# MOLECULAR SINULATION From Algorithms to Applications

# Introduction

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## Introduction

- Why to use a simulation
- Some examples of questions we can address

## **Molecular Simulations**

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- Molecular dynamics: solve equations of motion
- Monte Carlo: importance sampling
- Calculate thermodynamic and transport properties for a given intermolecular potential



Use: Exact= in the limit of *infinitely* long simulations the error bars can be made *infinitely* sm<sup>-1</sup>

If one could envision an experimental system of these N particles that interact with the potential.

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Pressure Heat capacity Heat of adsorption Structure

# Why Molecular Simulations

Paul Dirac, after completing his formalism of

quantum mechanics: "The rest is chemistry....".

This is a heavy burden the shoulders of "chemistry":

# Intermolecular potential

The intermolecular potential can:

- Mimic the experimental system as accurate as possible:
  - Replace experiments (dangerous, impossible to measure, expensive, ...)
- Make a model system:
  - Test theories that can not directly be tested with experiment

# If we know/guess the "true" intermolecular potential

### Example 1: Mimic the "real world" Critical properties of long chain hydrocarbons





To *predict* the thermodynamic properties (boiling points) of the hydrocarbon mixtures it is convenient (=Engineering models use them) to know the critical points of the hydrocarbons.

#### Critical points of long chain hydrocarbons



Hydrocarbons: intermolecular potential

# United-atom model Fixed bond length Bond-bending Torsion

• Non-bonded: Lennard-Jones

$$u(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right]$$





But my system is extremely small, is the statistic reliable?

#### Computational issue

- How to compute vapour-liquid equilibrium?
- How to deal with long chain

But C48 moves much slower than methane (C1). Do I have enough CPU time

#### **Critical Temperature and Density**



# Example 2: Computational Carbon Capture

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#### **Carbon Capture and Sequestration**





# Metal Organic Frameworks



Zn<sub>4</sub>O(1,4-benzenedicarboxylate)<sub>3</sub> MOF-5

- BET surface areas up to 6200 m<sup>2</sup>/g
- Density as low as 0.22 g/cm<sup>3</sup>
- Tunable pore sizes up to 5 nm
- Channels connected in 1-, 2-, or 3-D
- Internal surface can be functionalized
- BASF production on ton scale

# **Computation Challenge**

#### Chemical Flexibility of MOFs

- We can change the metal: Fe, Mg, Ca, Zn, Cu, etc
- We can change the linker
- We can change the pore topology





Out of these many many millions of structures, which one is the best for Carbon Capture?



#### Working capacity & Henry coefficient



Increasing the working capacity: temperature



#### Increasing the working capacity: pressure



We can increase the working capacity, but at which cost?

#### Performance metric: parasitic energy

Energy penalty for Carbon Capture and Sequestration: compression work and the heating energy:

- Heating energy (Q): heat necessary to regenerate a given sorbent:
  - Sensible heat: heats and cools bed. Provides driving force to produce CO<sub>2</sub>
  - Desorption heat: desorbs  $CO_2$  (equal to heat of adsorption,  $\Delta h$ ).

$$Q = \underbrace{(C_p \rho_{sorbent} \Delta T + \Delta h_{CO2} \Delta q_{CO2} + \Delta h_{N2} \Delta q_{N2})}_{\text{Sensible heat requirement}} / CO_{2 \text{Produced}}$$

- Compressor work (W<sub>comp</sub>): Work to compress CO<sub>2</sub> to 150 bar (for transport)  $W_{eq} = \left(0.75 Q \cdot \eta_{carnot} + W_{comp}\right)$
- Parasitic energy calculated by discounting the heat requirement by the Carnot efficiency to simulate the effect of taking steam from a steam cycle

#### Zeolites



- 180 Known structures
- >3.000,000hypothetical structures
- Which is the best for carbon capture?





## **Zeolites for Carbon Capture**

Equivalent Energy for those all silica structures with experimental data



What is the best structure?

What is the lowest energy?

# Zeolites (MFI)



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# All known zeolites



## What is the best zeolite structure?

#### Hypothetical zeolites

~2.7  $10^6$  unique structures were enumerated, with roughly 10% within the +30 kJ/mol Si energetic band above R-quartz in which the known zeolites lie



Deem et al. J. Phys. Chem. C 2009, 113, 21353.



#### How to predict 1 million isotherms? CPU: one isotherm 5-10 days



- Less than 20 cores
- Designed for general programming

#### GPU

trade-off between memory, # threads, and work load

- Energy calculation in parallel
- Monte Carlo in parallel for different pressures

J. Kim and B. Smit, J. Chem. Theory Comput. 8 (7), 2336 (2012) GPU: one isotherm in 1 minute

**GPU** 

DRAM

- Optimized for SIMD (same-

instruction-multiple-data) problems

- More than 500 cores

# Screening: zeolites







Screening: > 300,000 structures Identified many structures with a significantly lower parasitic energy compared to the current technology L.-C. Lin, et al, *In silico screening of carbon-capture materials* Nat Mater **II** (7), 633 (2012)

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## Example 3: make a mode'

?

Your theory is WRONG it disagrees with the experiments

> Attrac forces ar liquid equin.

My theory is **RIGHT**: tive int but this experimentalist refuses to use molecules that do not have any attractive interactions

- Theories predict the
- **BUT**:
  - There no molecules with only attractive interactions

How to test the theory?

#### But we can simulate hard spheres ..

- Bernie Alder carried out Molecular Dynamics simulations of the freezing of hard spheres
- But, .... did the scientific community accept this computer results as experimental evidence ...
  - ... during a Gordon conference it was proposed to vote on it
  - ... and it was voted against the results of Alder



#### Experiments are now possible

... But not on molecules

but on colloids:



From the following article:

A colloidal model system with an interaction tunable from hard sphere to soft and dipolar Anand Yethiraj and Alfons van Blaaderen Nature 421, 513-517 (30 January 2003)



- Compute the forces on the particles
- Solve the equations of motion
- Sample after some timesteps

## Monte Carlo

What is the correct probability? Statistical Thermodynamics

 Generate a set of configurations with the correct probability

How to compute these

properties from a simulation?

 Compute the thermodynamic and transport properties as averages over all configurations



**Classical and Statistical Thermodynamics** 

Problem: we have a set of coordinates and velocities -what to do with it?

- Statistical Thermodynamics
  - The probability to find a particular configuration
  - Properties are expressed in term of averages
  - Free energies
- Thermodynamics: relation of the free energies to thermodynamic properties