Molecular Simulation

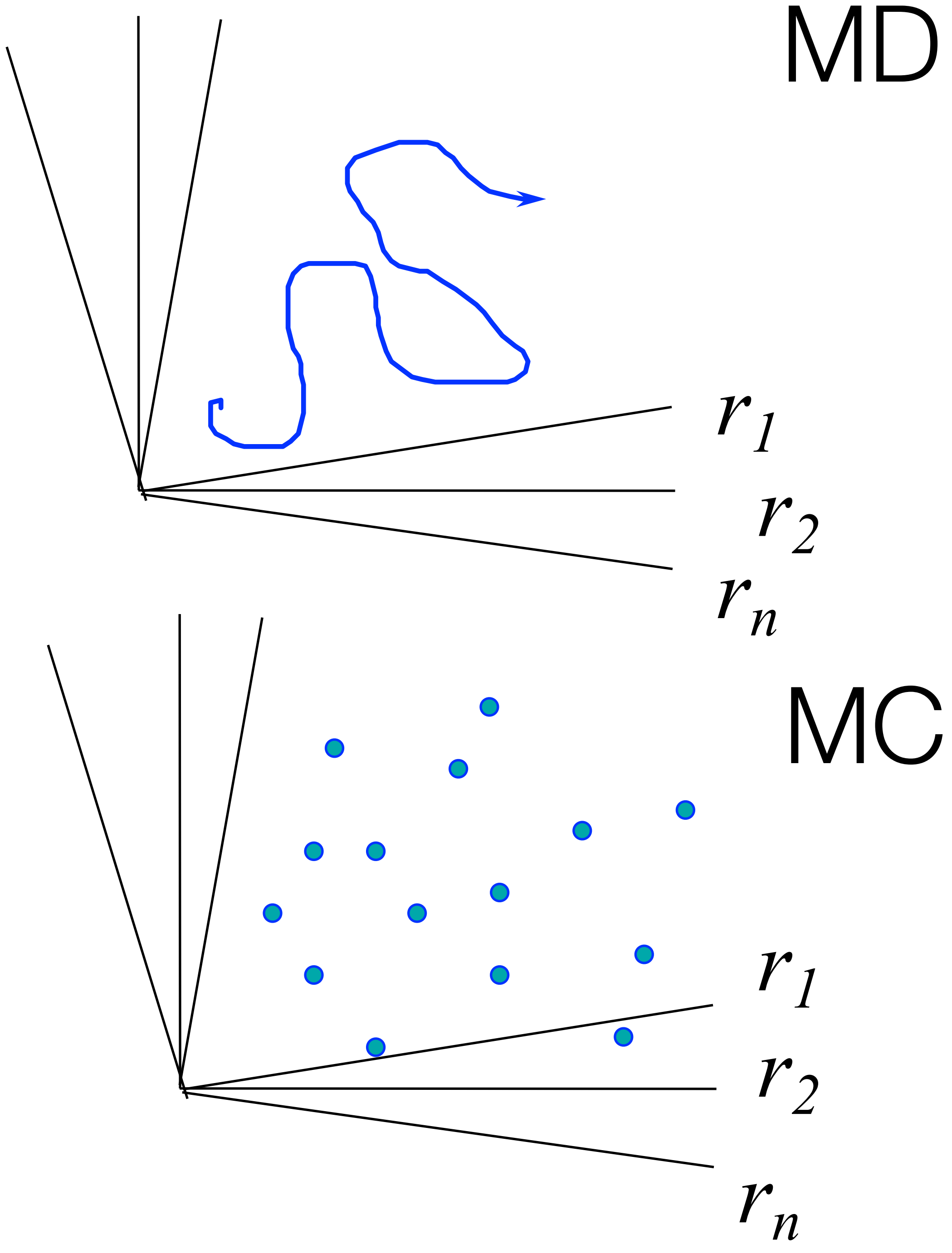
Introduction

Introduction

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

Molecular Simulations

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



Uses of Molecular Simulations

We assume the interactions between the particles are known!

Exact= in the limit of infinitely long simulations the error bars can be made infinitely small

The idea for a given ***intermolecular potential*** “***exactly***” compute the ***thermodynamic*** and ***transport*** properties of the ***system***

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

Pressure
Heat capacity
Heat of adsorption
Structure
....

Diffusion coefficient
Viscosity
…

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”:

The “*rest*”:

amounts to the ***quantitative description*** of the world around us and the prediction of all every-day phenomena ranging from the chemical reactions of small molecules to the integrated description of living organisms.

Intermolecular potential

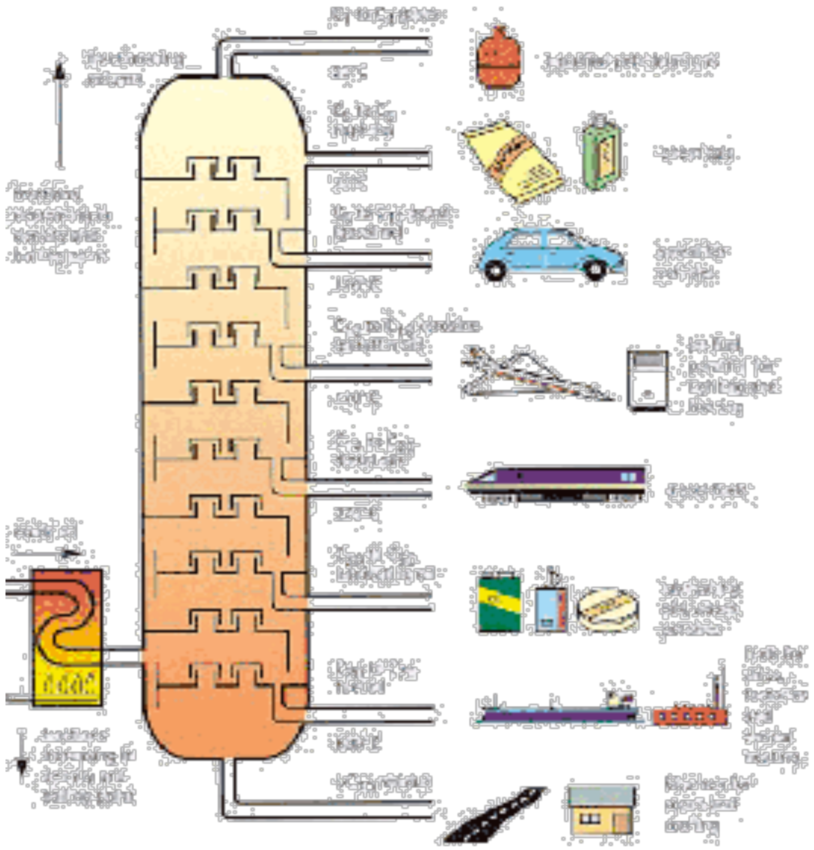
The intermolecular potential can:

- 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

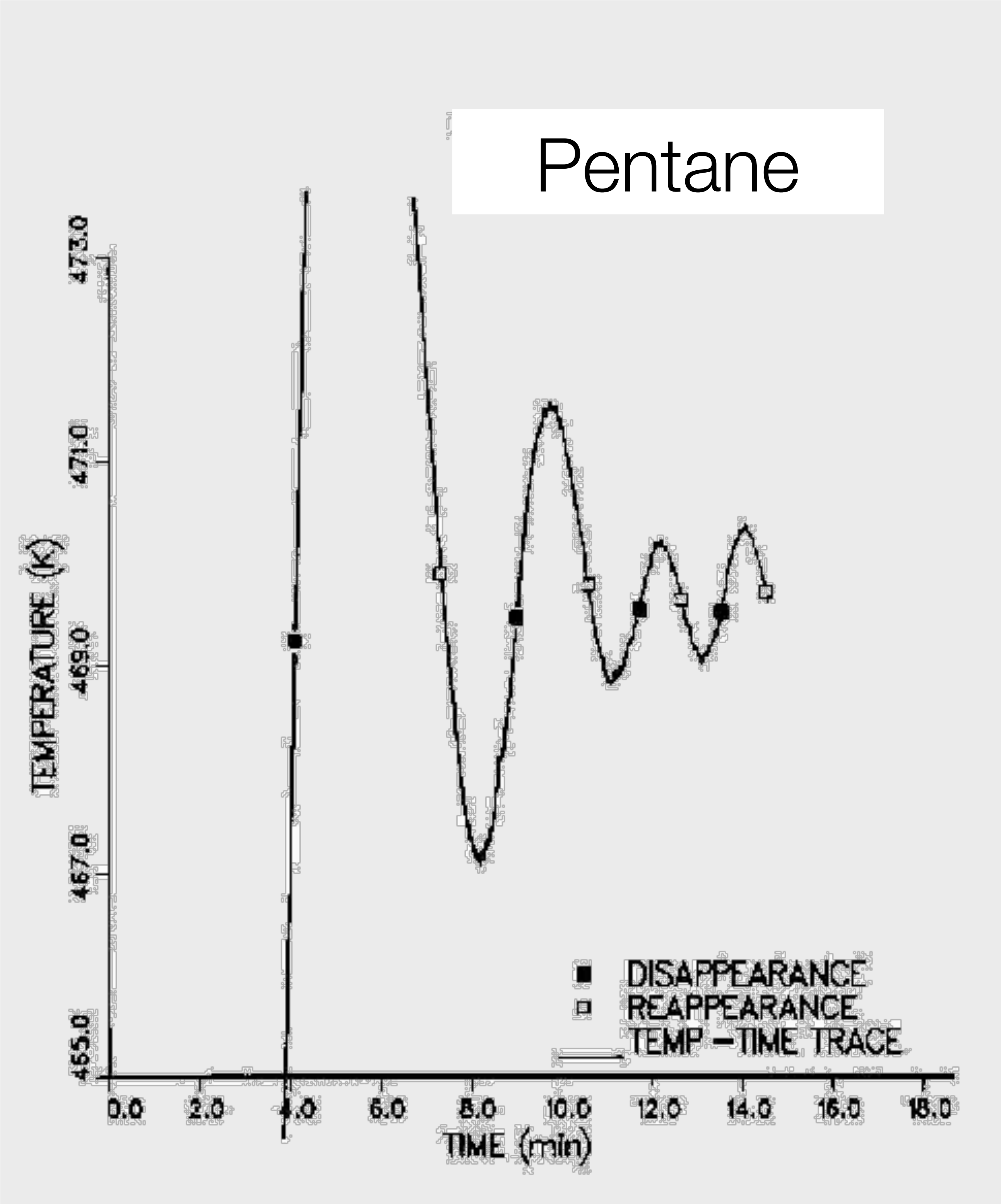
Example 1: Mimic the “real world”

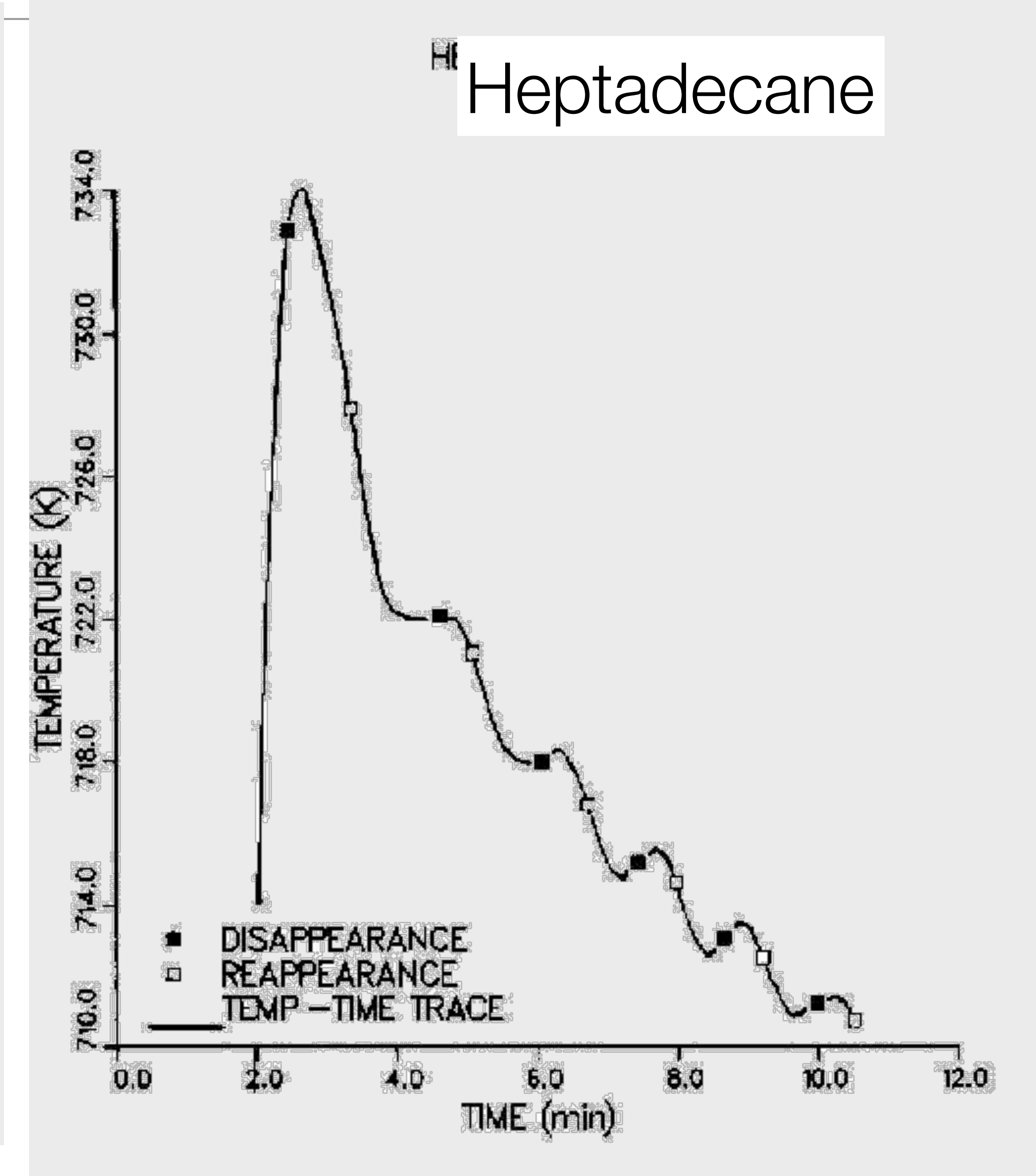
Critical properties of long chain hydrocarbons



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


Pentane

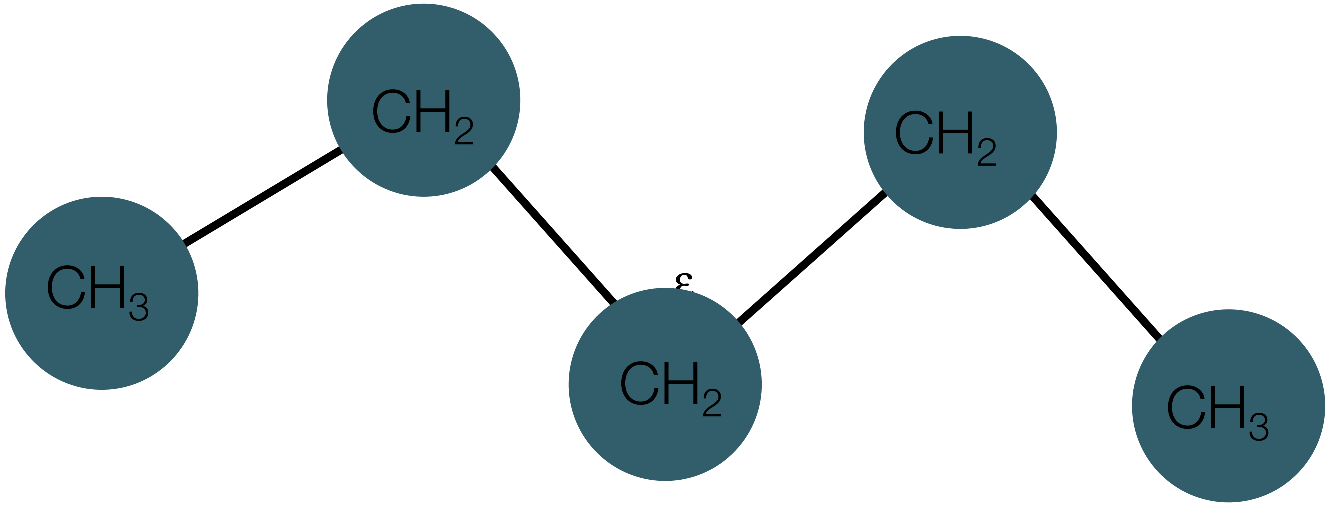

Heptadecane

Understanding Molecular Simulation

Hydrocarbons: intermolecular potential

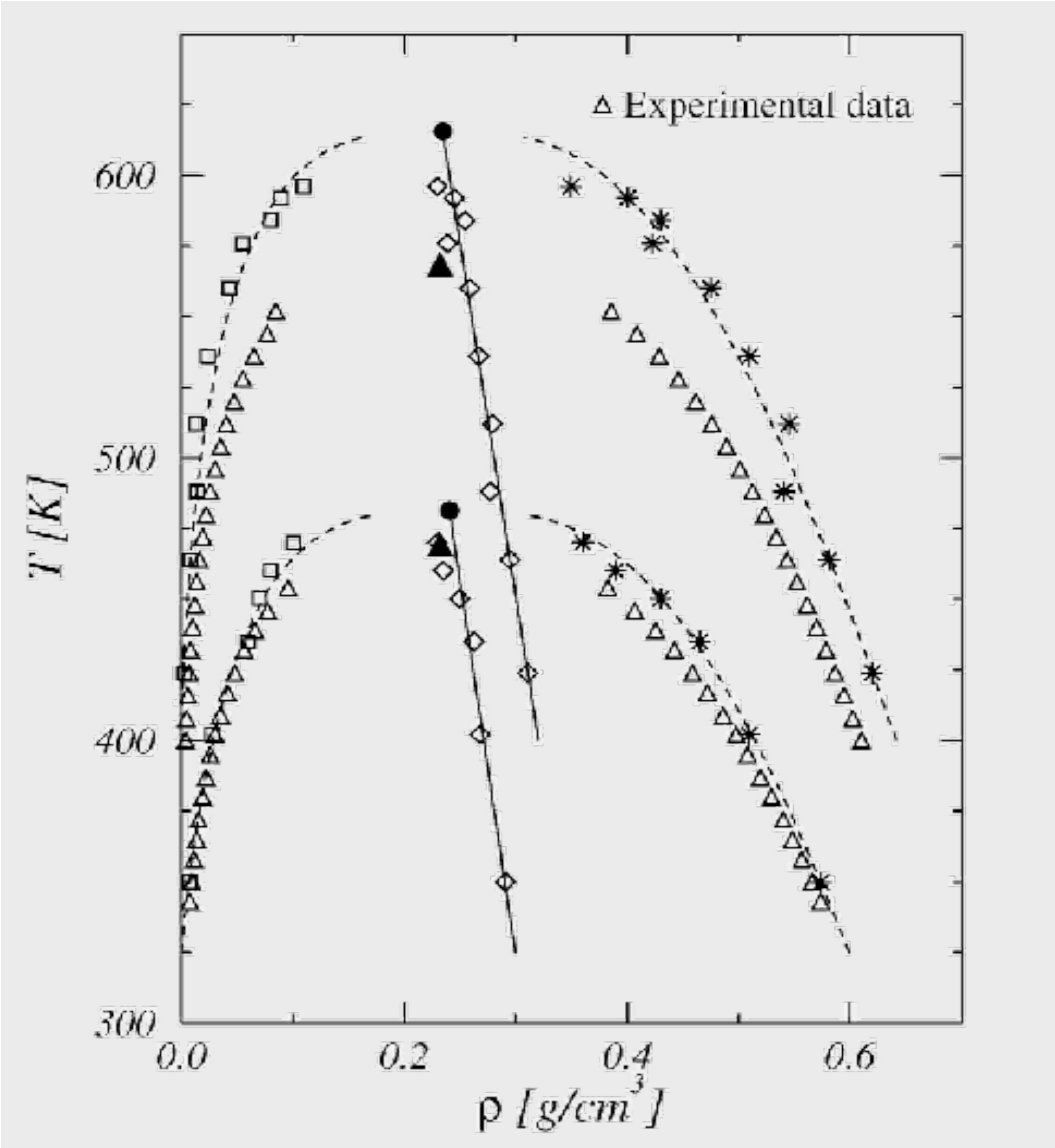
United-atom model

- Fixed bond length
- Bond-bending
- Torsion
- Non-bonded: Lennard-Jones

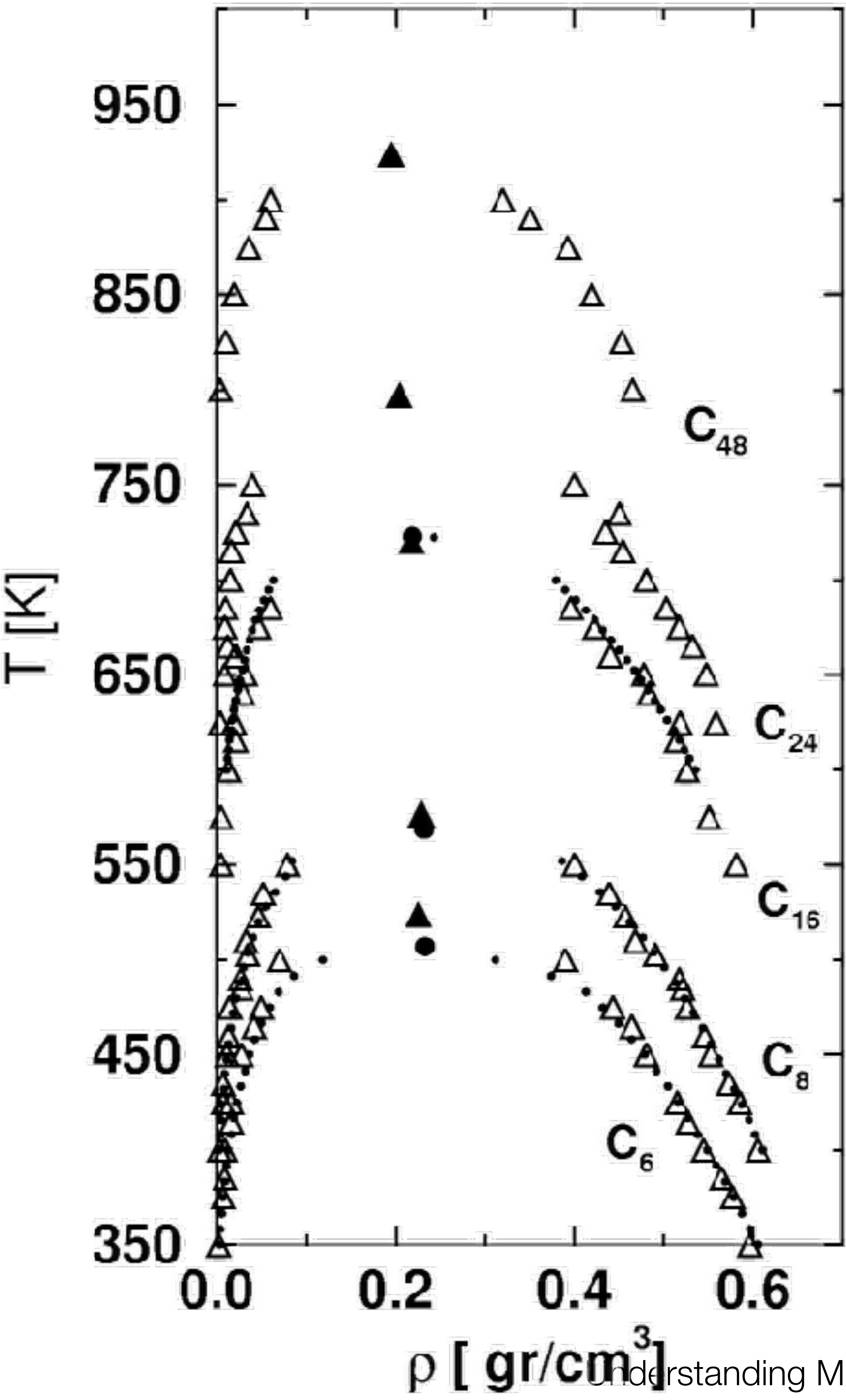


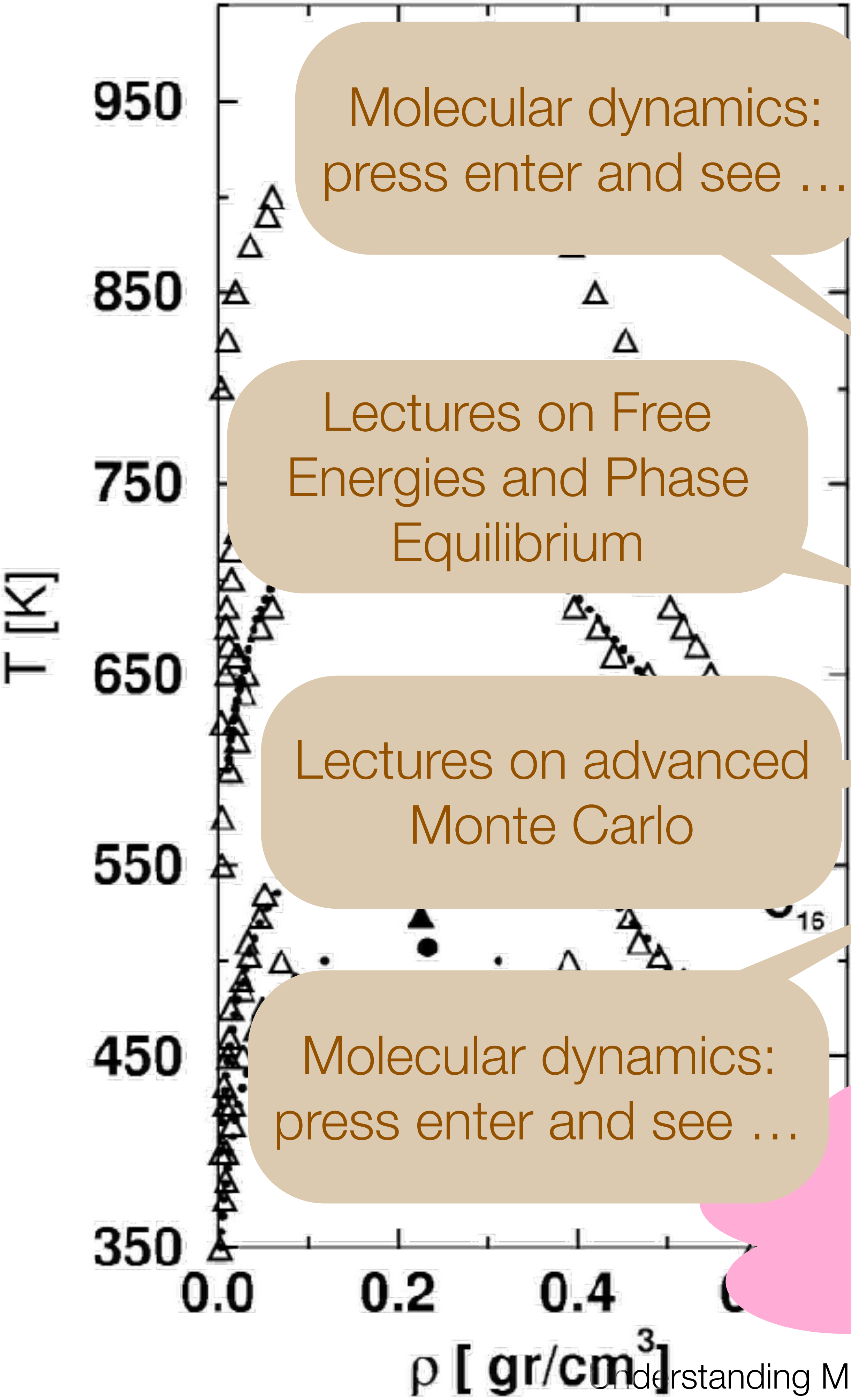
$$u(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]$$

OPLS (Jorgensen) Model



Understanding Molecular Simulation


950
850
750
650
550
450
350
T [K]
0.0
0.2
0.4
0.6
ρ [gr/cm^3]
C_{48}
C_{24}
C_{16}
C_8
C_6



Molecular dynamics: press enter and see …

Lectures on Free Energies and Phase Equilibrium

Lectures on advanced Monte Carlo

Molecular dynamics: press enter and see …

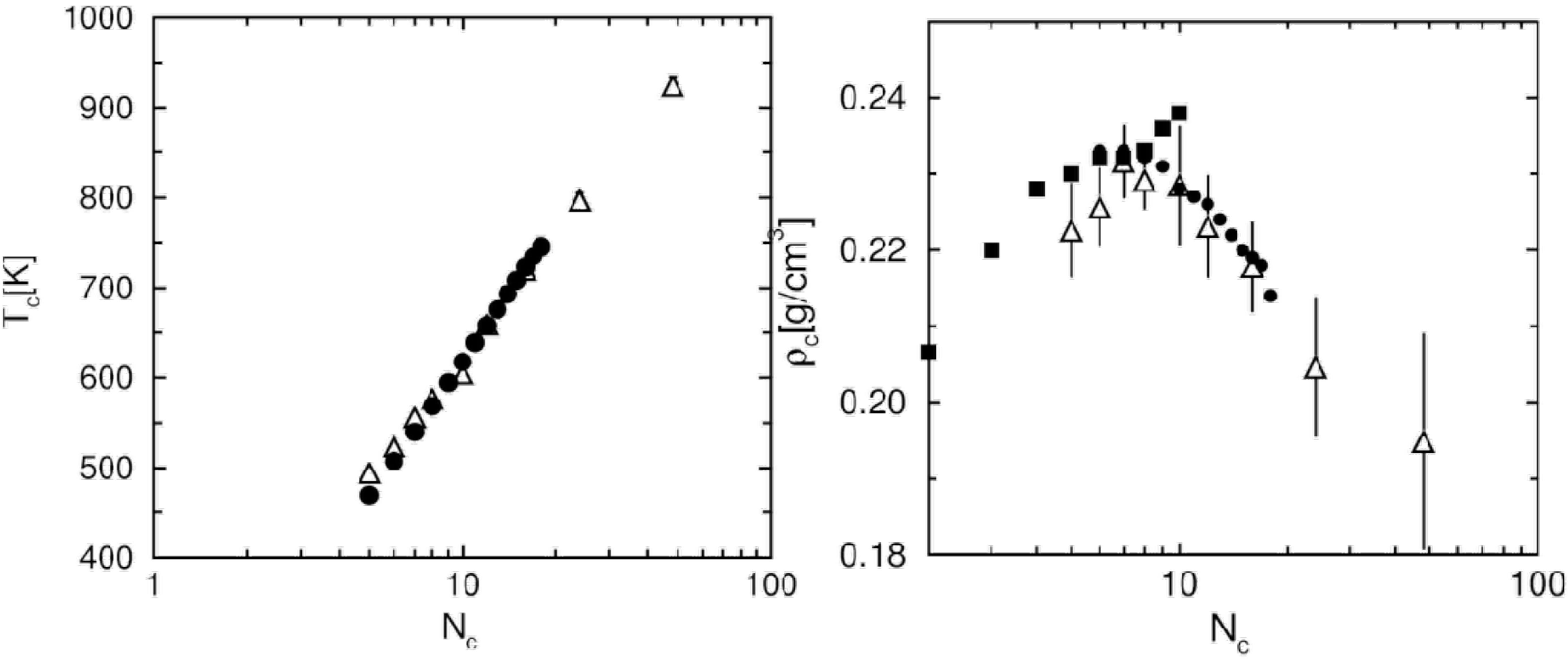
But my system is extremely small, is the statistic reliable?

Computational issues:

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

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

Critical Temperature and Density



Nature **365**, 330 (1993).

Methane storage

Methane cars: the technological obstacle

CH_4

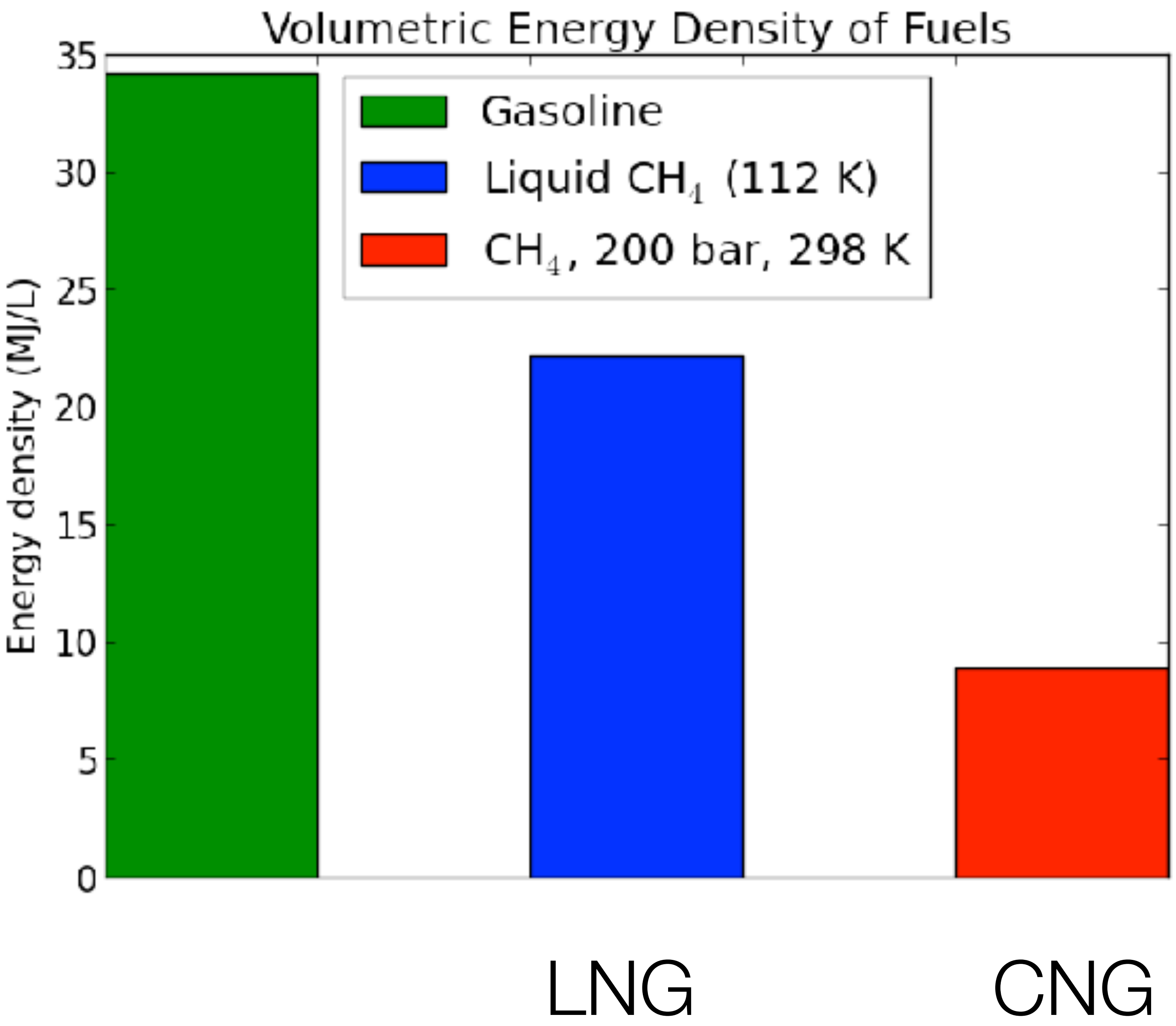
1 liter

0.036 MJ

Gasoline, 1 liter

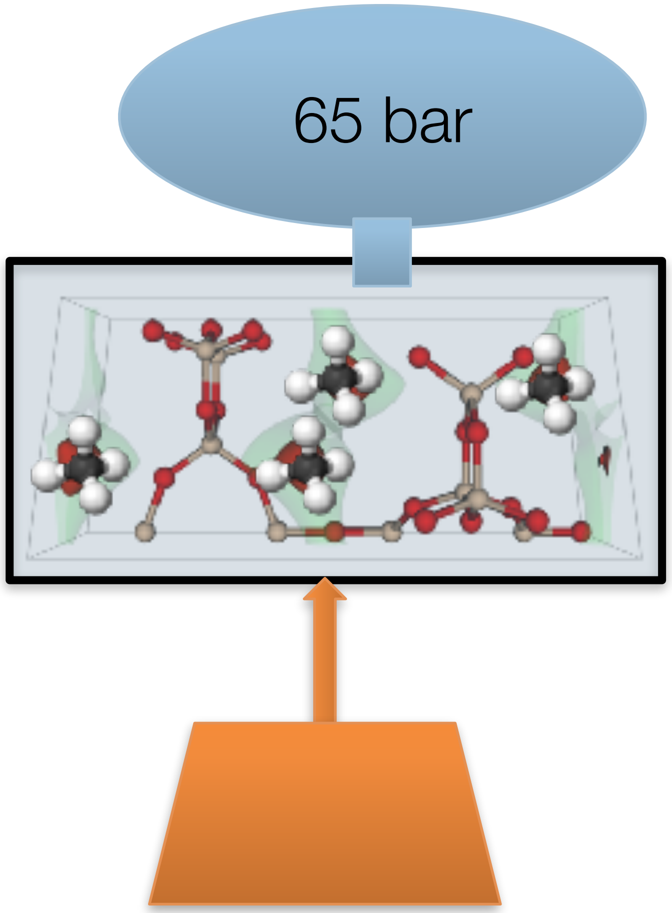
34.2 MJ

Methane versus gasoline

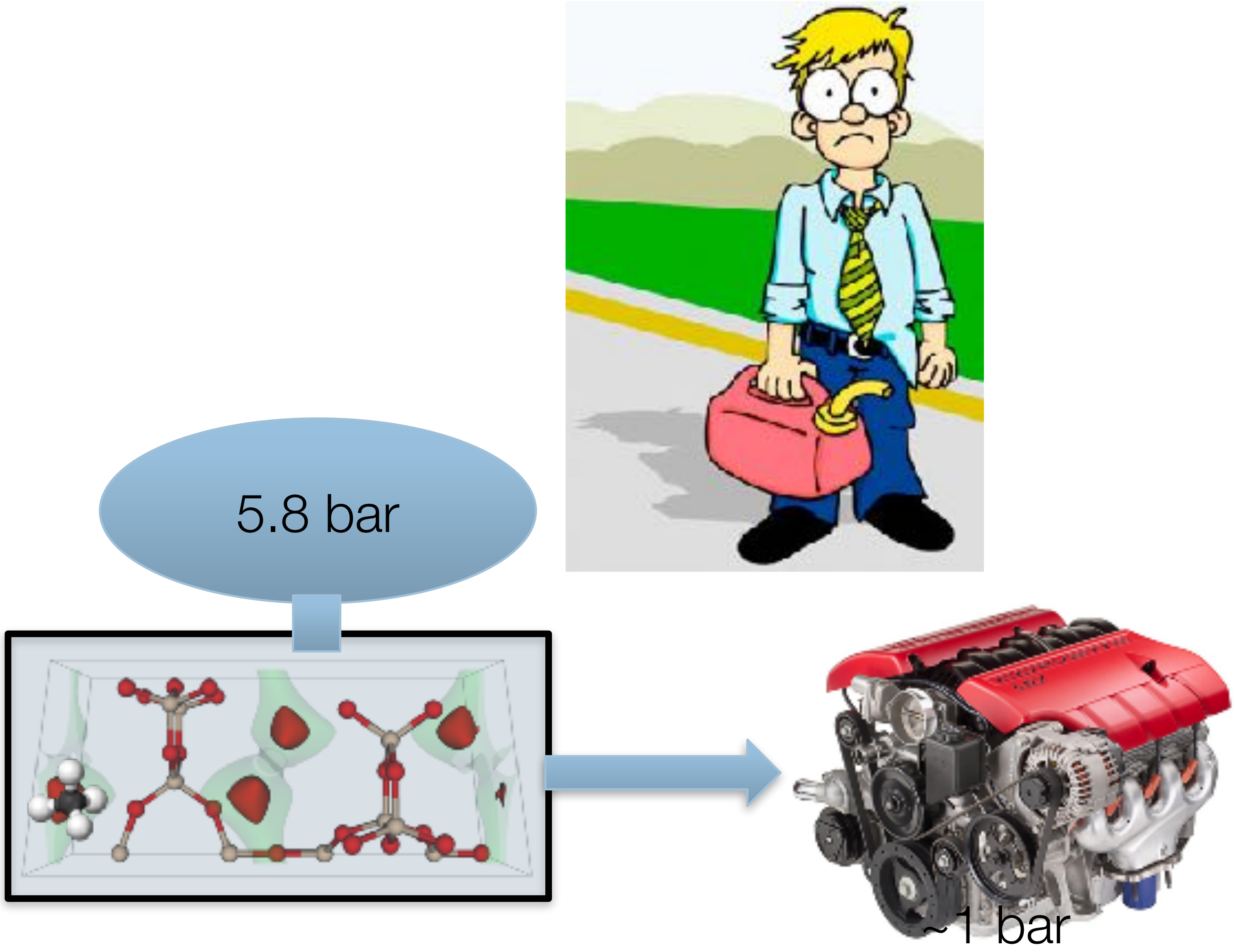


Makal *et al*. *Chem. Soc. Rev.* **2012** 41.23, 7761-7779.

Pressure swing adsorption



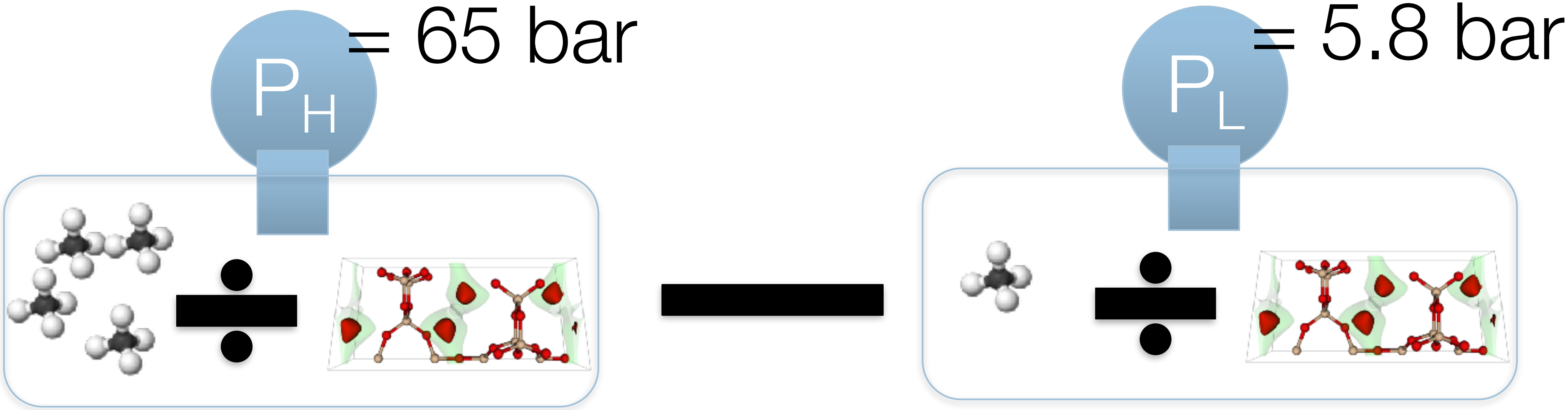
$P_H = 65$ bar



Insufficient flow

$P_L = 5.8$ bar

The deliverable capacity



$P_H = 65$ bar

Methane adsorbed
(v STP/v)
at tank charging
pressure

−

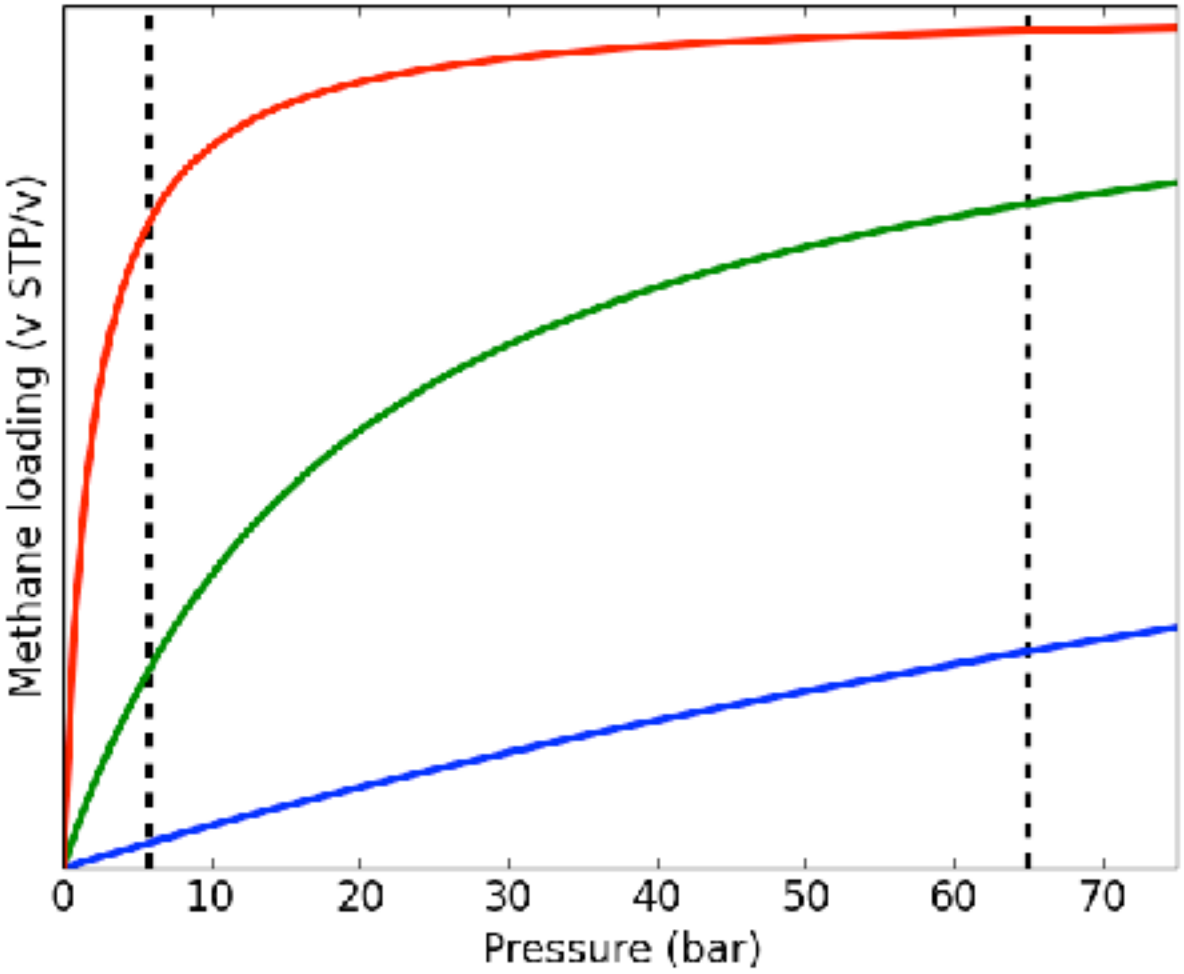
$P_L = 5.8$ bar

Methane adsorbed
(v STP/v)
at tank discharge
pressure

ARPA-E (DOE) target: 315 m^3 STP methane/m^3 adsorbent

An optimal heat of adsorption?

Goal: maximize deliverable capacity



"For methane, an optimal enthalpy change of [16.2] kJ/mol is found."

[redacted]

Langmuir 2006, 22, 1688−1700

Optimum Conditions for Adsorptive Storage

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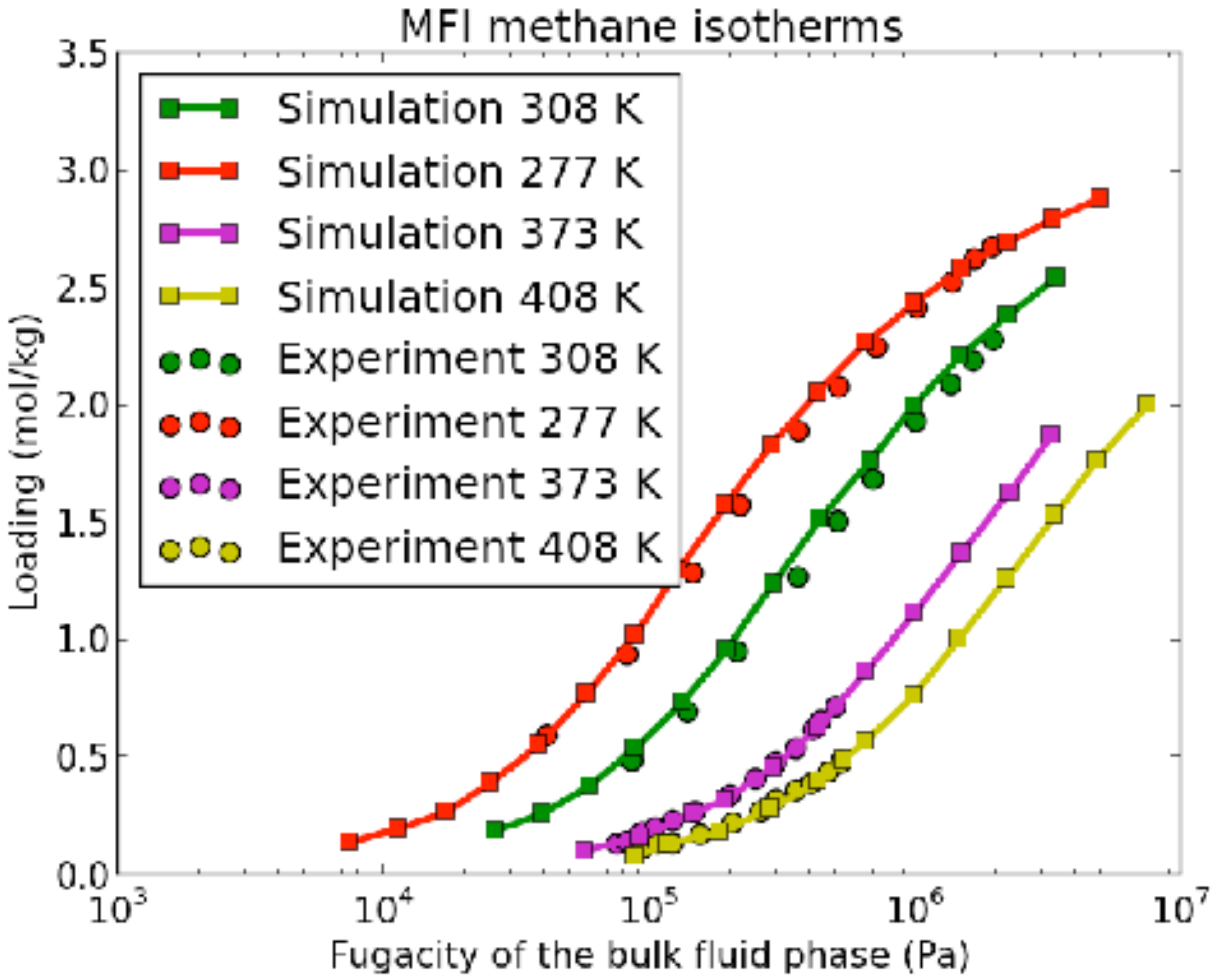
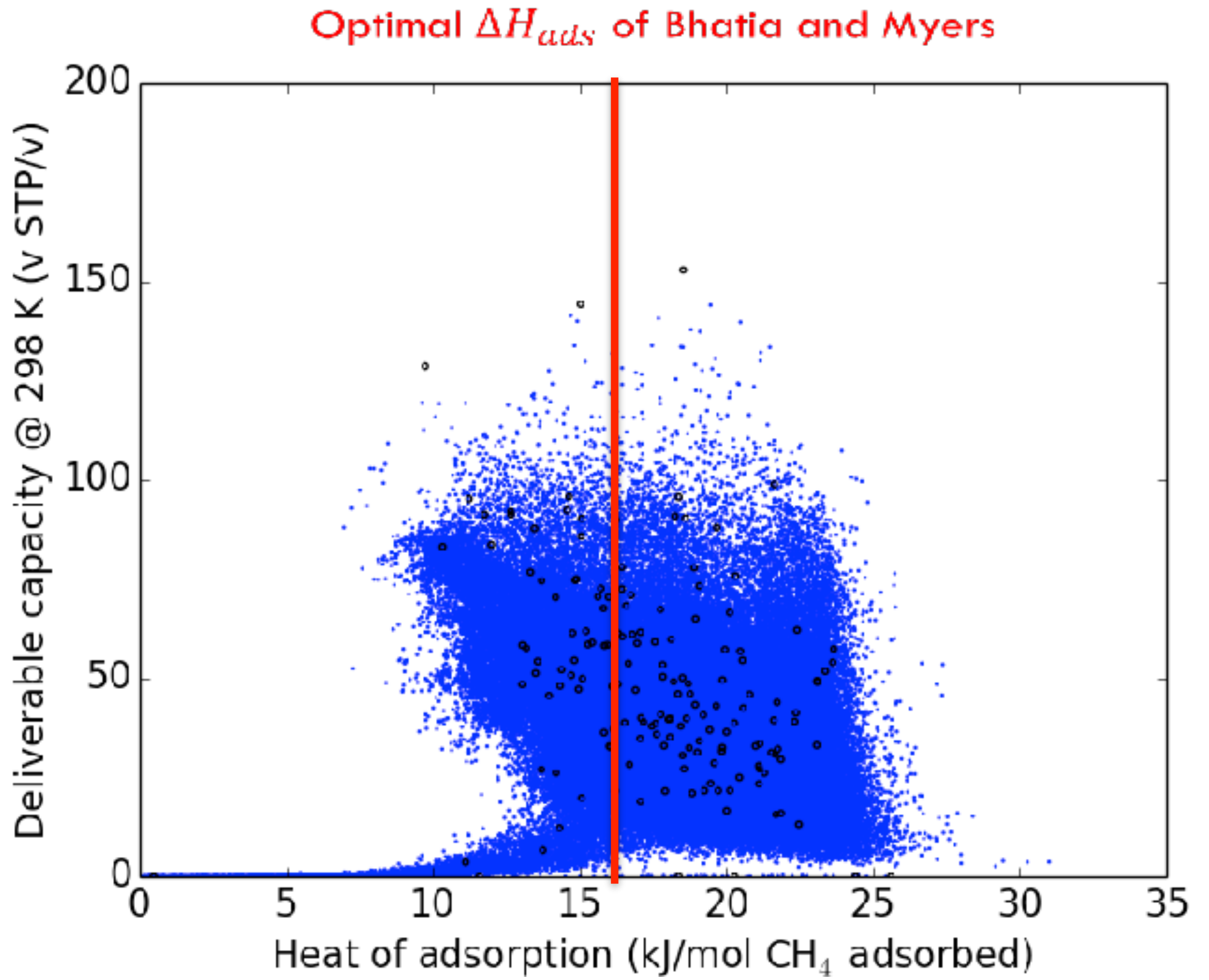
In silico screening of zeolites



MFI expt'l data: Sun *et al*. (1998) *J. Phys. Chem. B.* 102(8), 1466-1473.
Zhu *et al.* (2000) *Phys. Chem. Chem. Phys.* 2(9), 1989-1995.
Force field: Dubbeldam *et al*. (2004) *Phys. Rev.* 93(8), 088302.

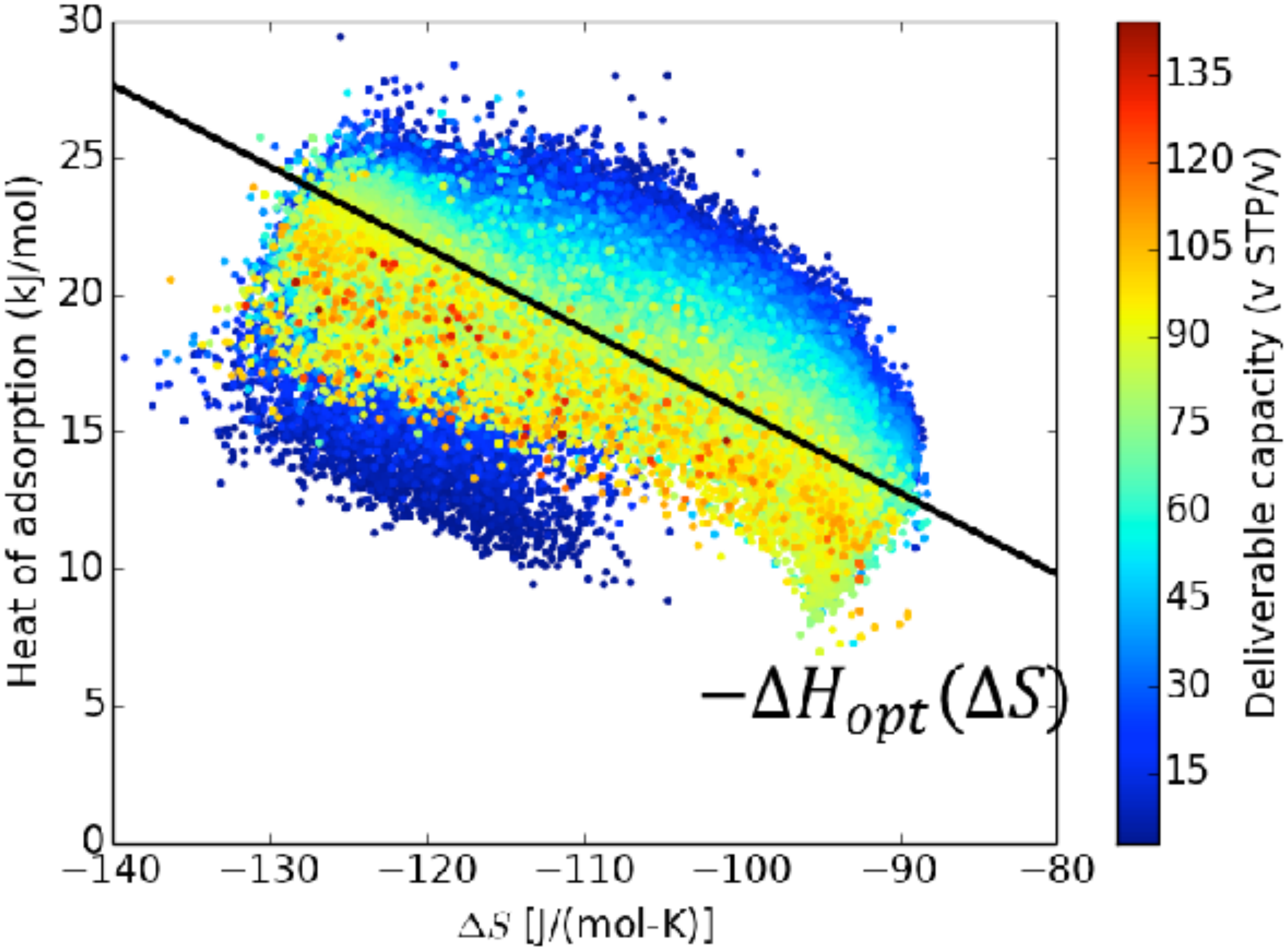
In silico screening of zeolites



C. Simon *et al*. (2014) *Phys. Chem. Chem. Phys*. 16 (12), 5499-5513

Enthalpy vs. entropy

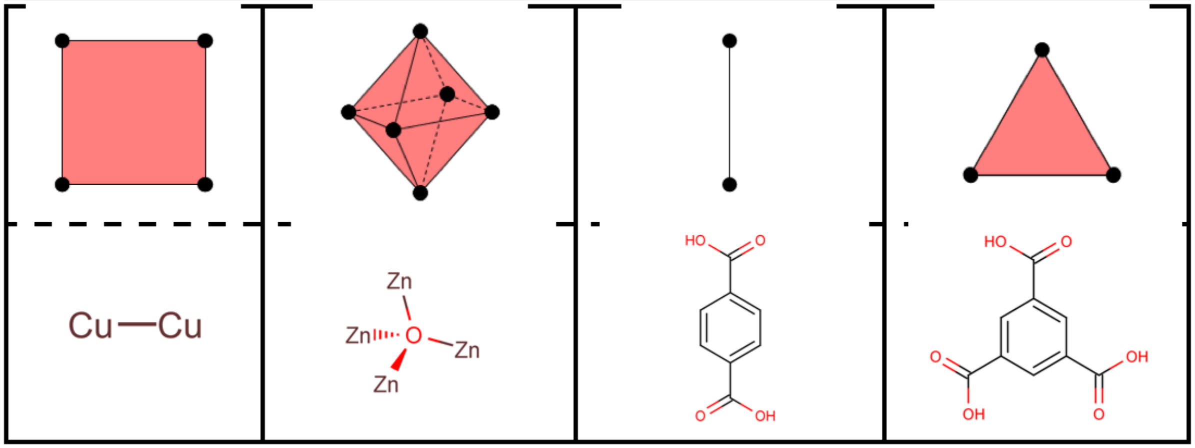
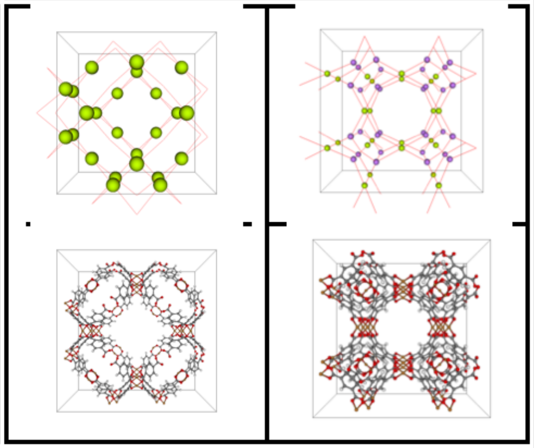
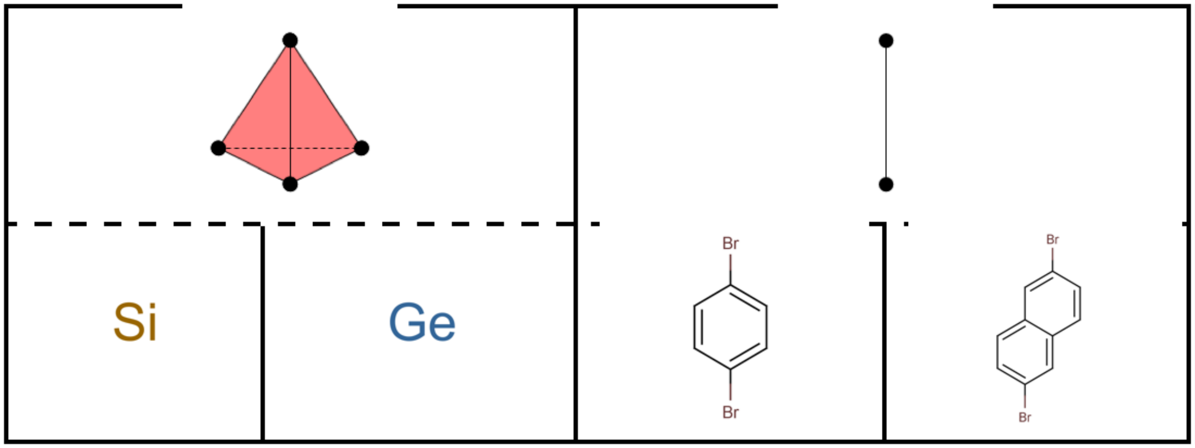
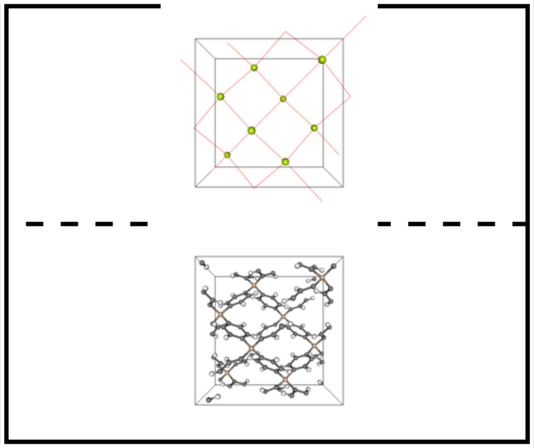
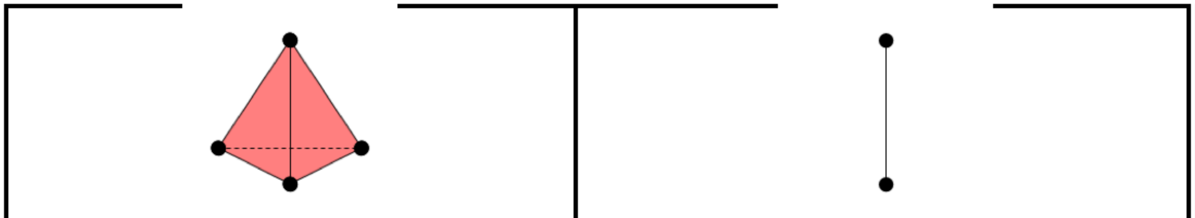
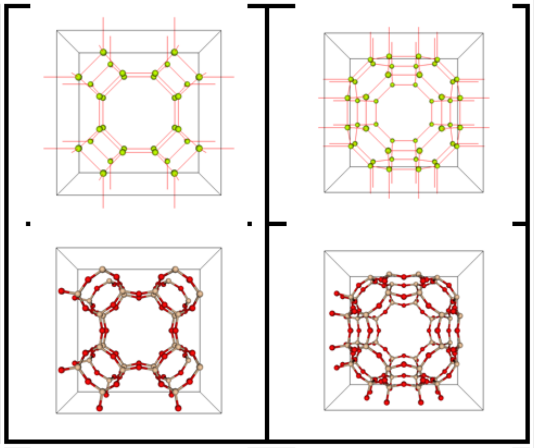
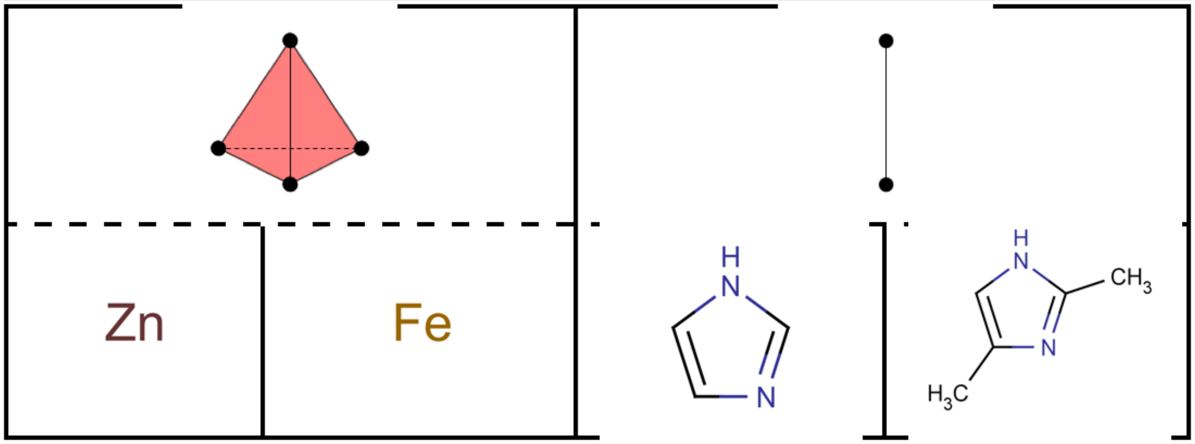
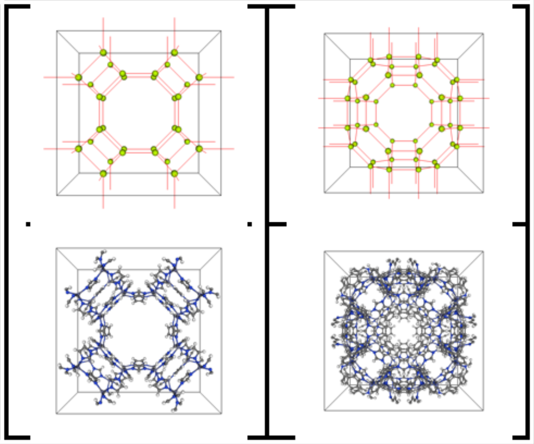
- ΔS not the same for all materials
- Wide range of ΔH that yields optimal material



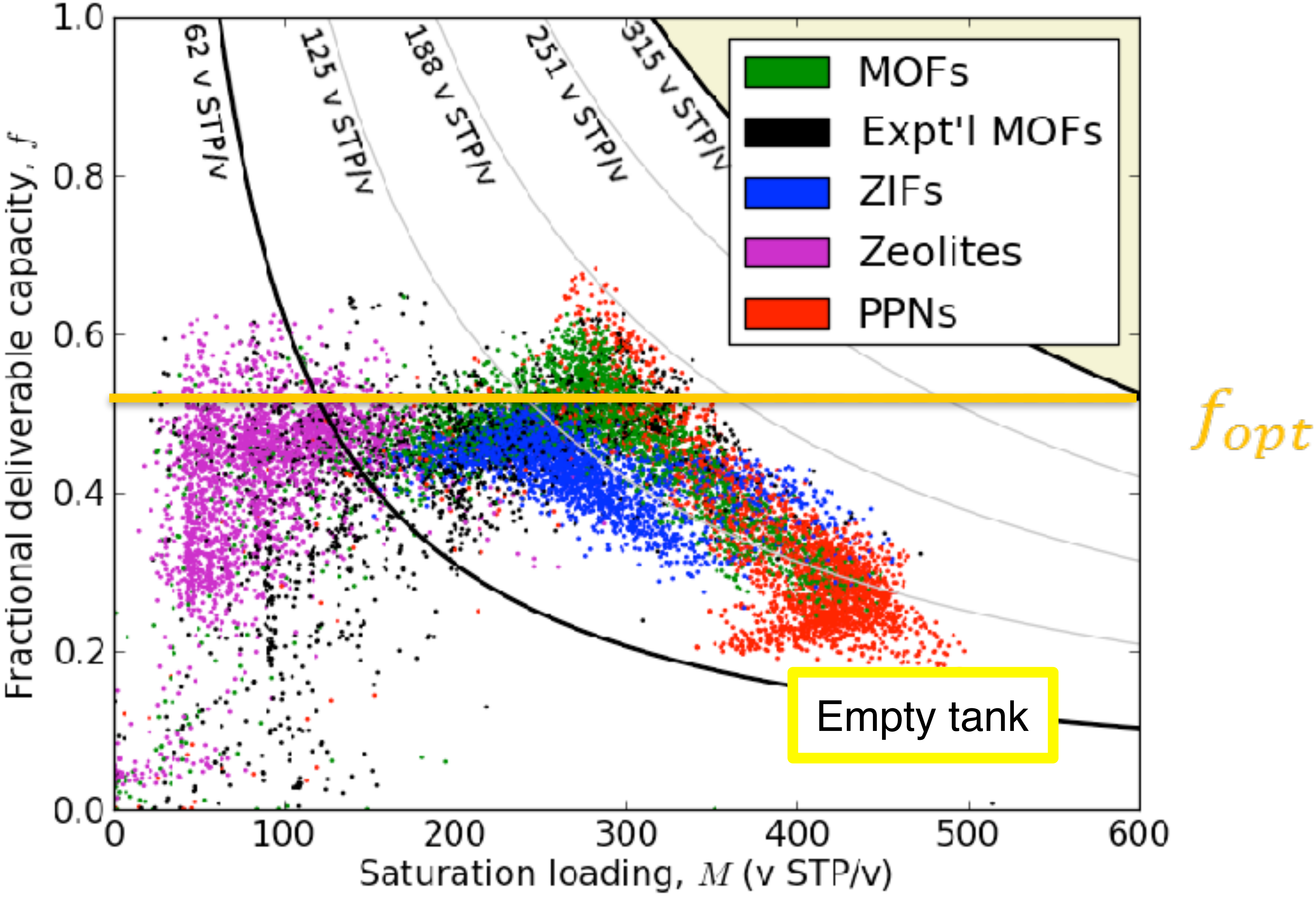
Can we find a material that meets the DOE target?

Screening > 100,000 materials

- zeolites
- Metal organic Frameworks, MOFs (Snurr and co-workers)
- zeolitic imidazolate frameworks, ZIFs, (Haranczyk)
- Polymer Porous Networks, PPNs (Haranczyk)

Material class	Building blocks	Topologies
MOFs	 Cu—Cu	
PPNs	 Si Ge	
Zeolites	 Si O	
ZIFs	 Zn Fe	

Insight from the model



Example 3: make a model syst

Question: are attractive interacti
phase?

YES:

- Attractive forces are needed
- Theories predict this ..

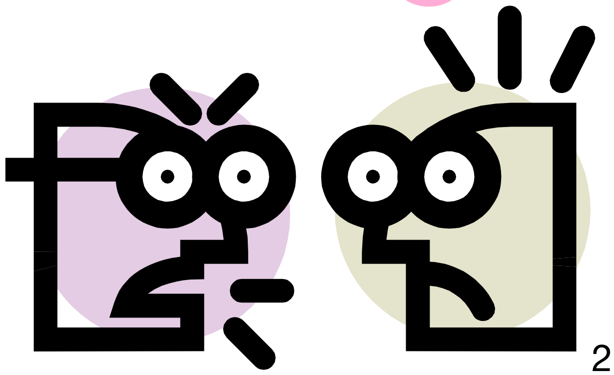
BUT:

- There no molecules with *only* attractive interaction

How to test the theory?

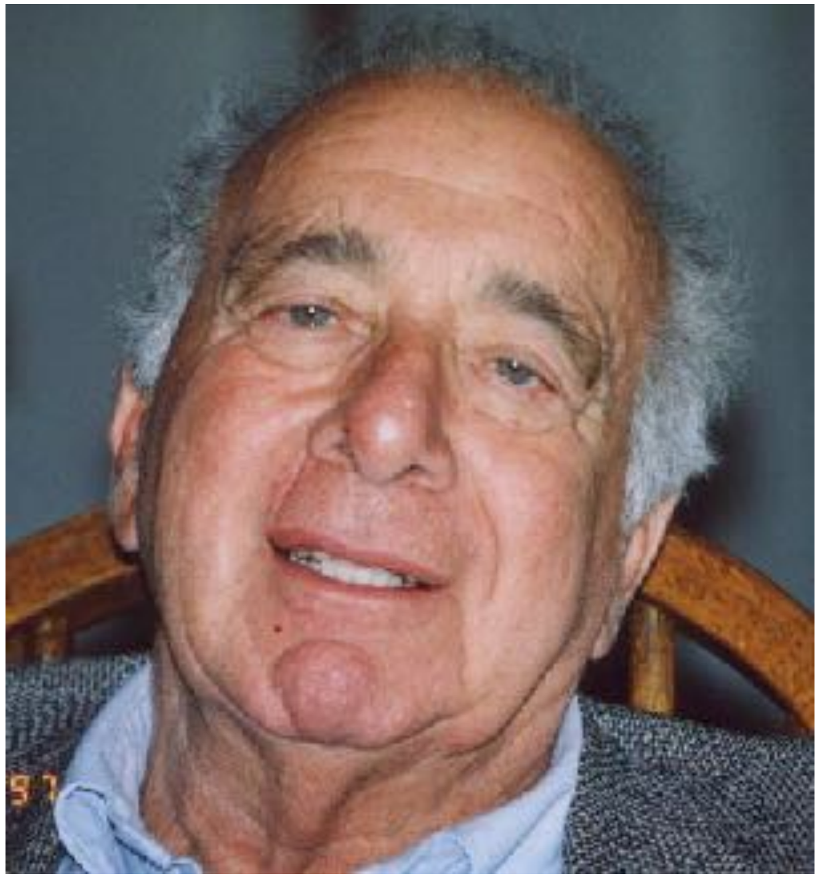
My theory is **RIGHT**: but this experimentalist refuses to use molecules that do not have any attractive interactions

Your theory is **WRONG** it disagrees with the experiments



But we can simulate hard spheres ..

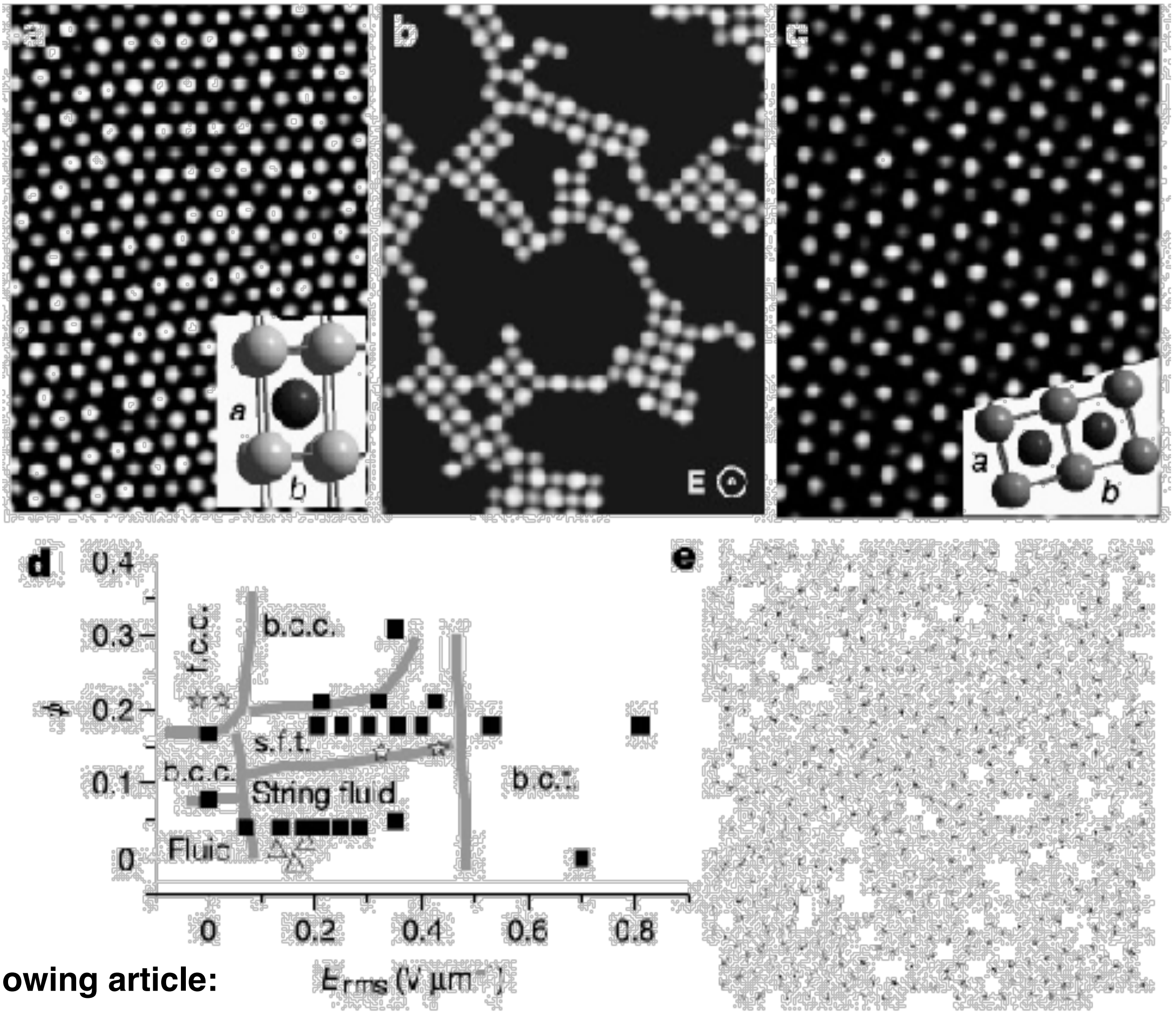
- Bernie Alder carried out Molecular Dynamics simulations of the freezing of hard spheres
- But, …. did the scientific community accept this computer results as experimental evidence …
- … during a Gordon conference it was proposed to vote on it …
- … and it was voted against the results of Alder



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]

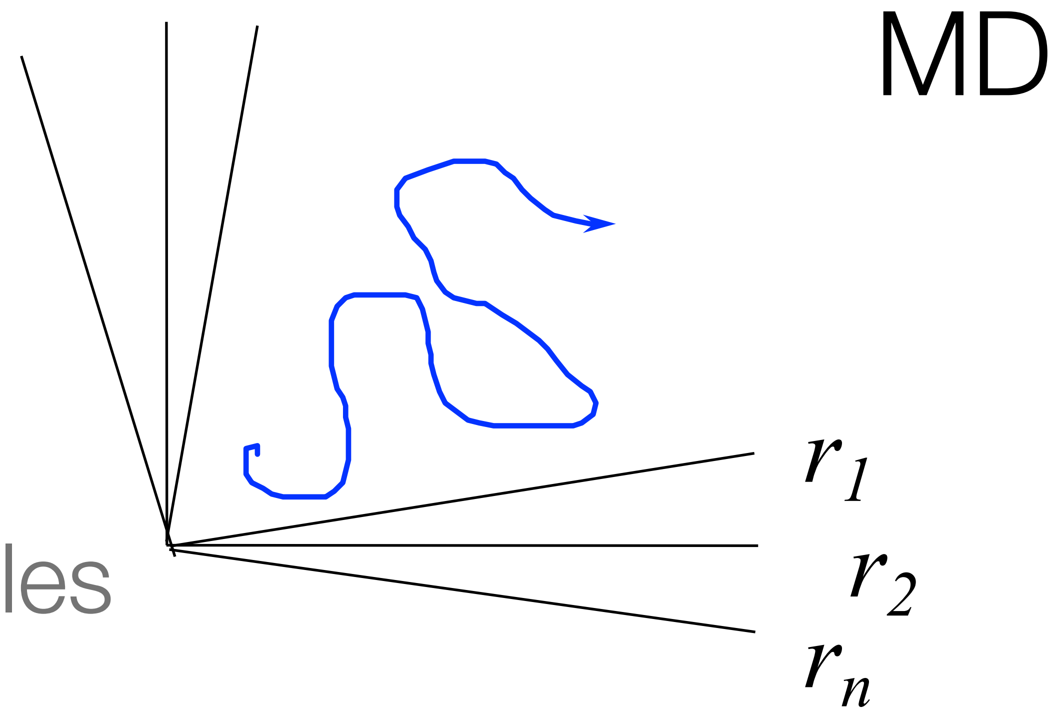
Anand Yethiraj and Alfons van Blaaderen
Nature 421, 513-517 (30 January 2003)

Molecular Dynamics

- Theory:

$$\mathbf{F} = m\frac{d^2\mathbf{r}}{dt^2}$$

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

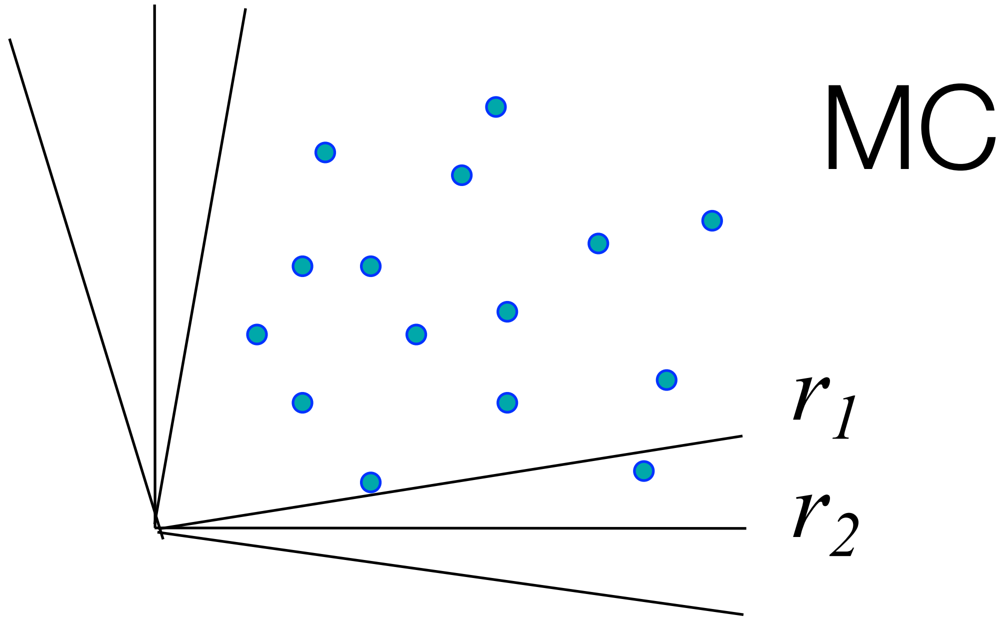


Monte Carlo

- Generate a set of configurations with the ***correct*** probability
- Compute the thermodynamic and transport properties as averages over all configurations

What is the correct probability? Statistical Thermodynamics

How to compute these properties from a simulation?



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