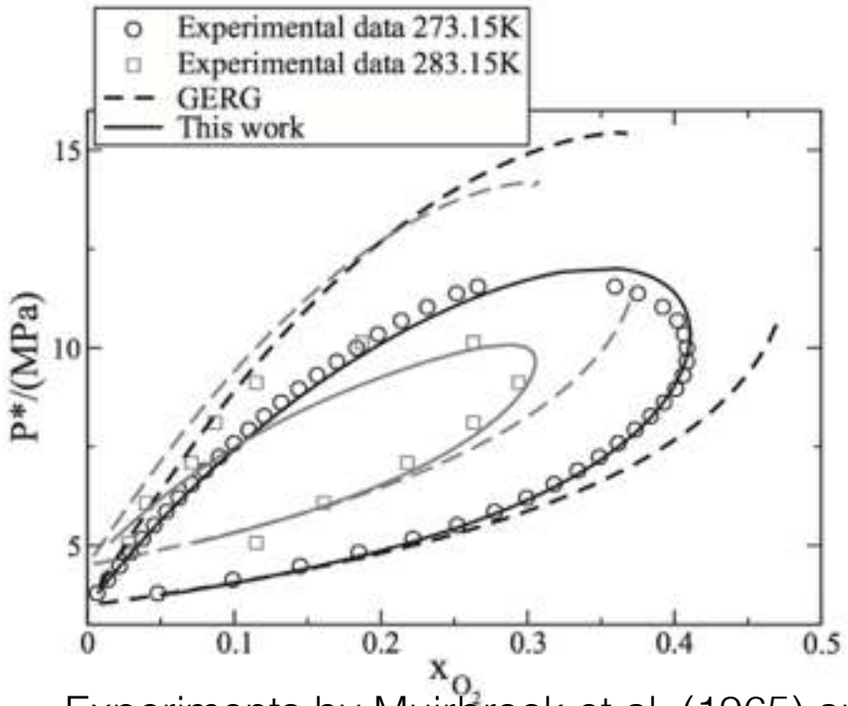
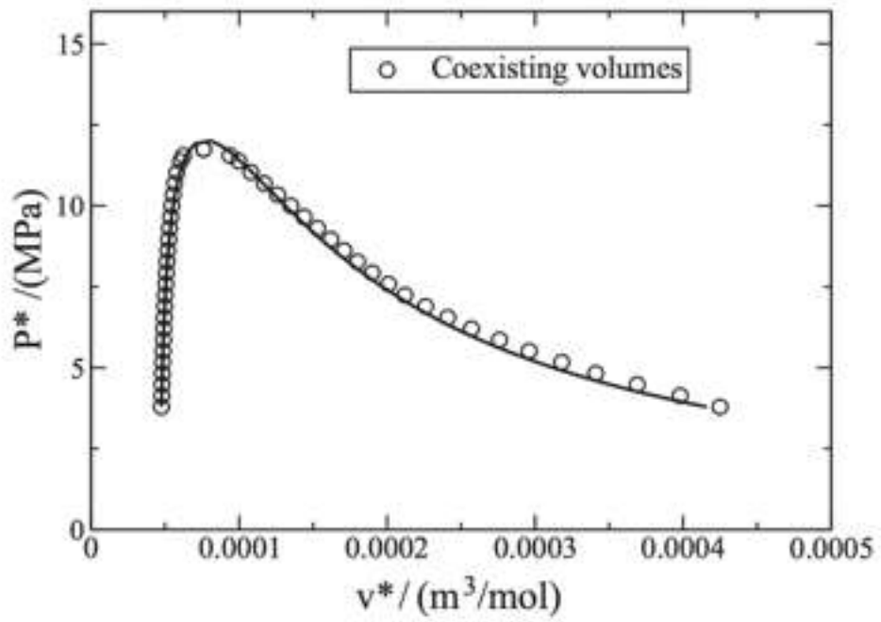
CO_2-O_2





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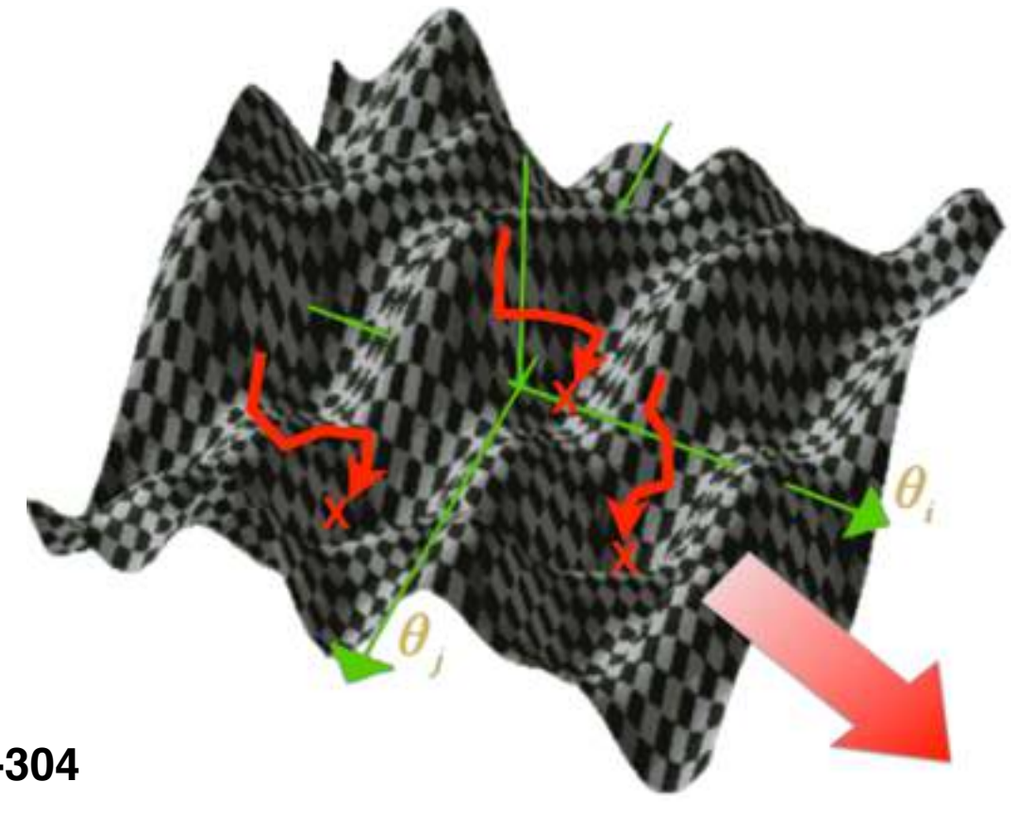

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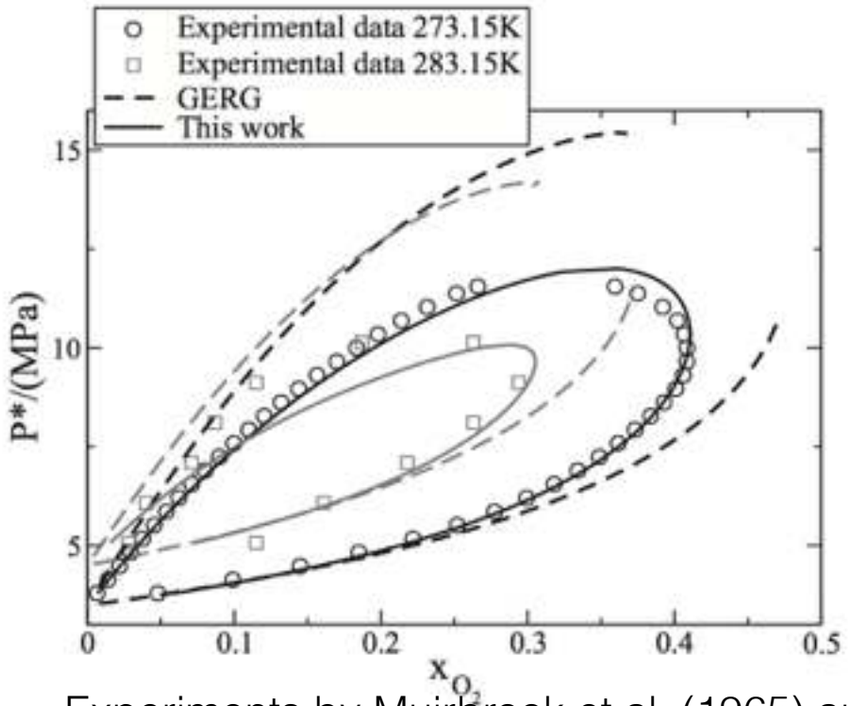

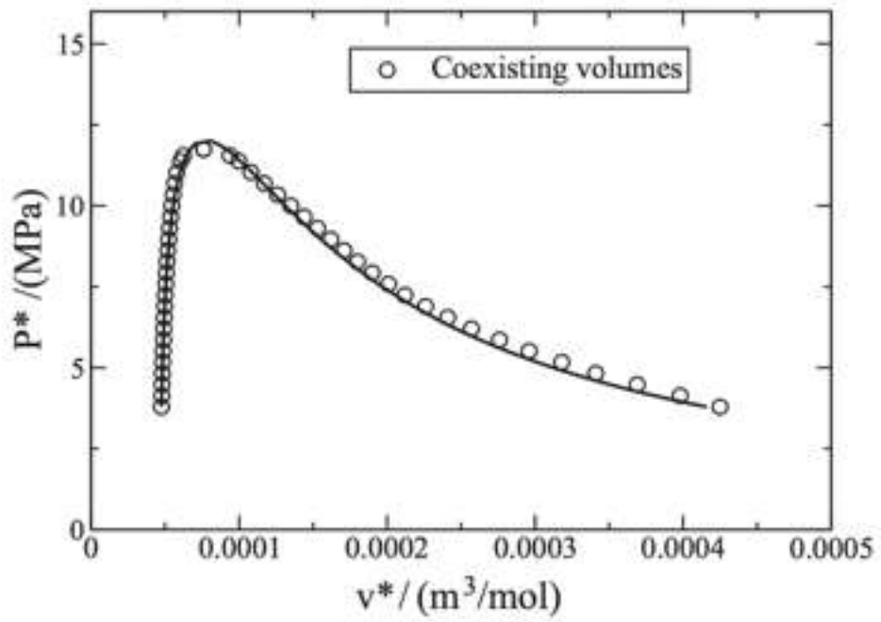

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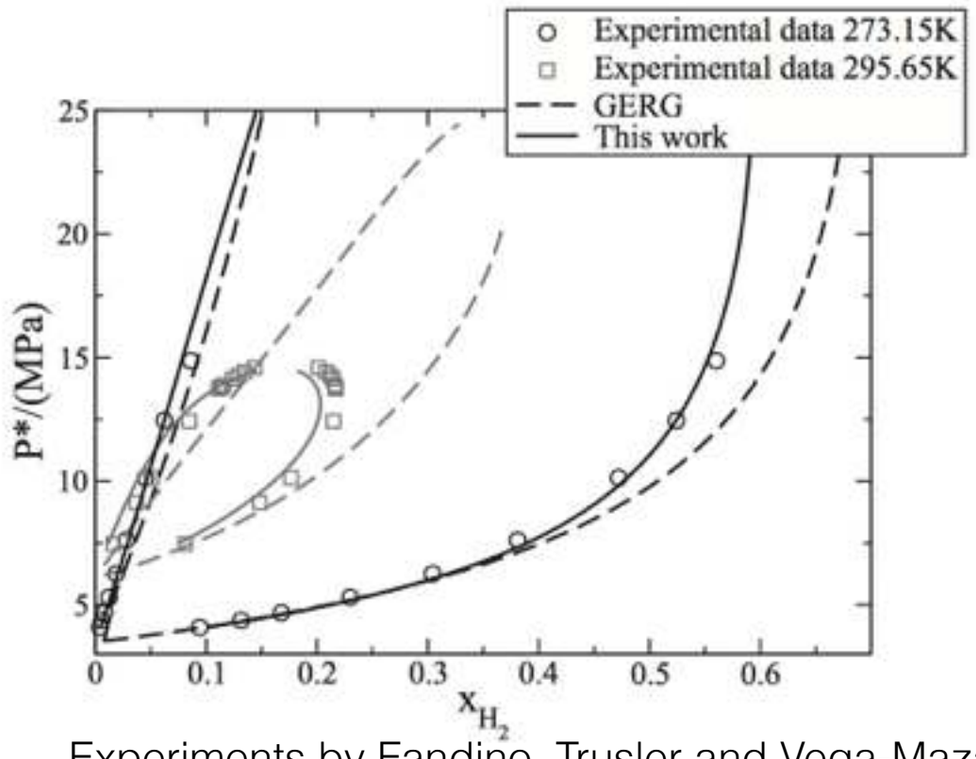

Experiments by Fandino, Trusler and Vega-Maza (2015).

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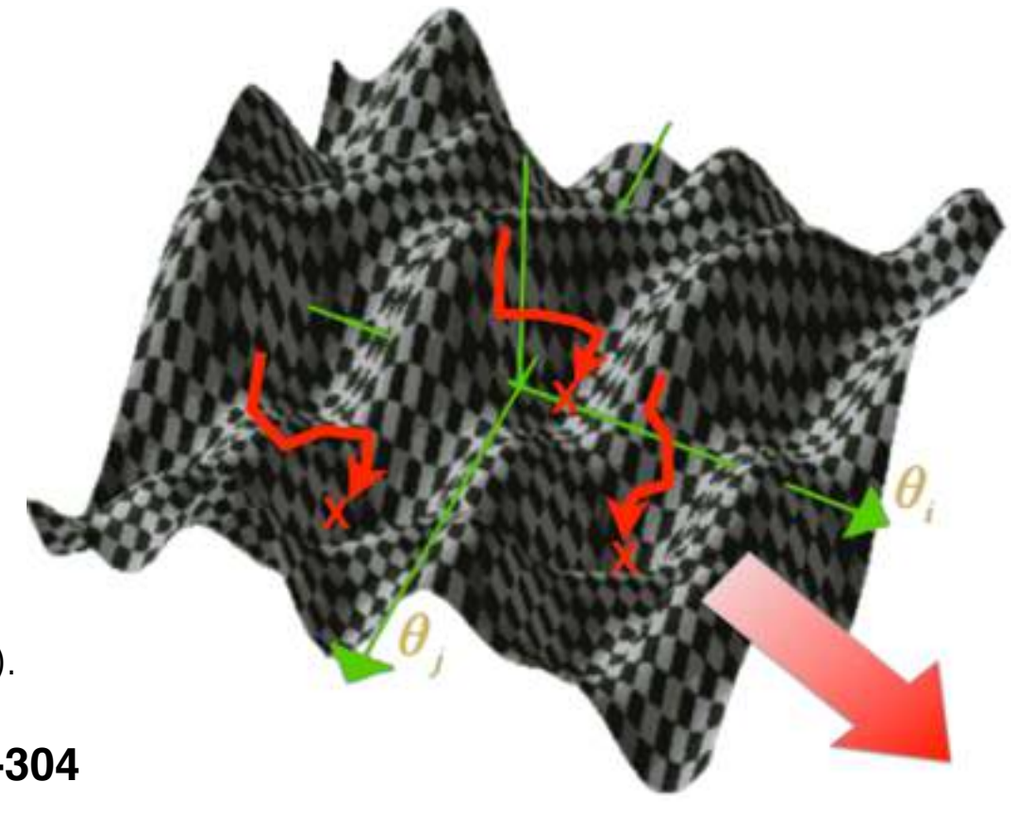

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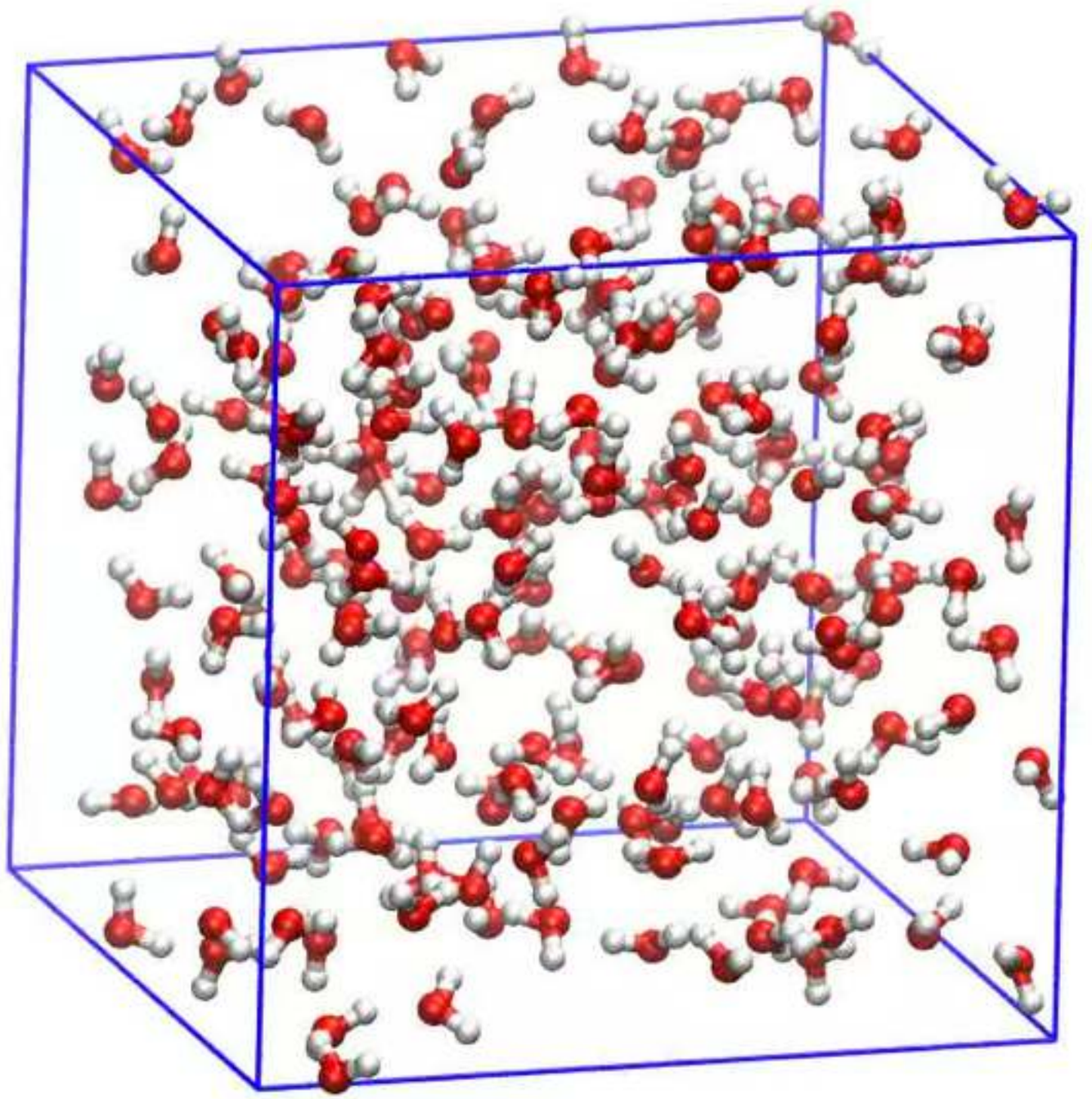
Molecular simulation



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

Can predict:

- Pressure-volume
- Coexistence
- Effect of impurity
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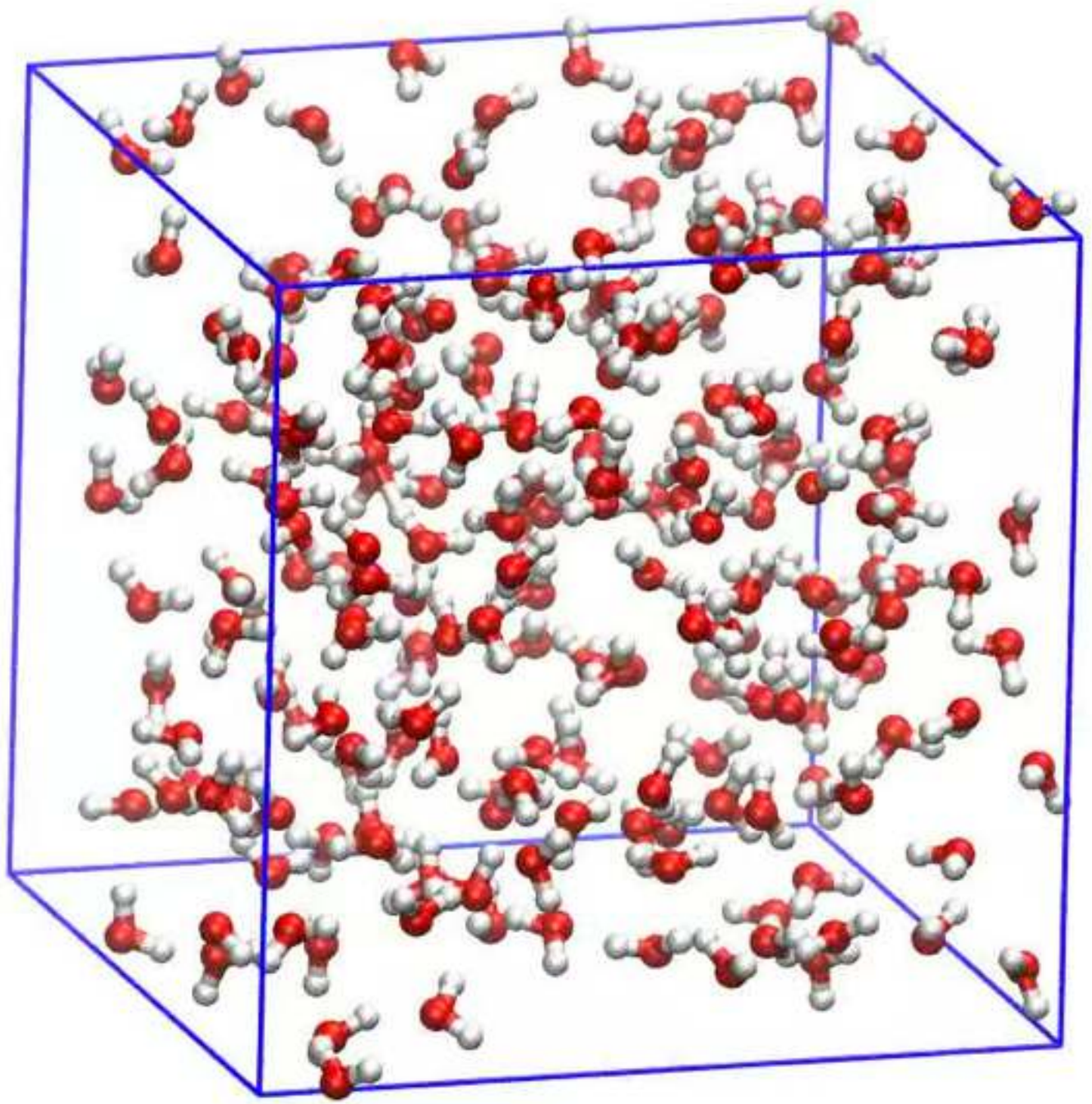

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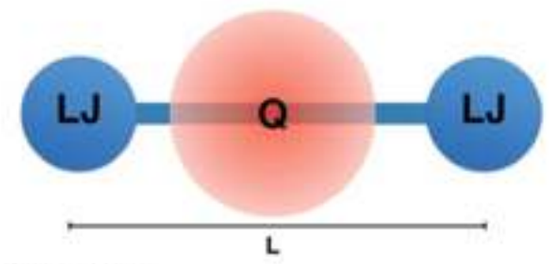
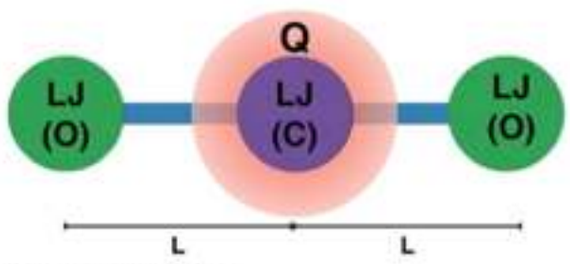


a) Diatomic



b) Carbon dioxide

Simplified picture of how molecules interact - fit a small number of interaction parameters

Results - molecular simulations with empirical force fields

Cresswell, Wheatley, Wilkinson and Graham, Faraday Discussions (2016) 192, 415-436.

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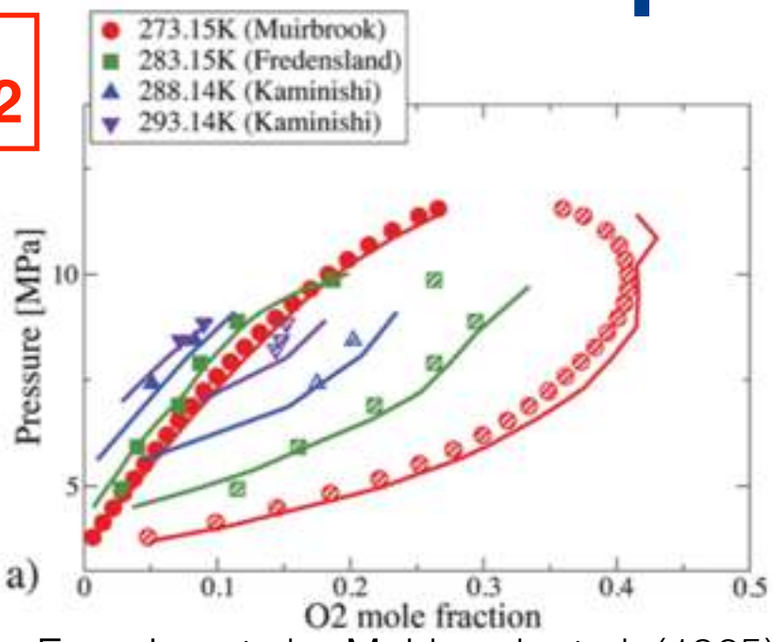

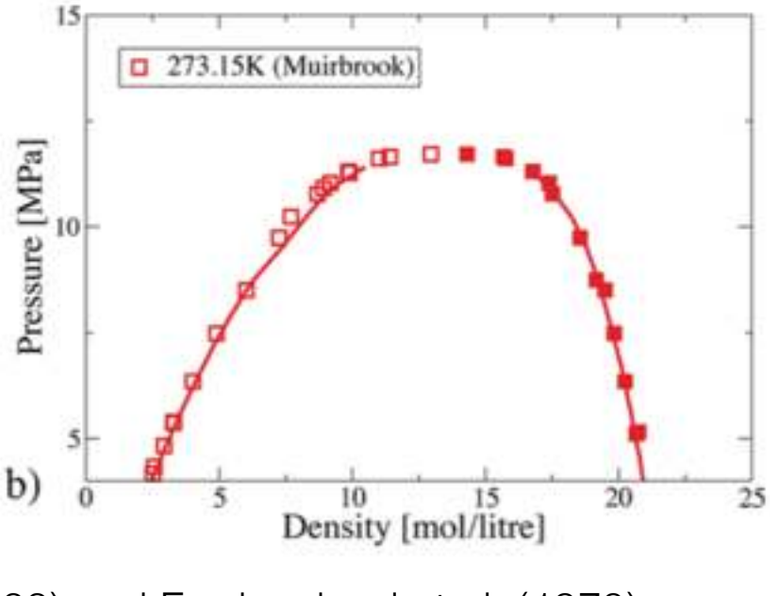

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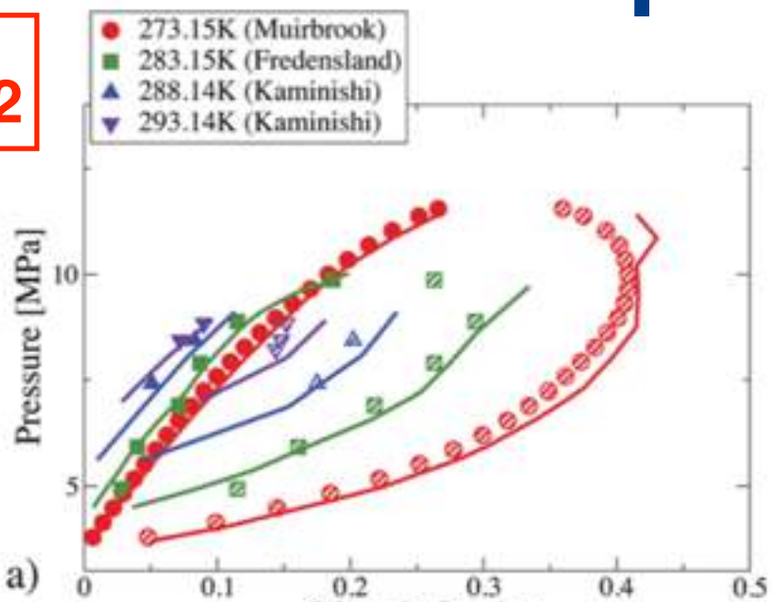

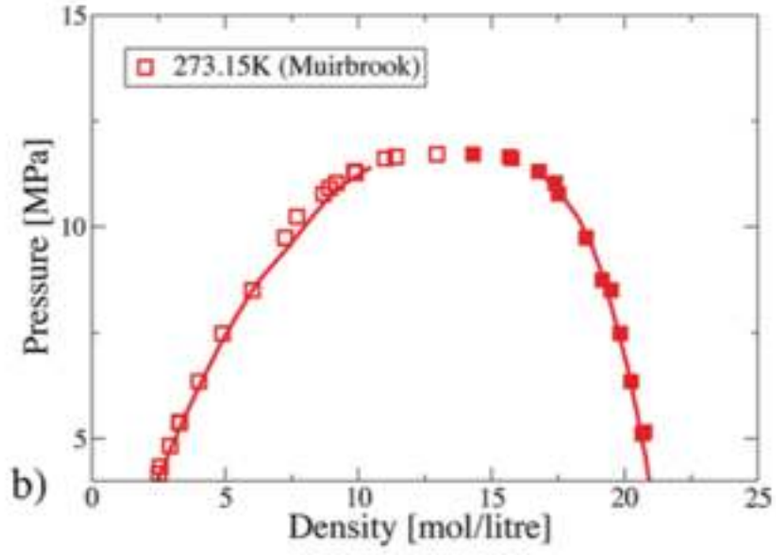

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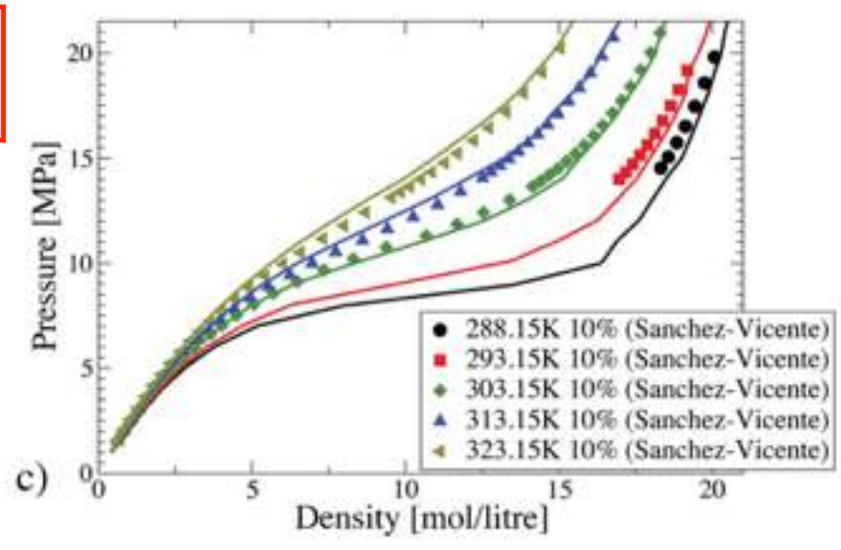

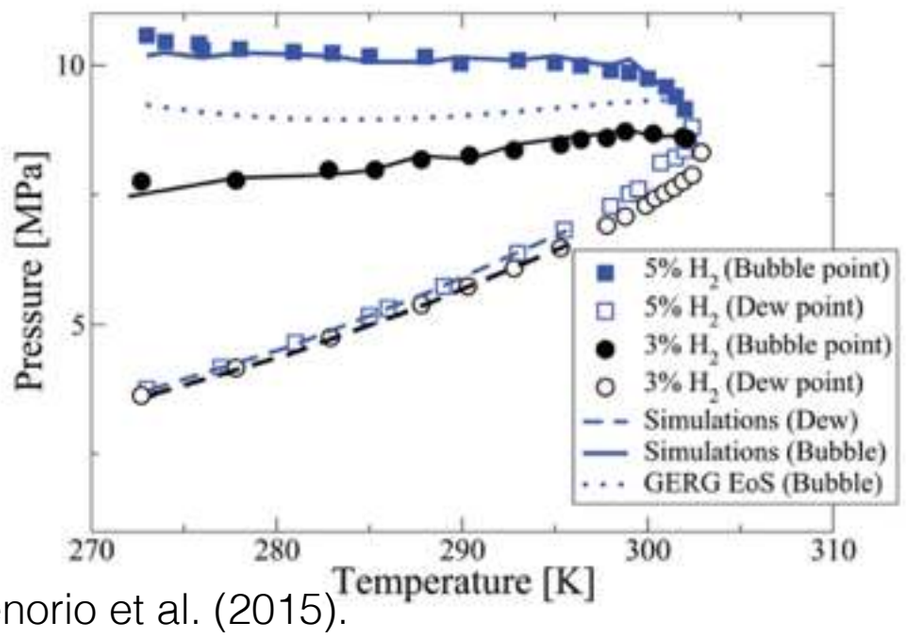

Experiments by Sanchez-Vicente et al. (2013) and Tenorio et al. (2015).

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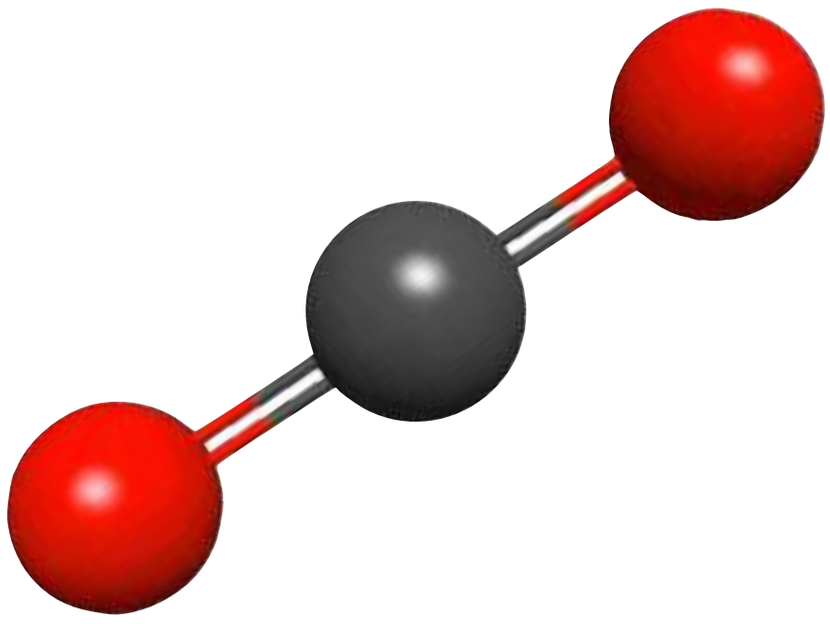
Molecular force-fields from first principles

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



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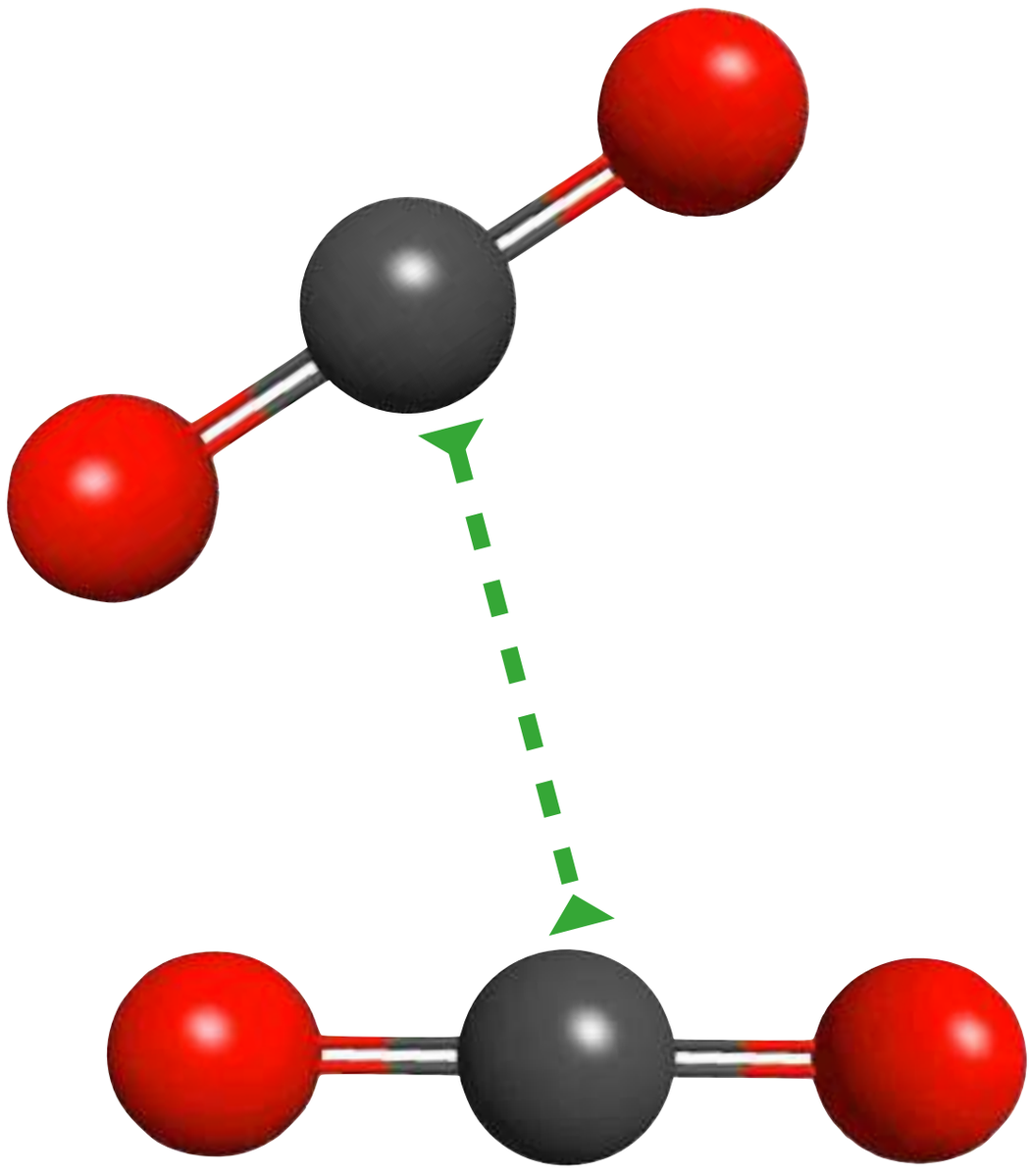

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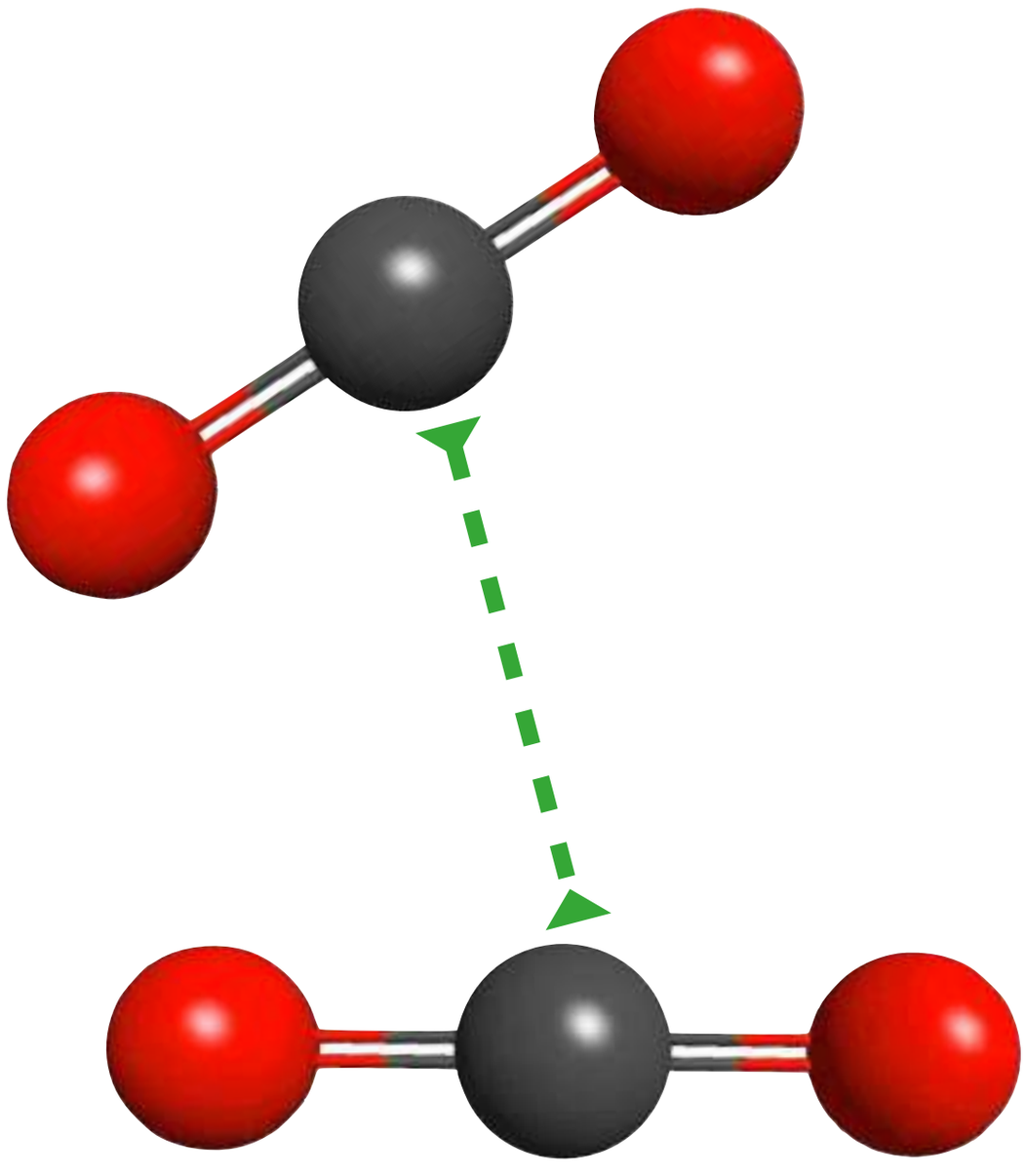
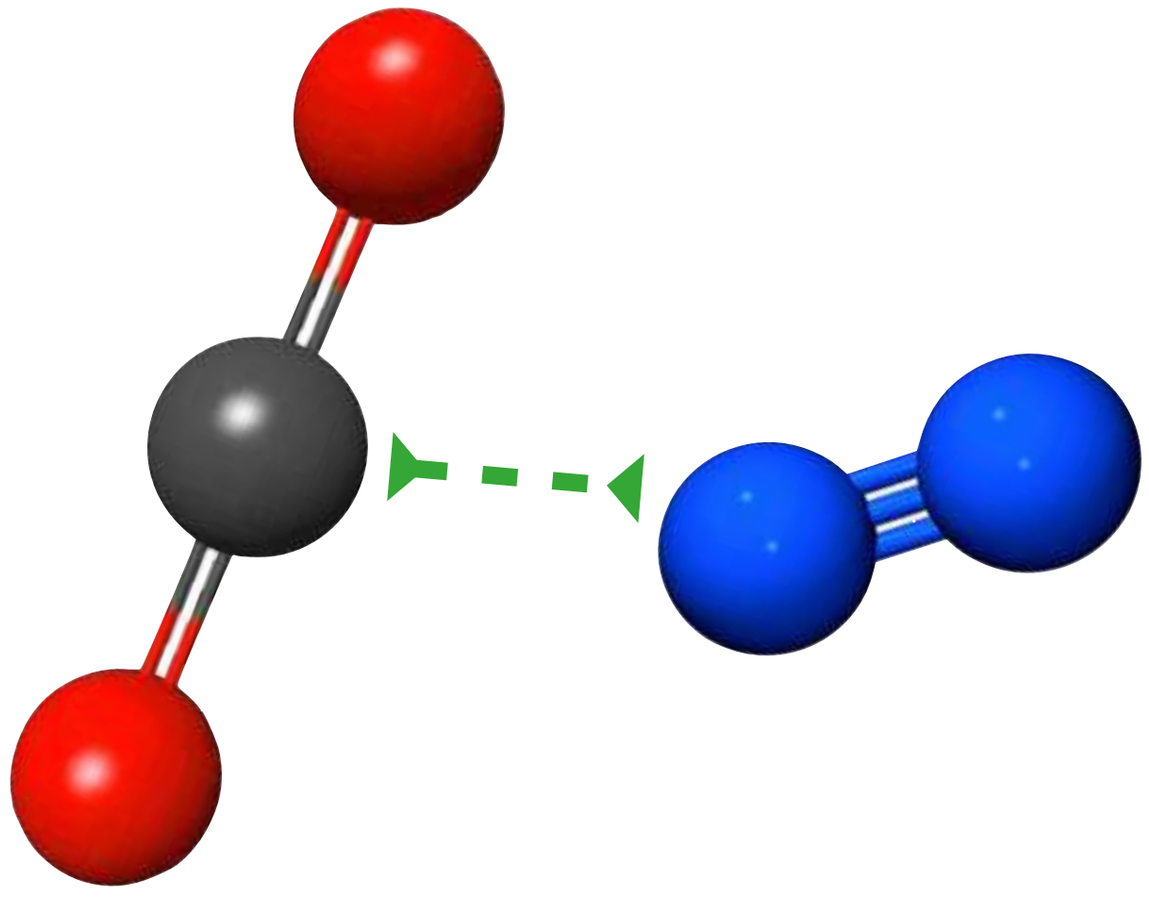
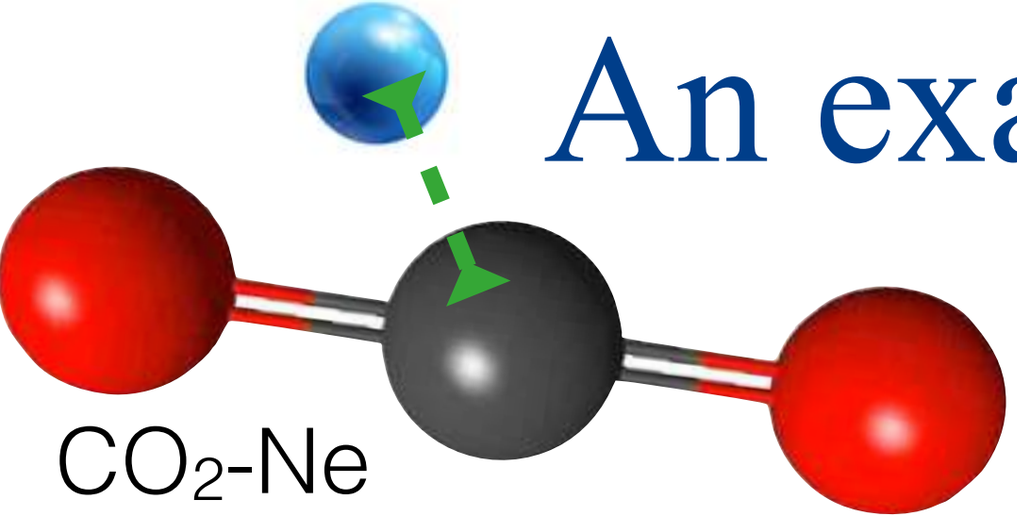




An example energy surface



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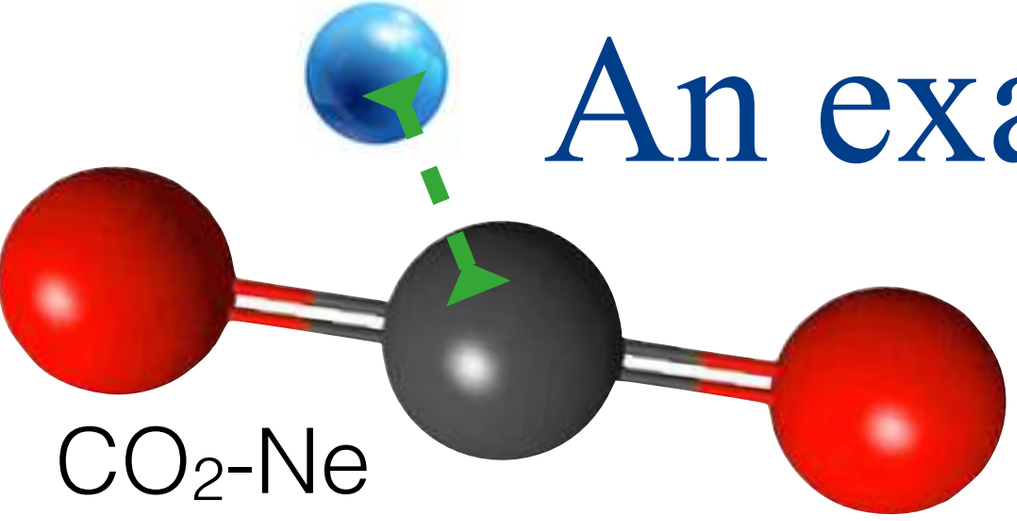

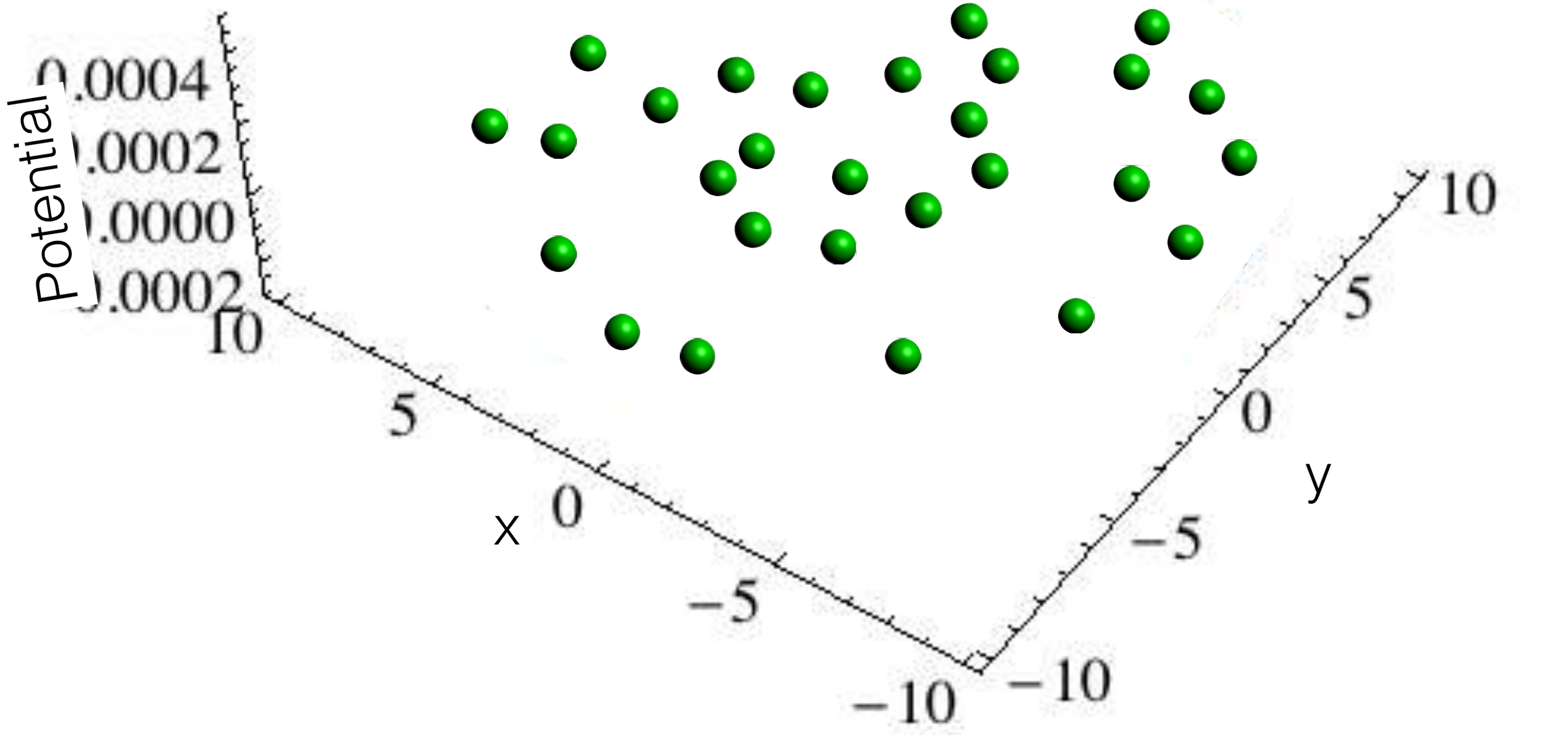

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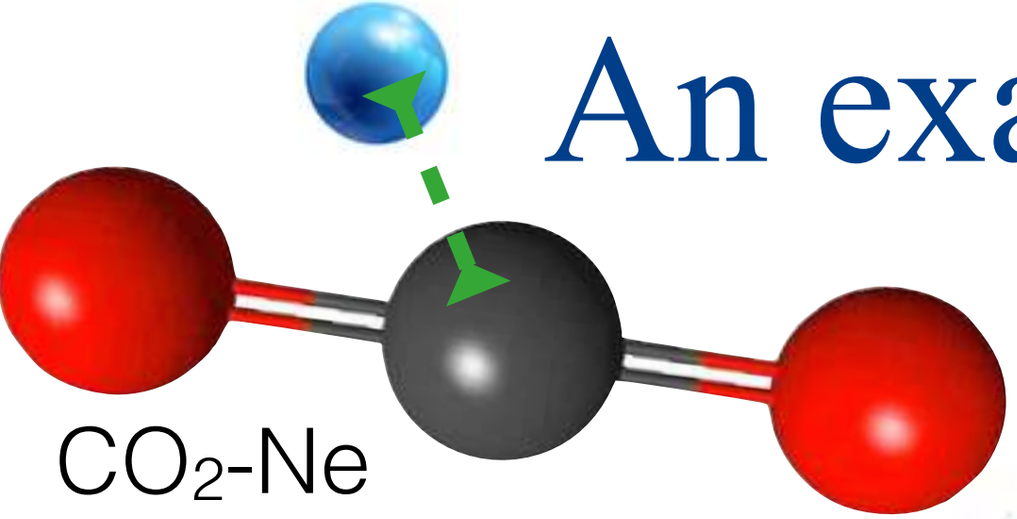
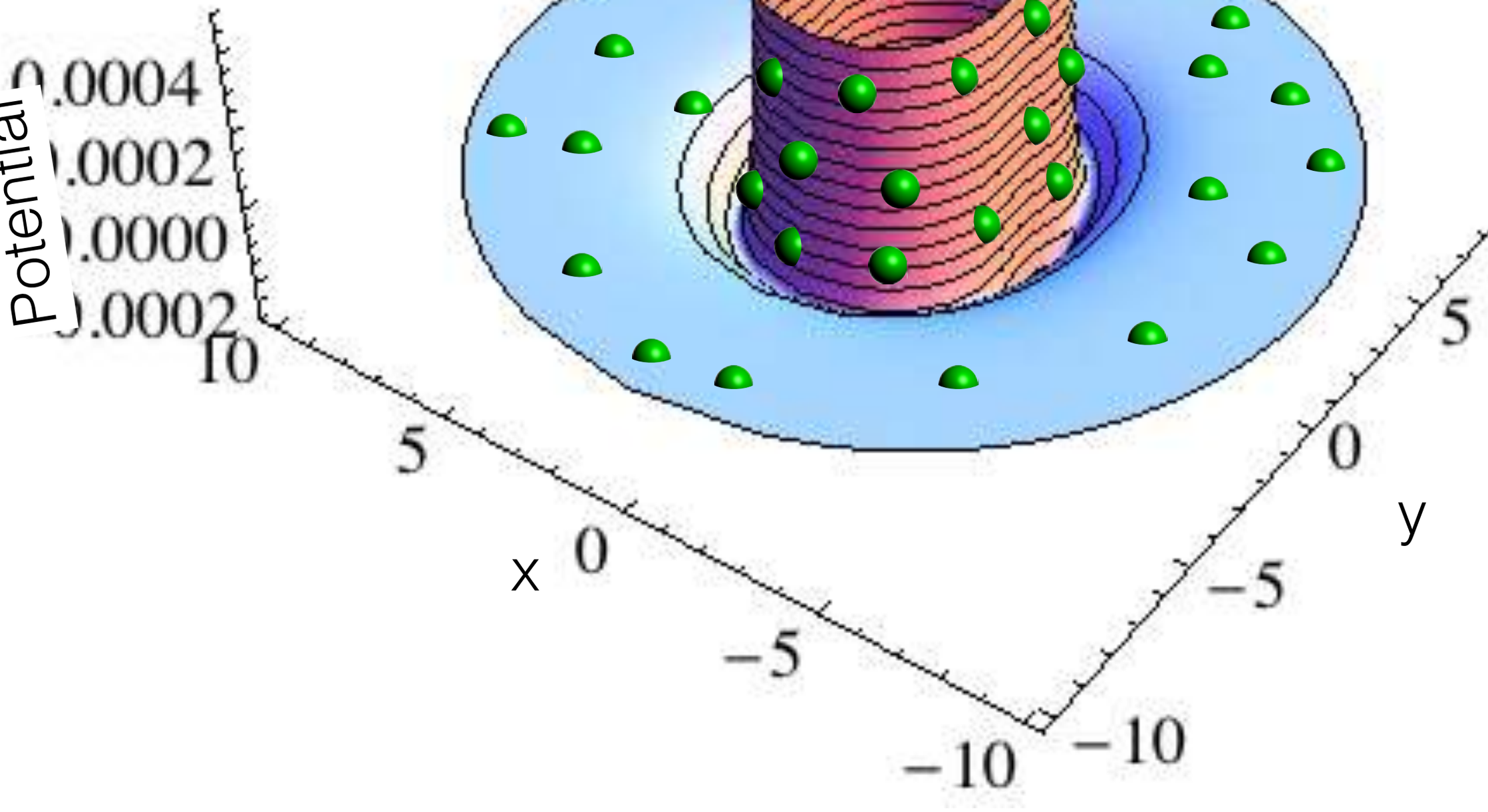
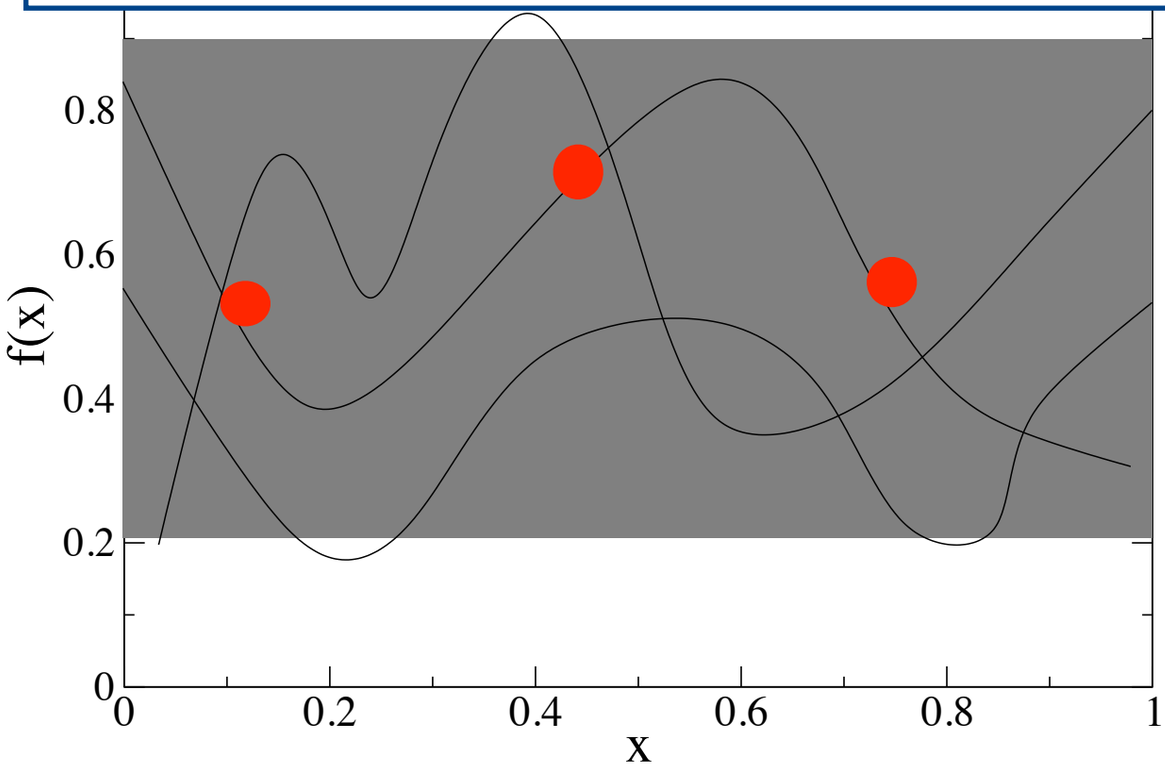




Gaussian processes

Interpretation 1: Average over functions



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

Gaussian processes

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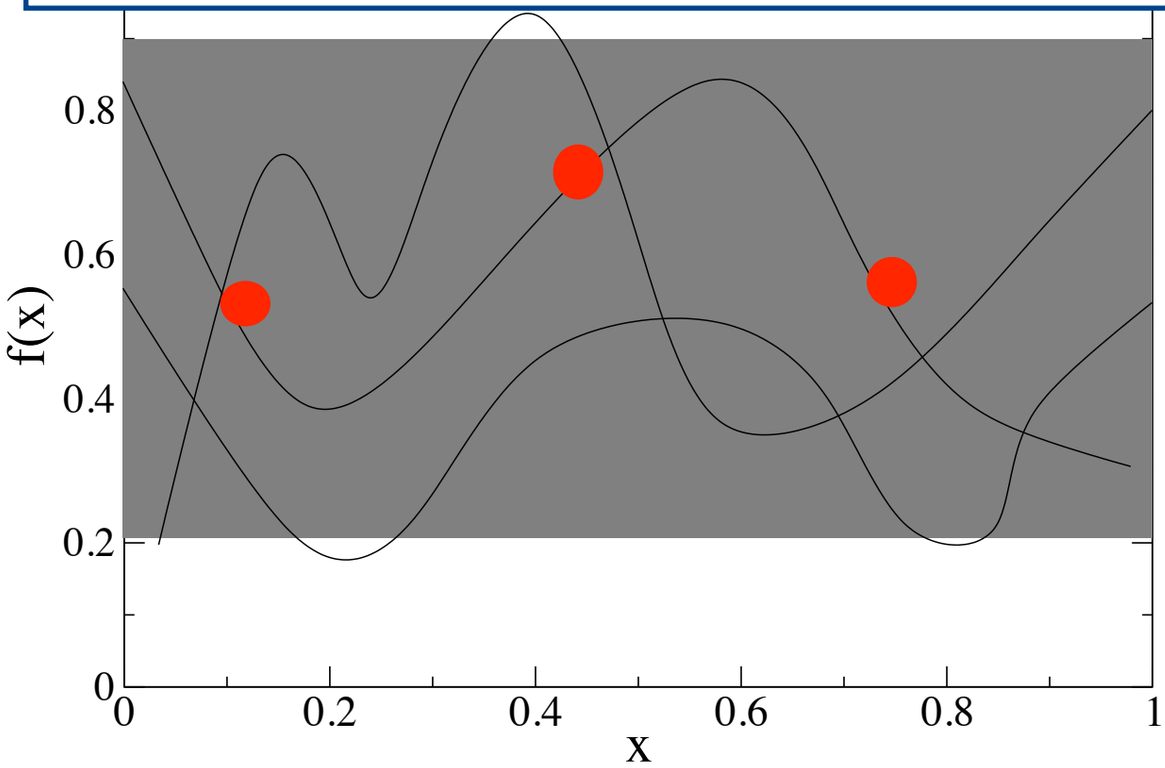

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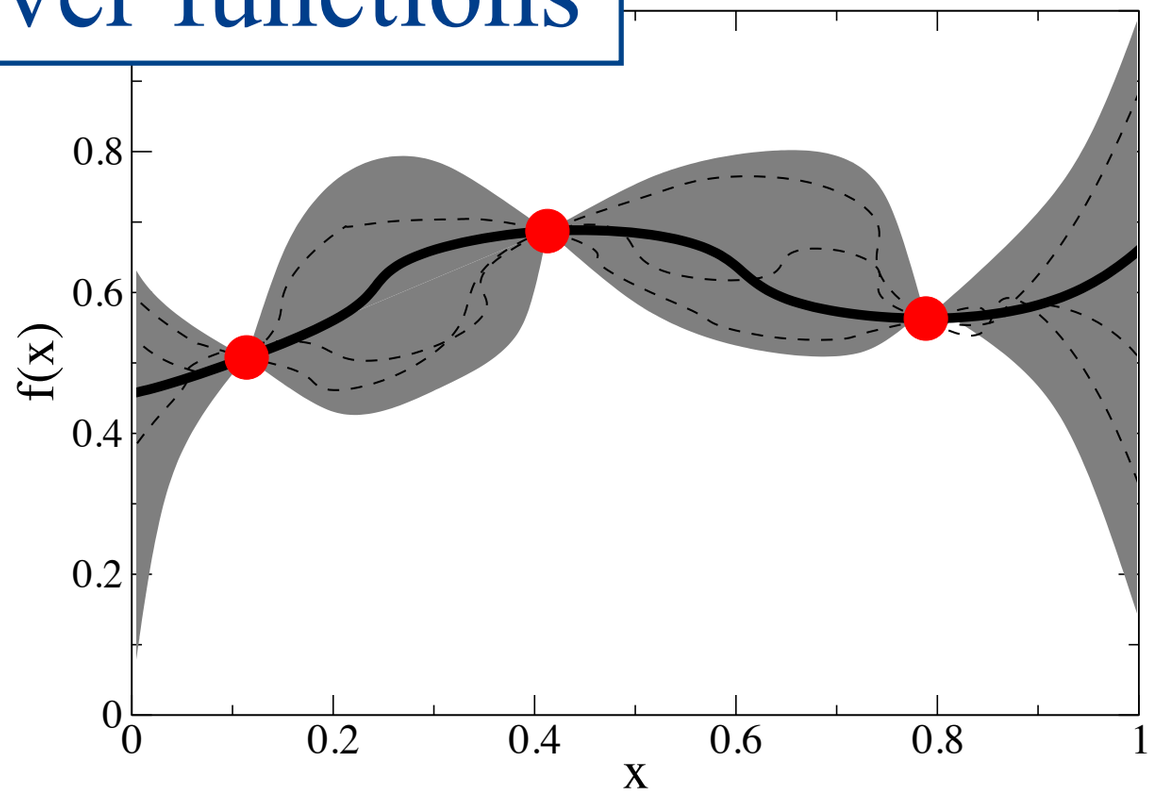

b) Keep only the functions that pass through the data points

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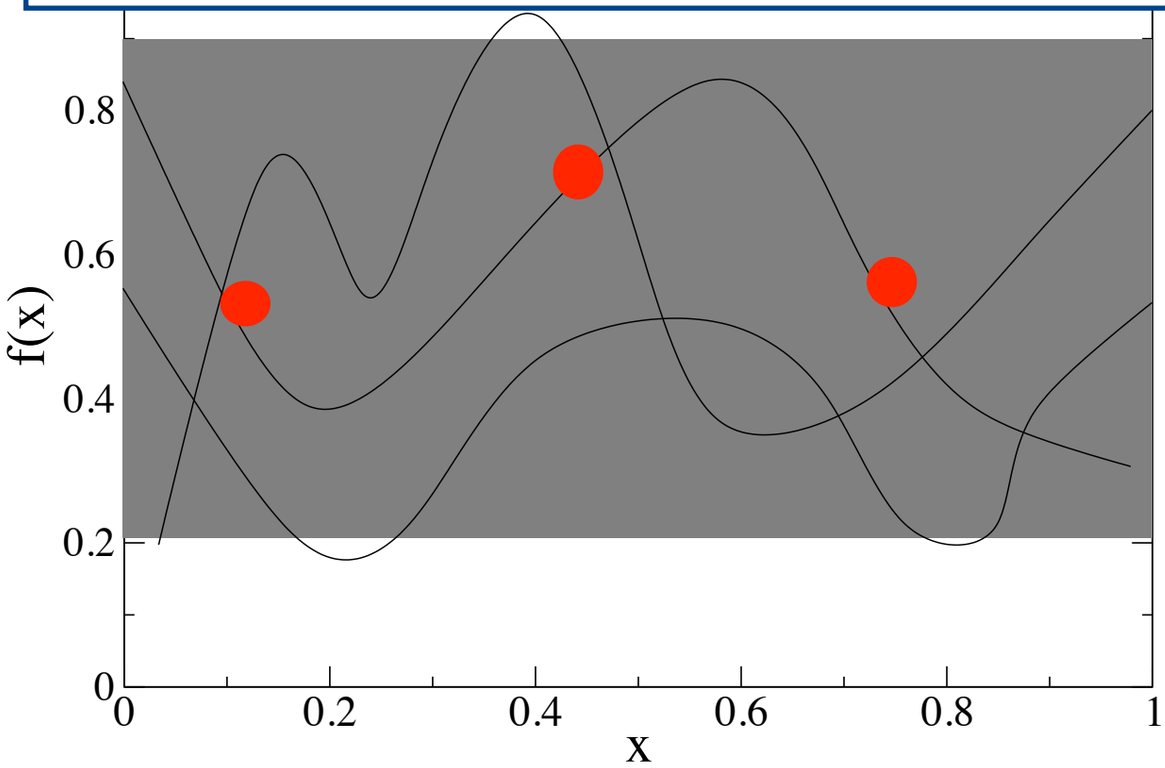

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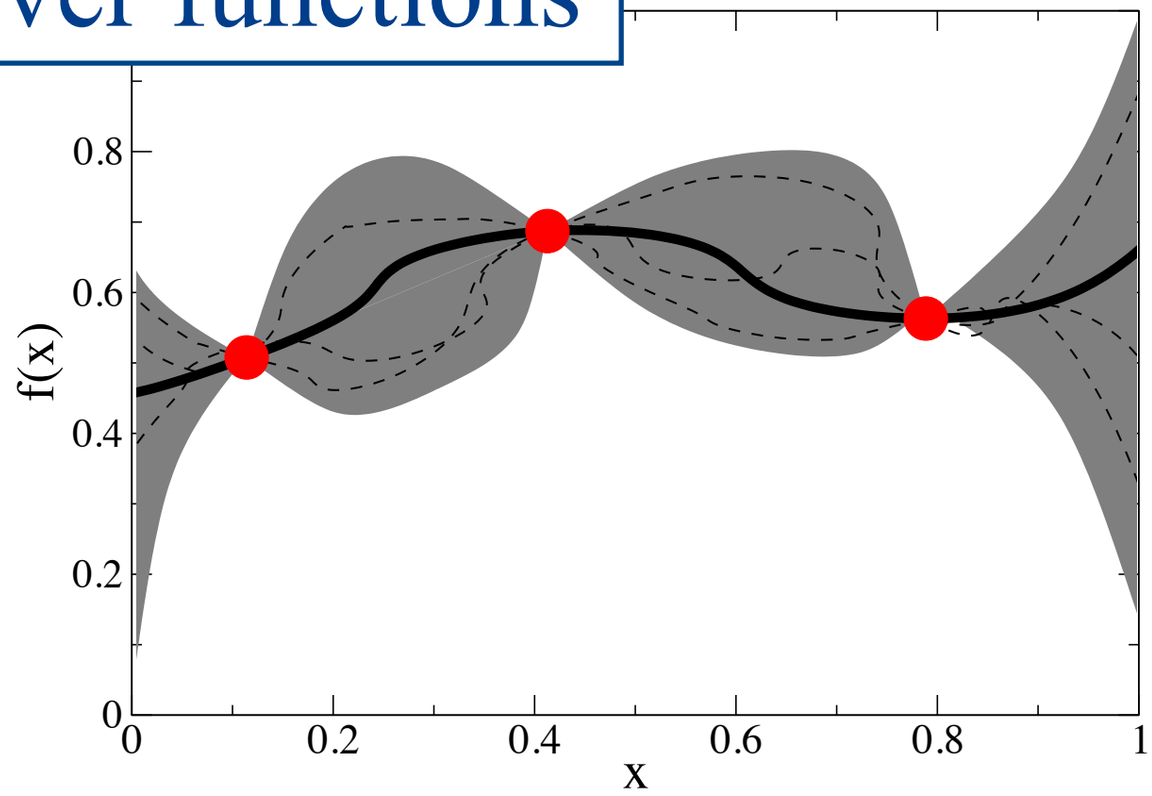

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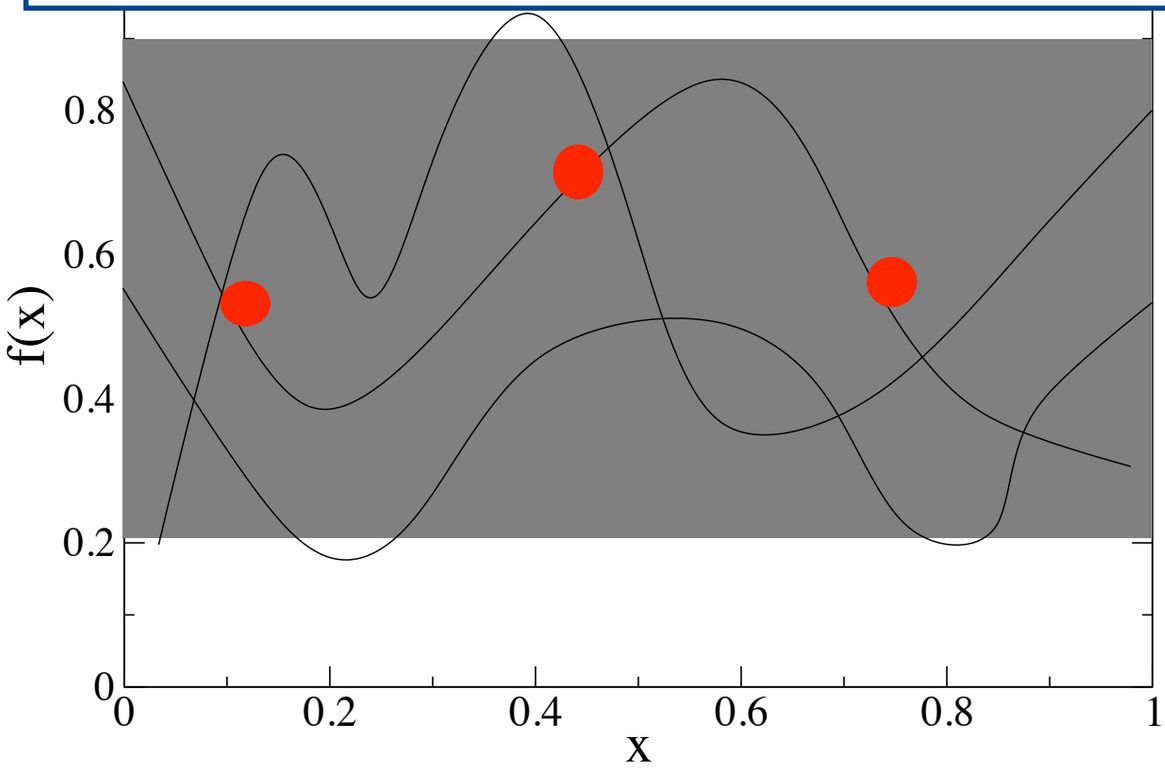

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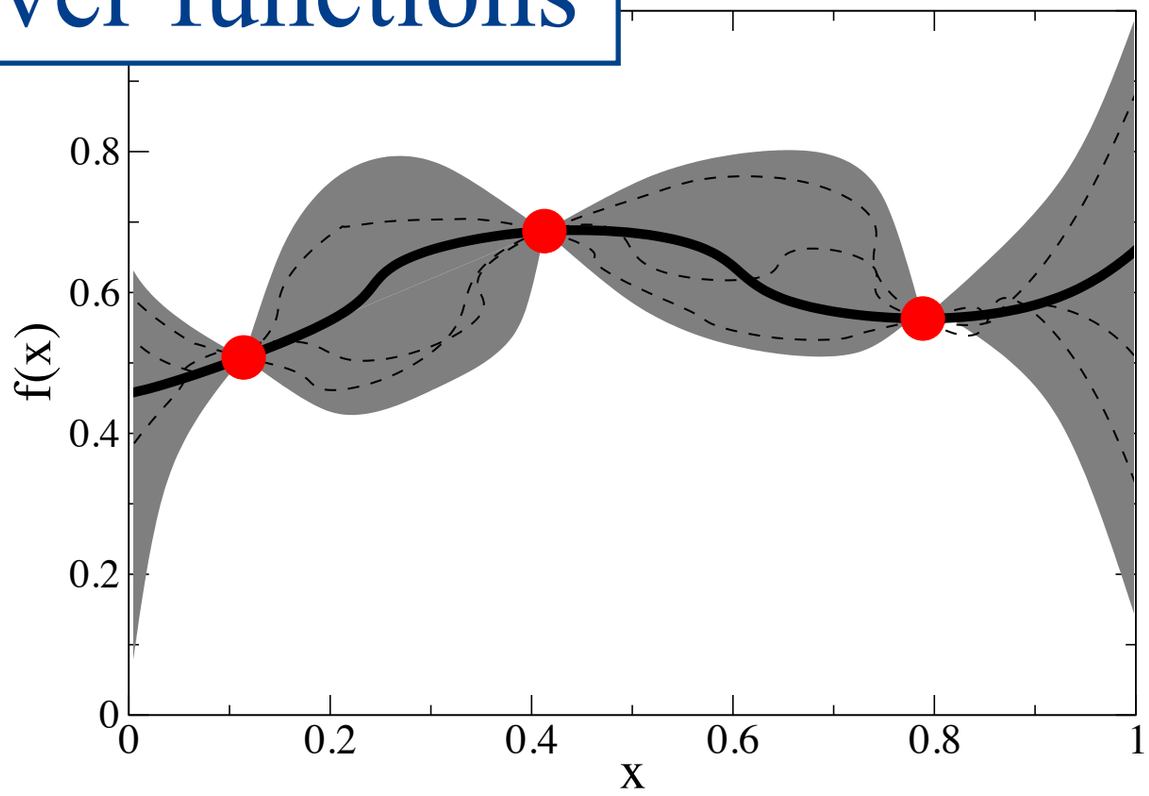

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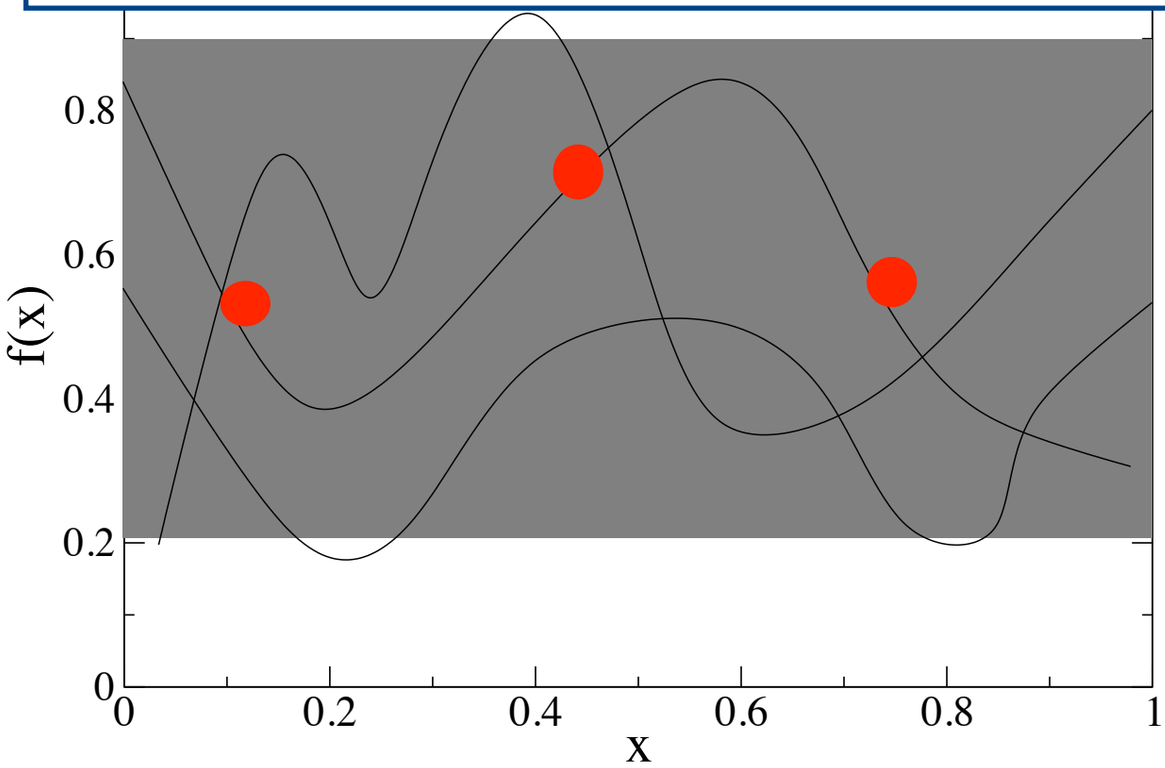

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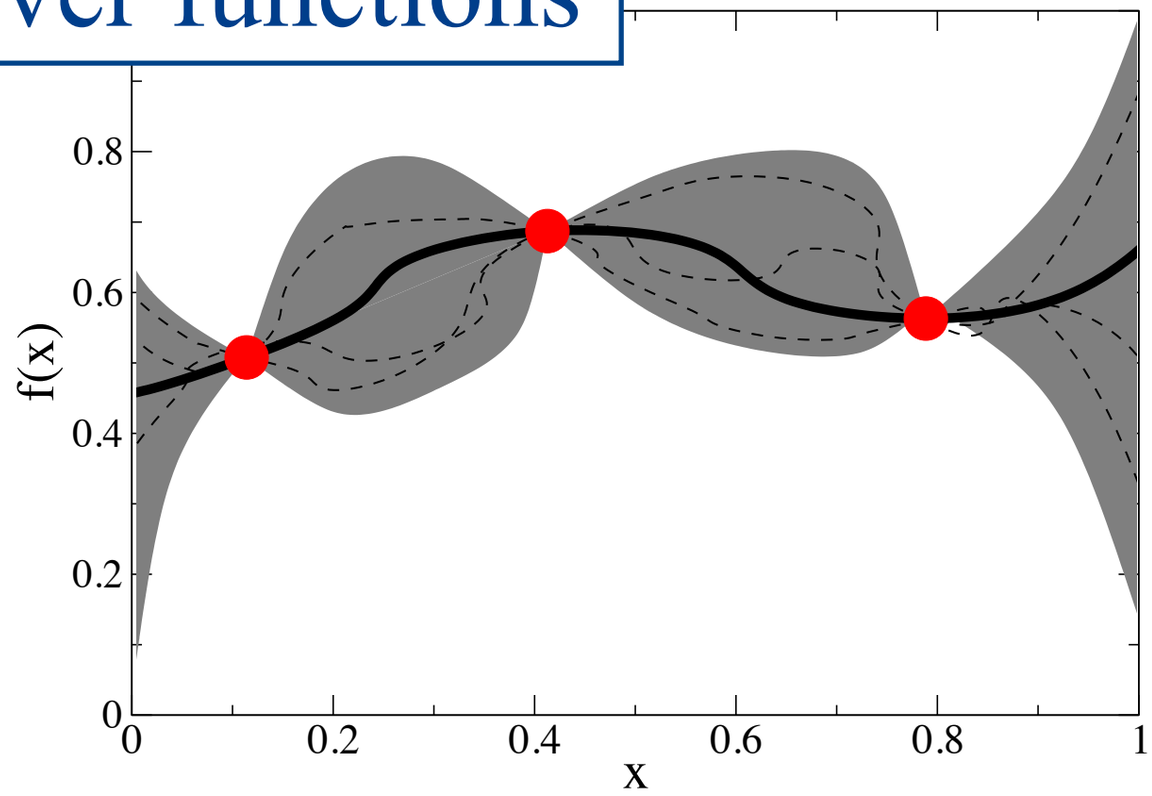

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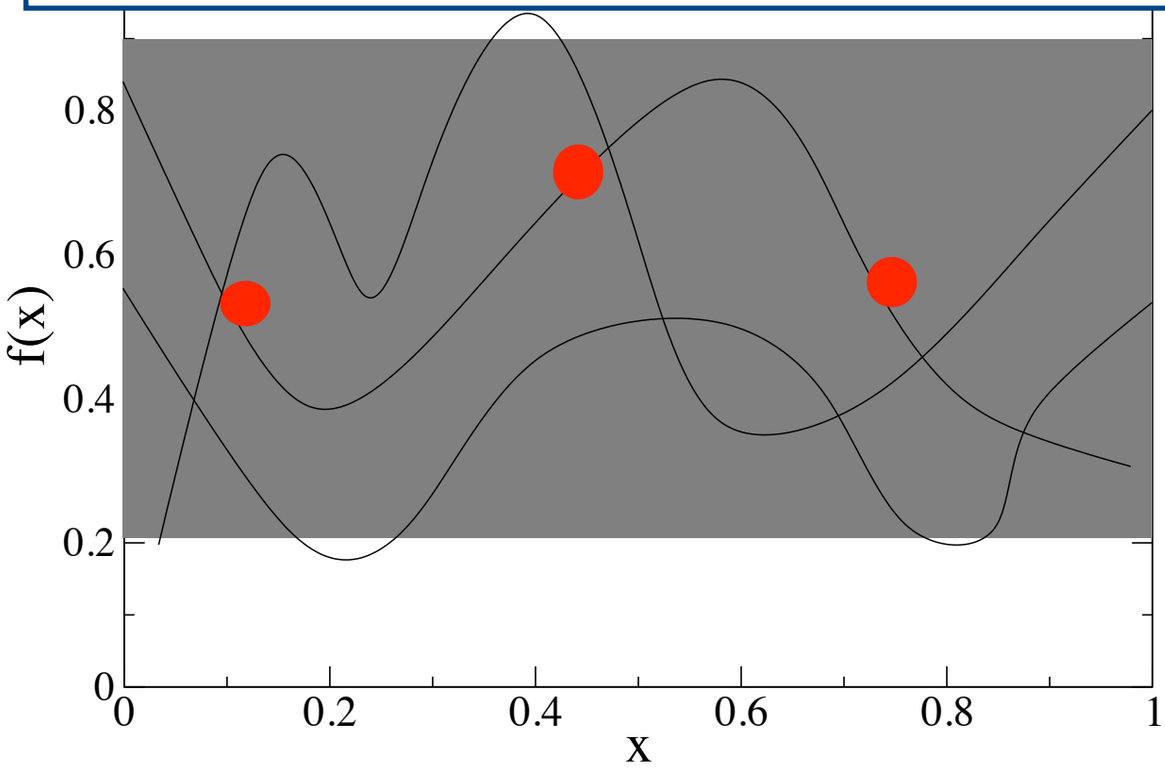
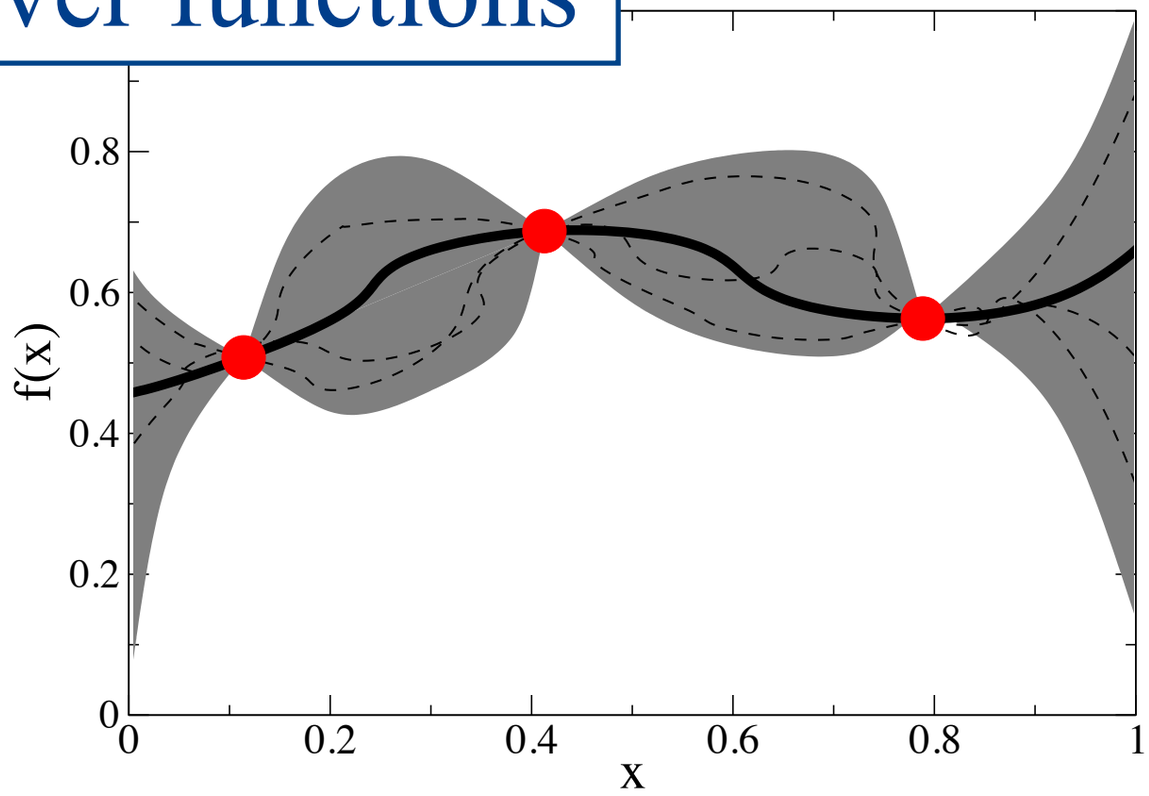
Basis functions eg x, x^2, exp(-x), etc

Gaussian processes

Interpretation 1: Average over functions



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



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

Interpretation 2: Sum of basis functions

Function to be interpolated

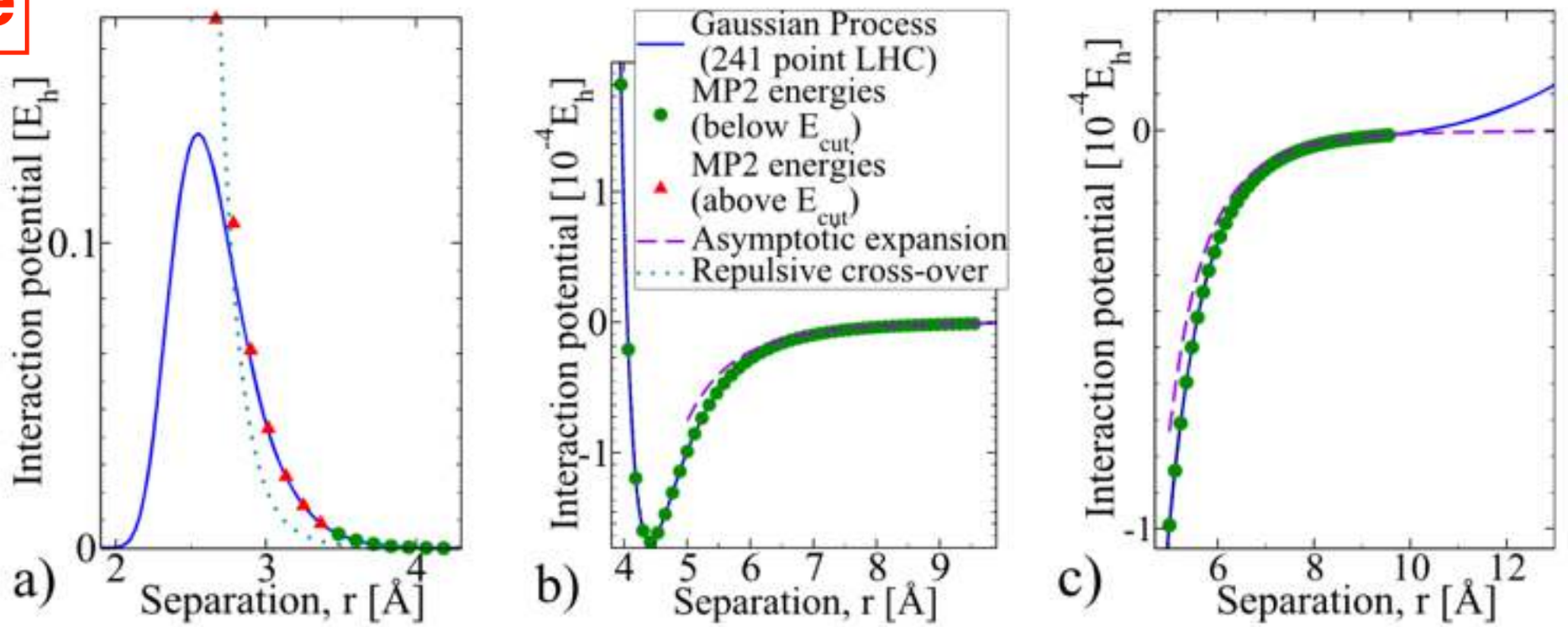
$$F(\mathbf{x}) = \sum_{i=1}^{N} \alpha_i u_i(\mathbf{x})$$

Coefficients (usually found by regression/ fitting)

Basis functions eg x, x^2, exp(-x), etc

Example force-fields

CO_2-Ne



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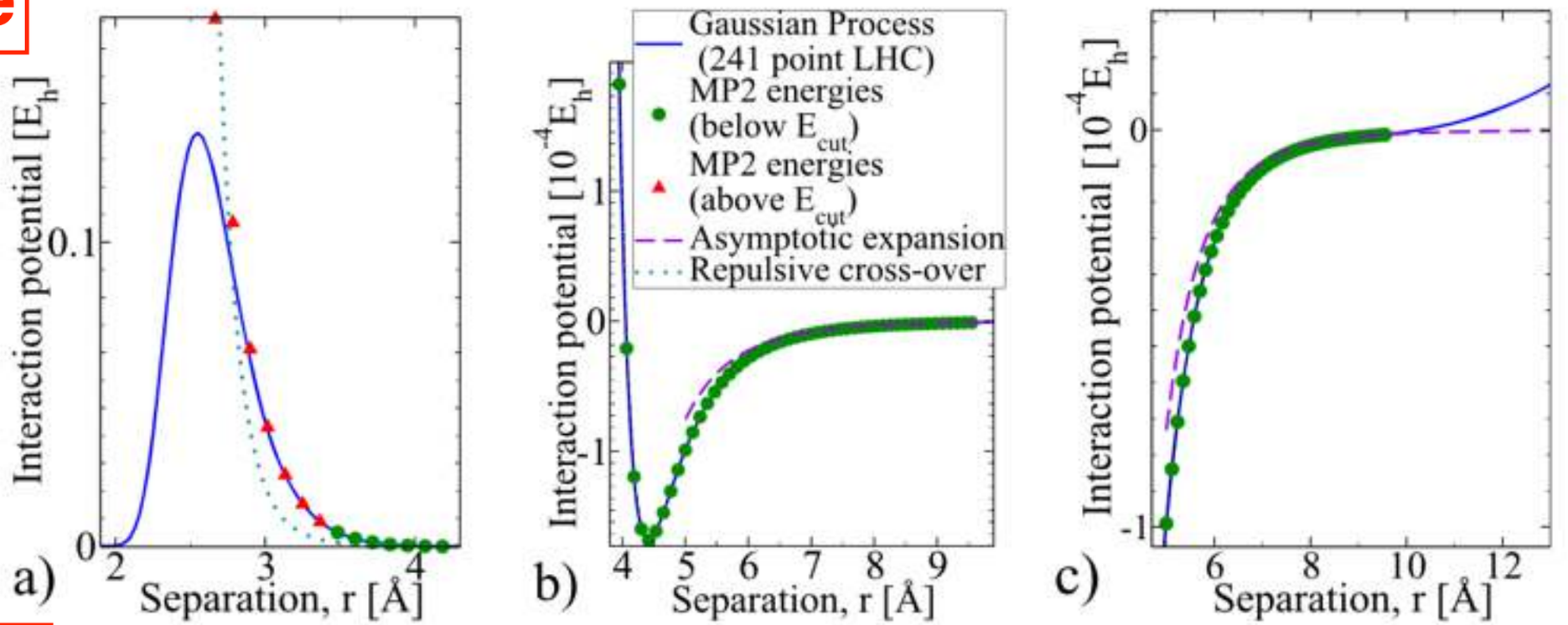
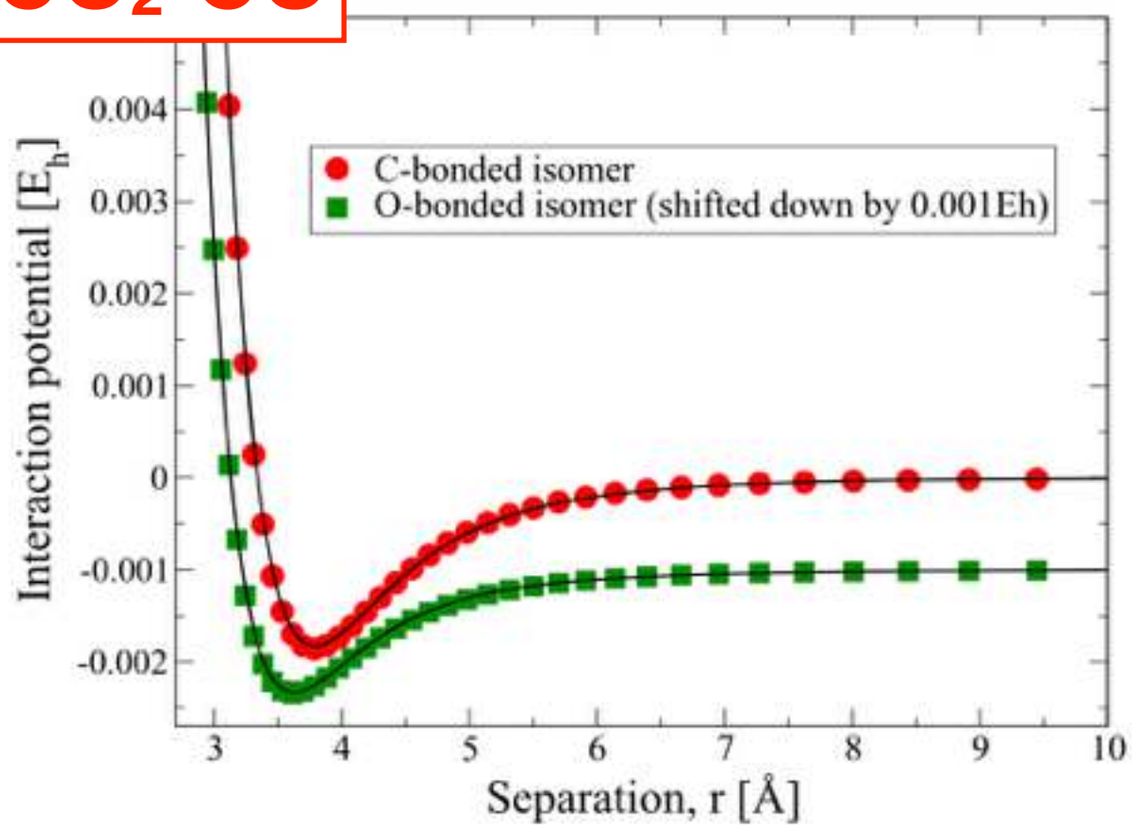


CO_2-CO



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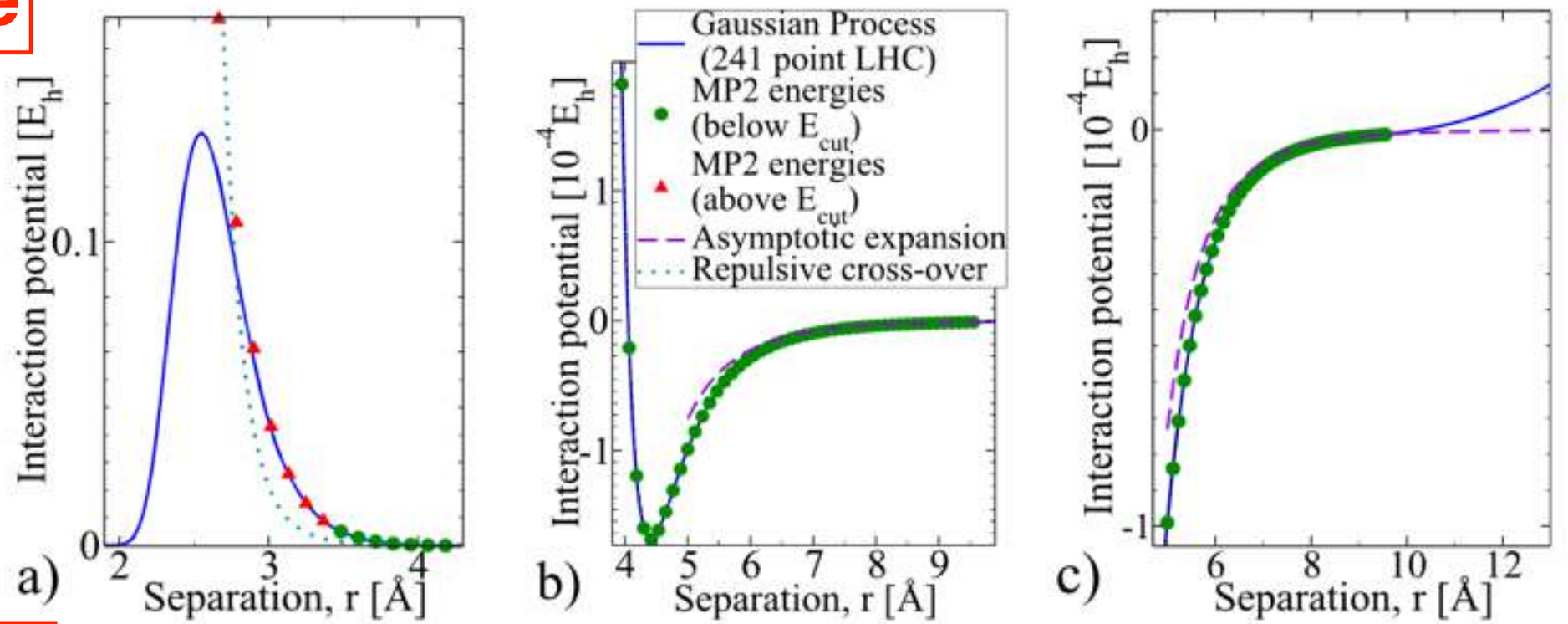

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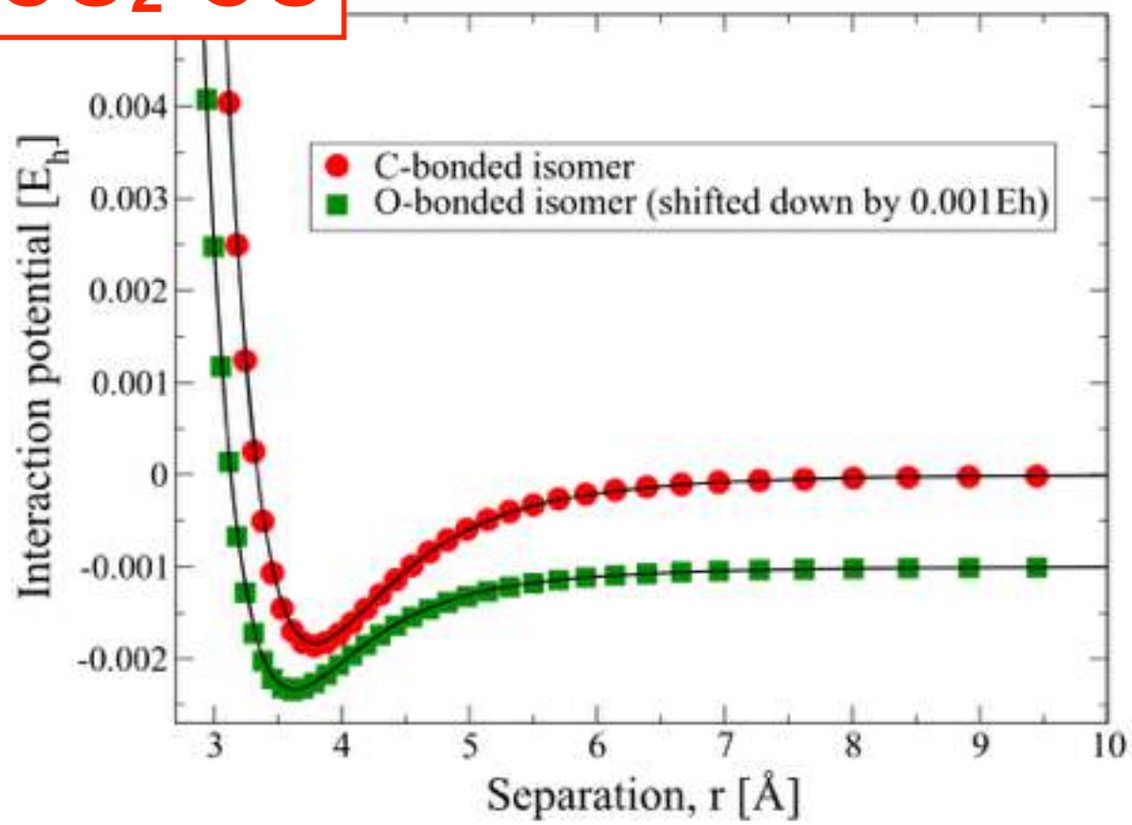
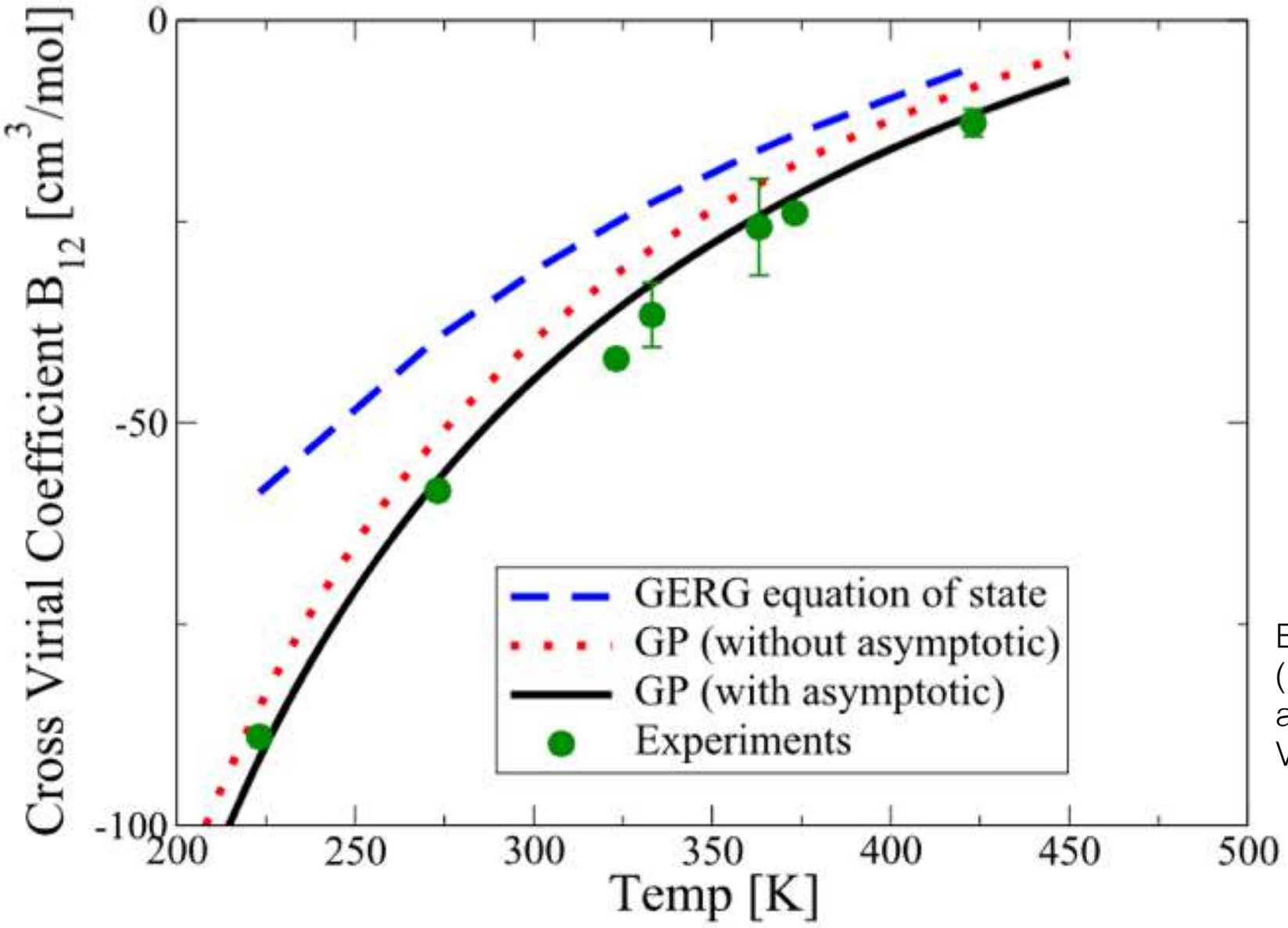


We have similar results for:

- CO2 with Ar, H_2 and N_2
- Hydrogen Fluoride (strong polar interaction) and Methane-Nitrogen (Many symmetries)

Results - first principles calculations

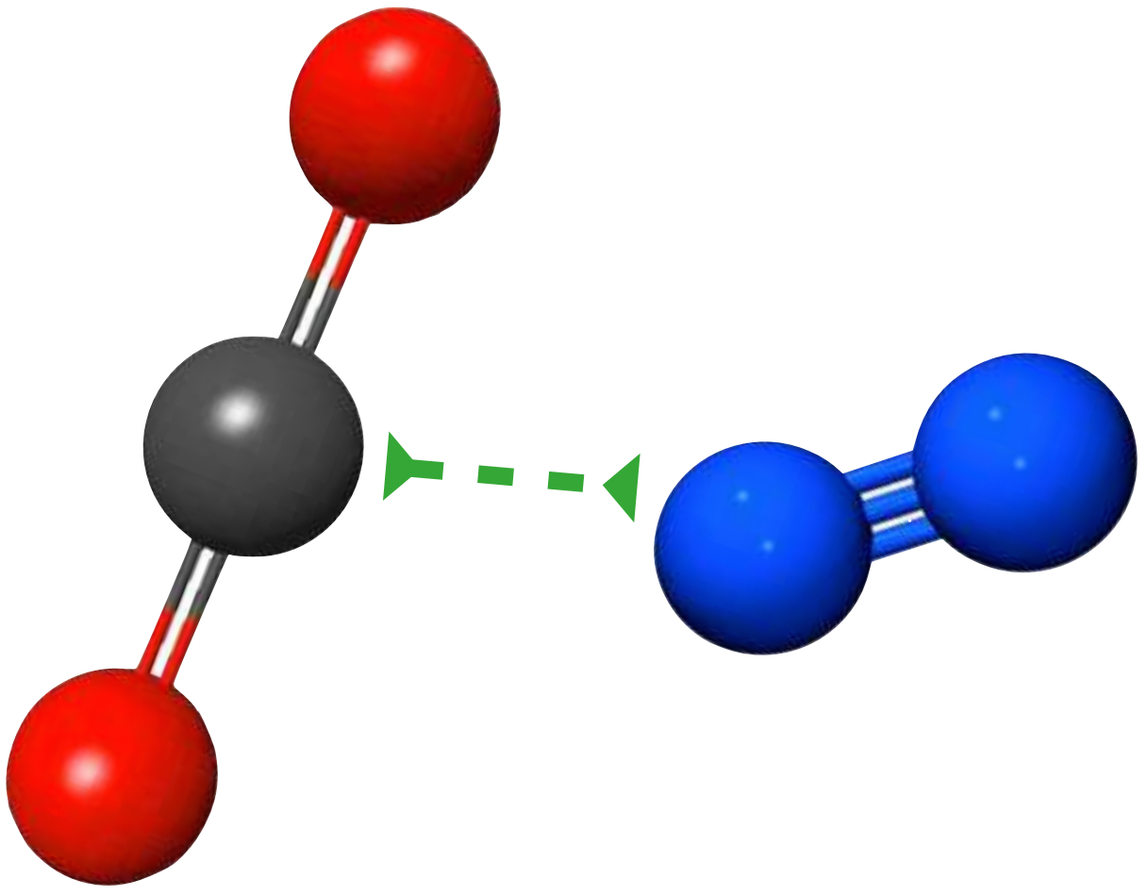


Experiments by Cottrell et al. (1956), Brewer and Vaughn (1969) and Mallu, Natarajan and Viswanath (1989).

Uteva, Graham, Wilkinson, Wheatley, J. Chem. Phys. (2017) 147, 161706.

The next steps

3 body interactions



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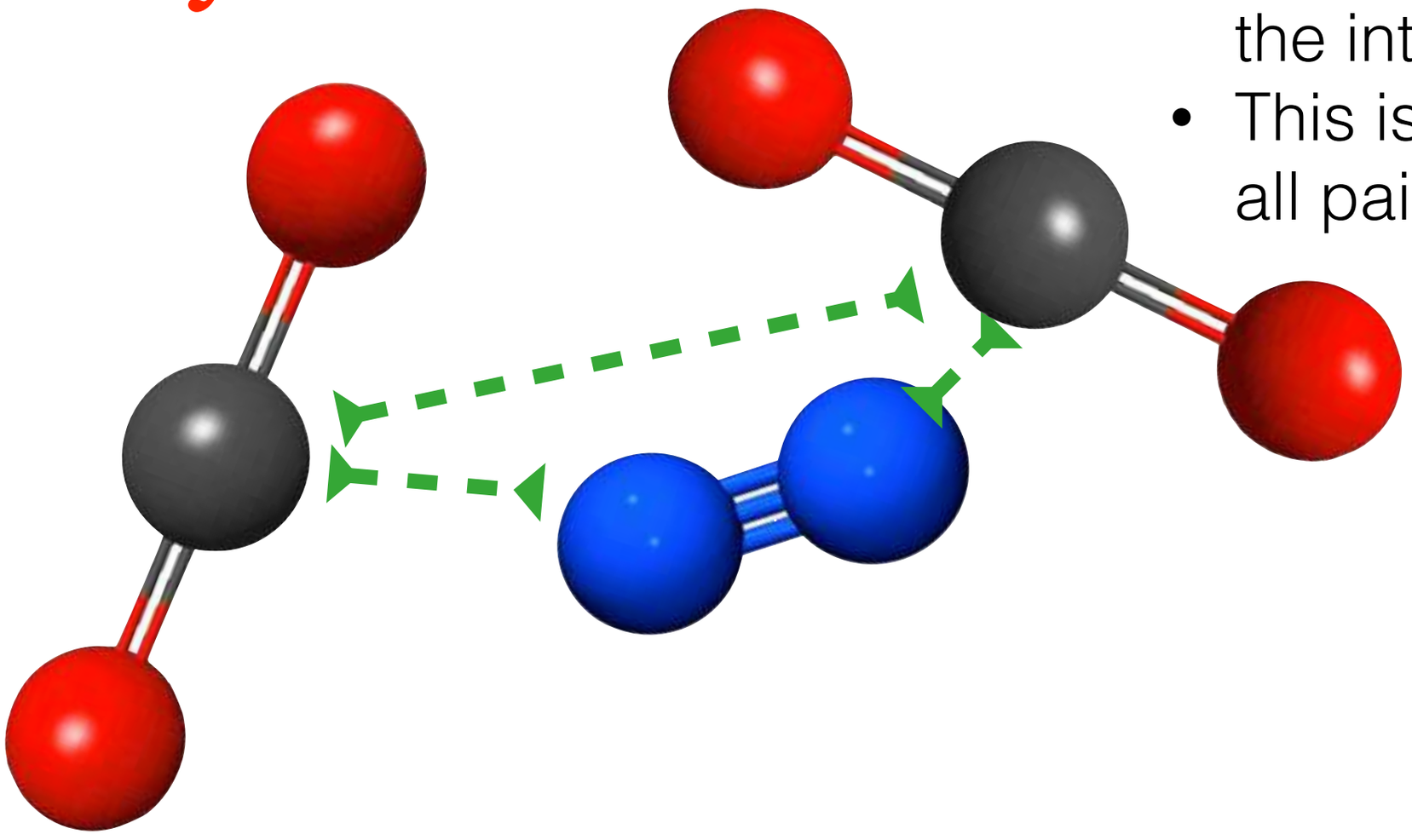

- A third molecule changes the interactions.
- This is not just the sum of all pairwise interactions.

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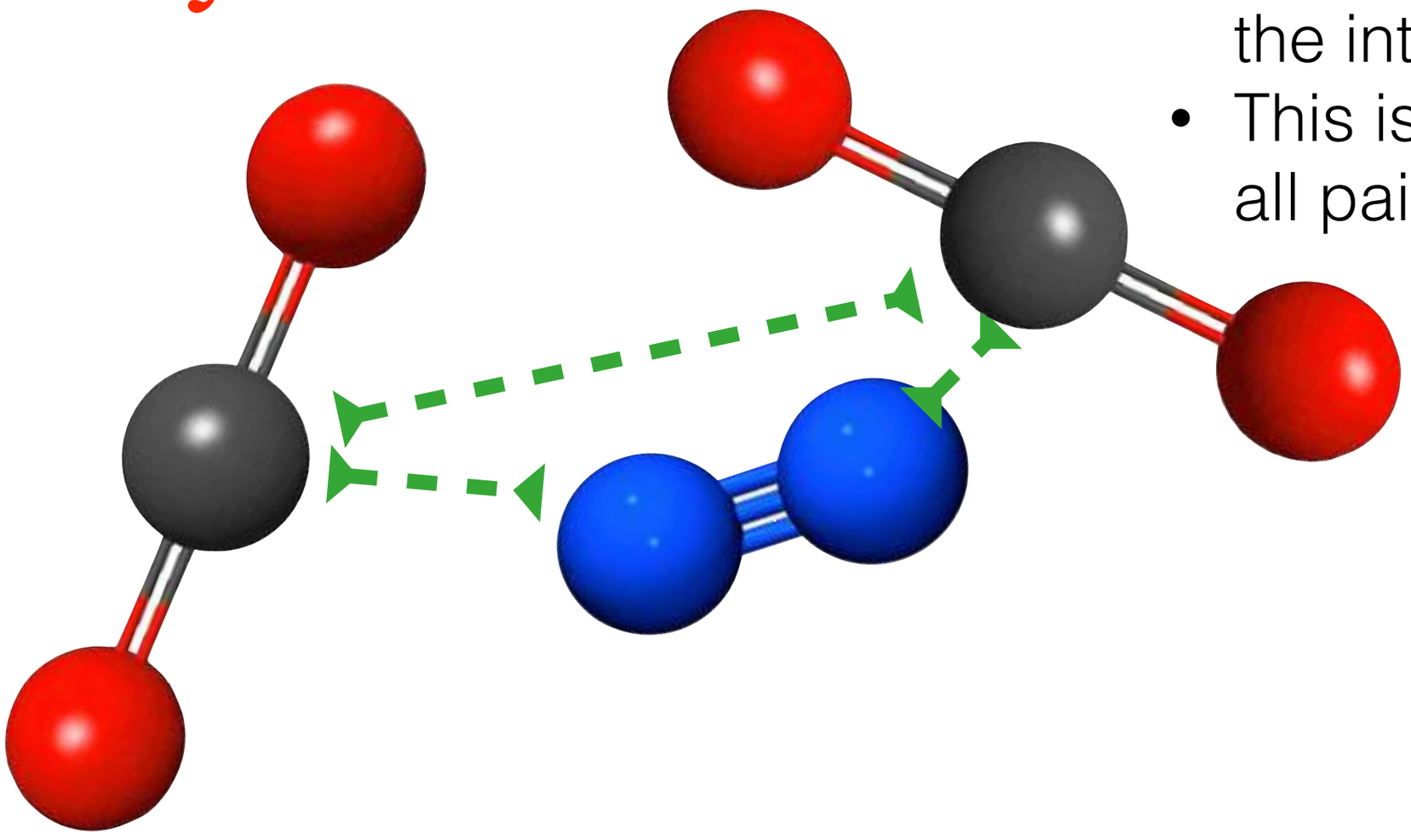
3 body interactions



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Predictions for CCS

- These non-additive interactions are important to predict dense gases and liquids.
- Our initial calculations shows that our interpolation works for non-additive interactions.

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Use first-principles calculations to fit EoS