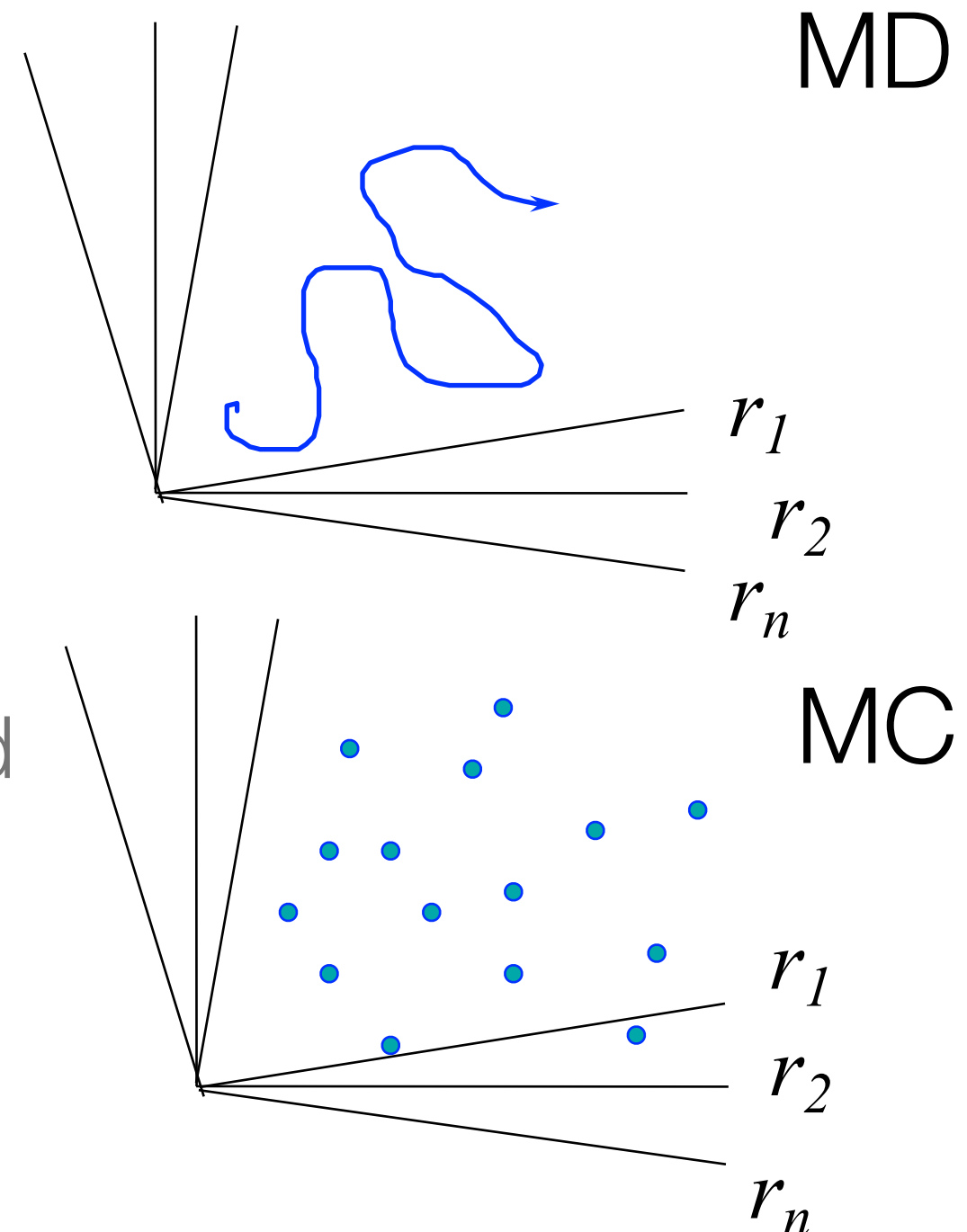# Molecular Simulation

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

MD

r_1

r_2

r_n

MC

r_1

r_2

r_n

Understanding Molecular Simulation

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
…

Understanding Molecular Simulation

4

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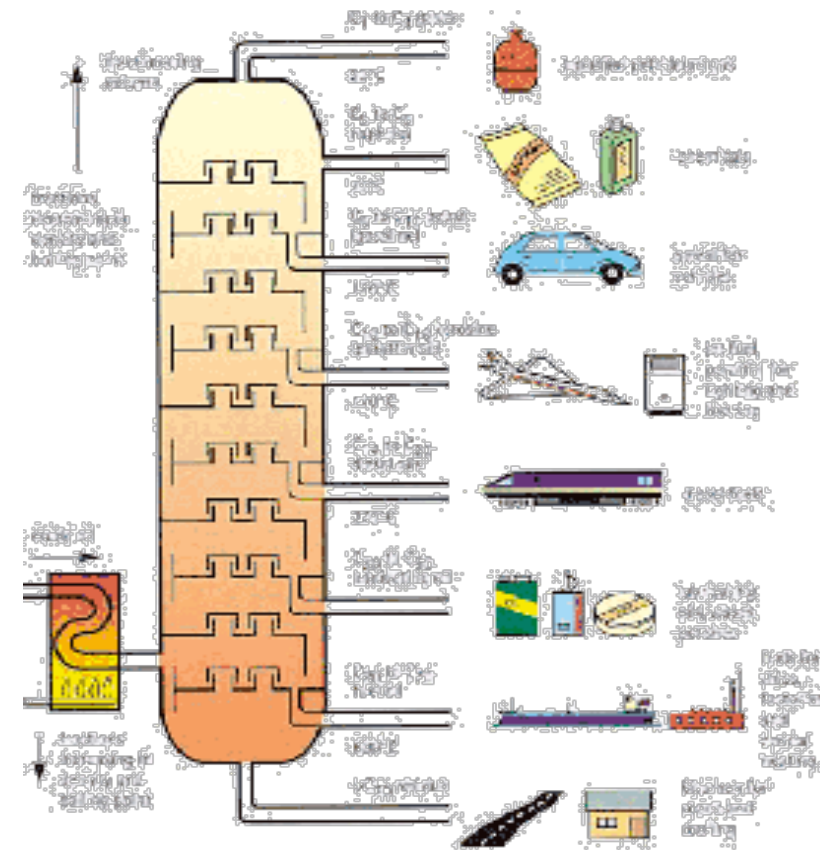
To *predict* the thermodynamic properties (boiling points) of the hydrocarbon mixtures it is convenient (=Engineering models use them) to know the critical points of the hydrocarbons.

Understanding Molecular Simulation

Critical points of long chain hydrocarbons

Pentane
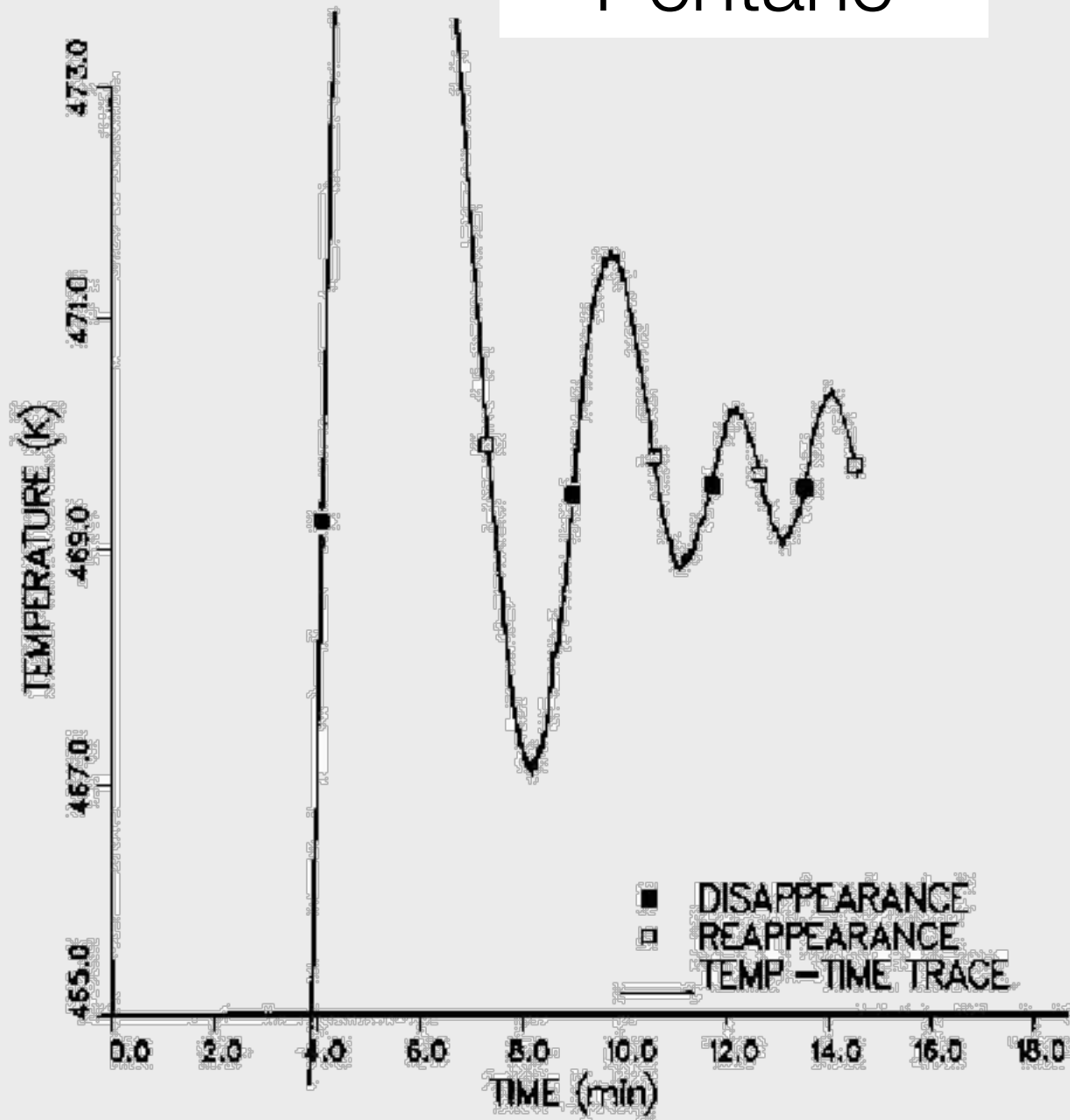
Heptadecane
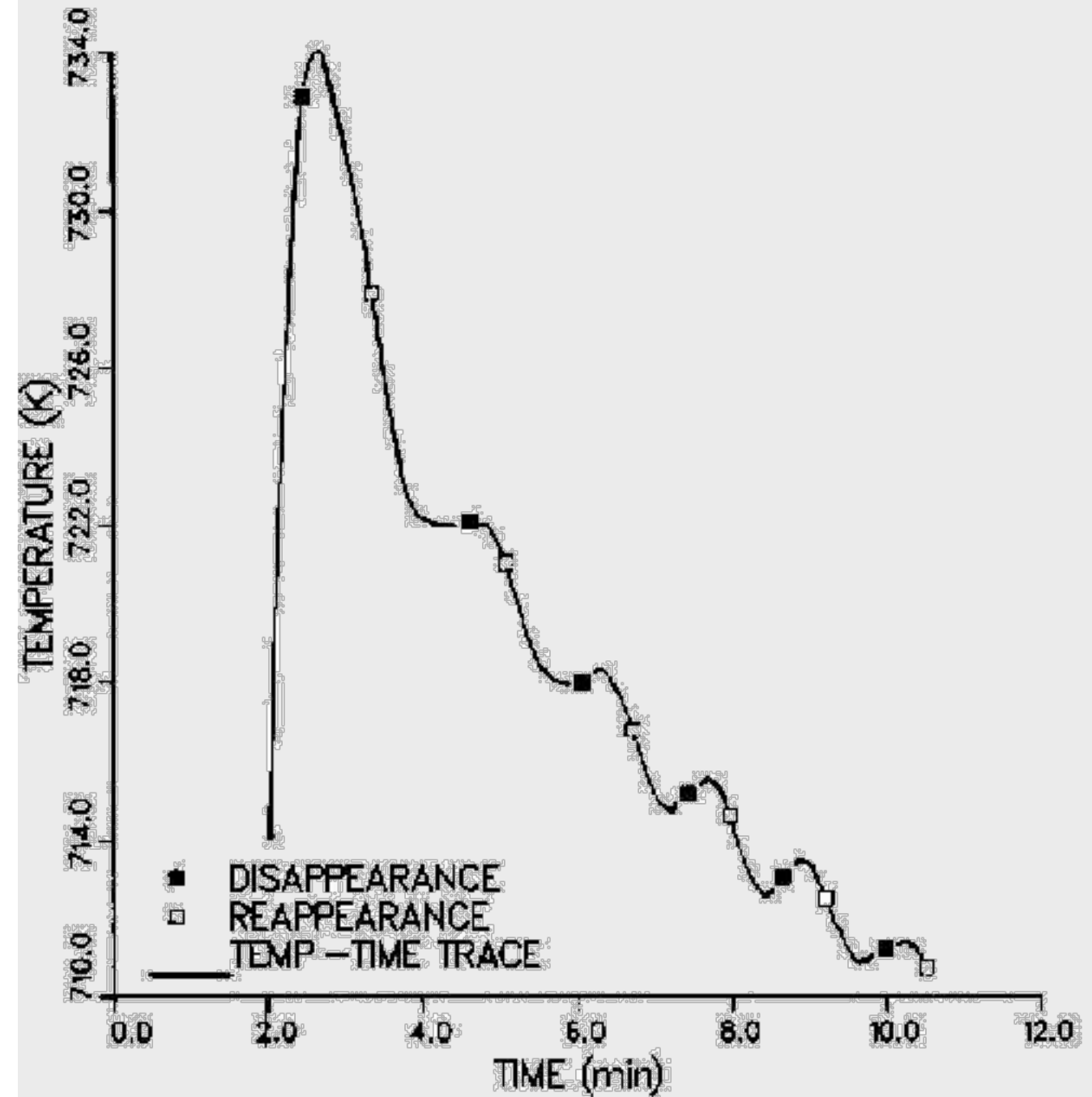
Hydrocarbons: intermolecular potential

United-atom model

- Fixed bond length

- Bond-bending

- Torsion

- Non-bonded: Lennard-Jones
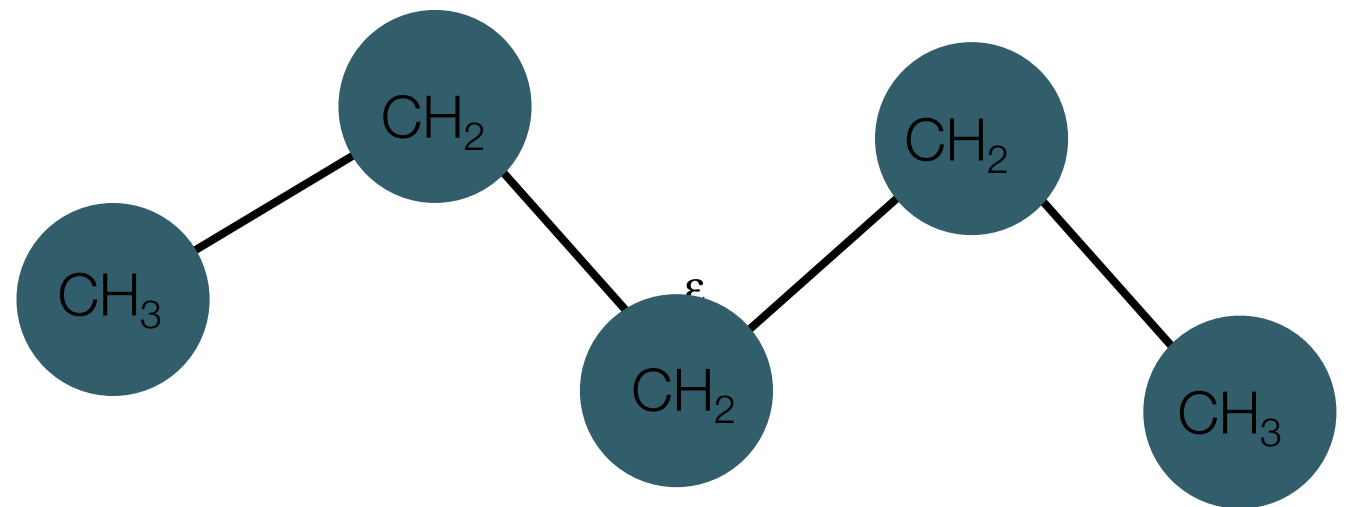
$$u(r) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^{6} \right]$$
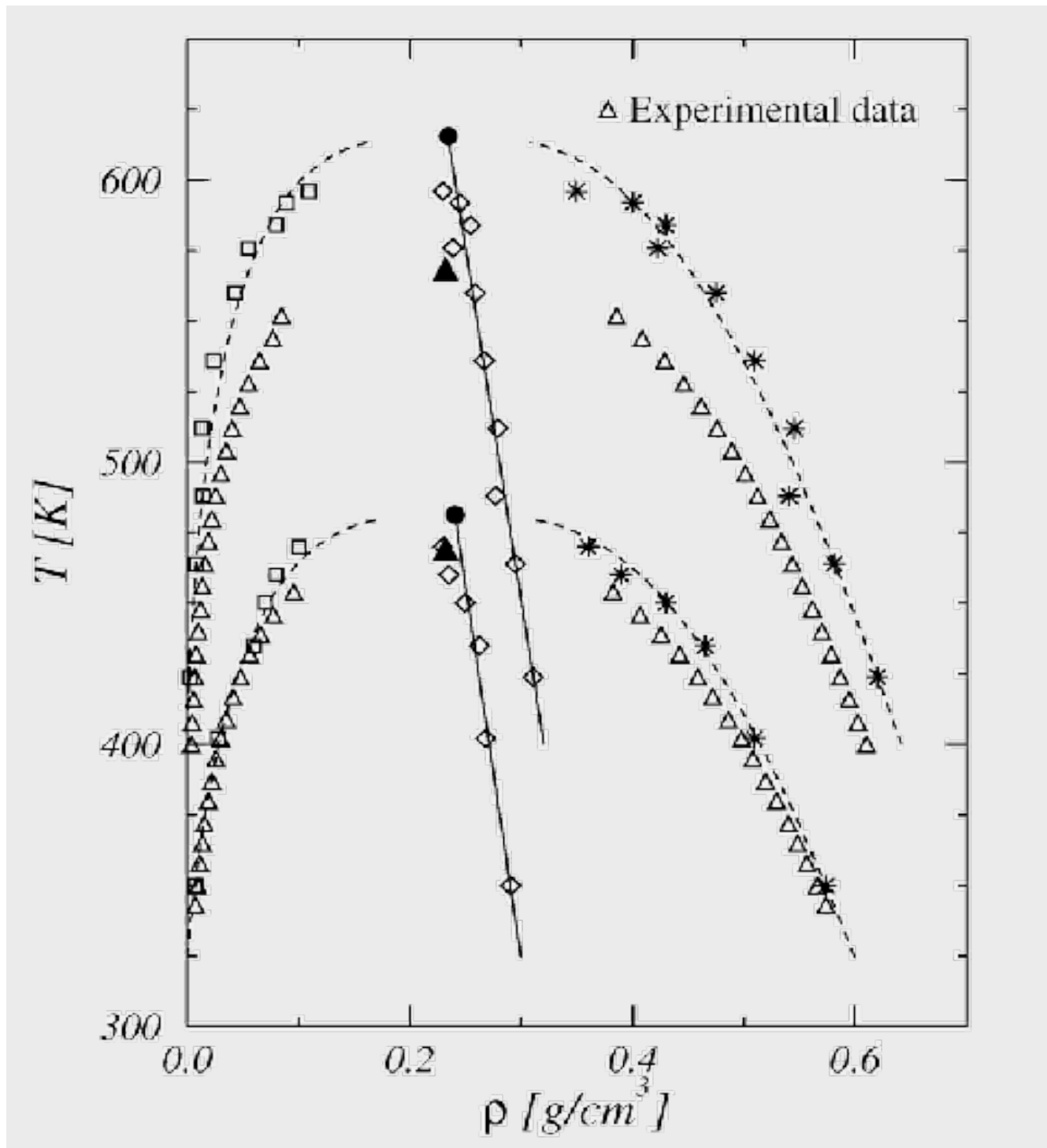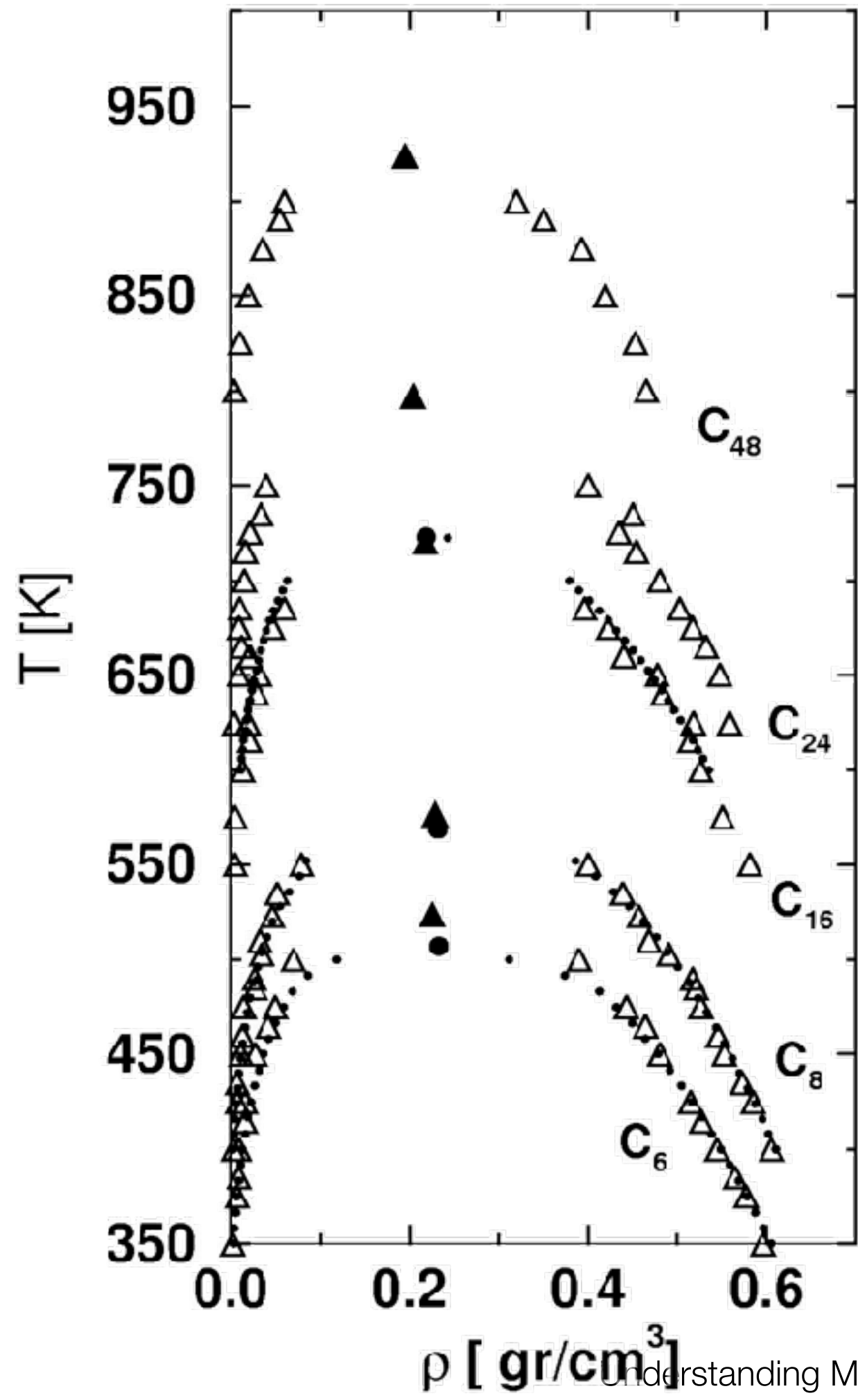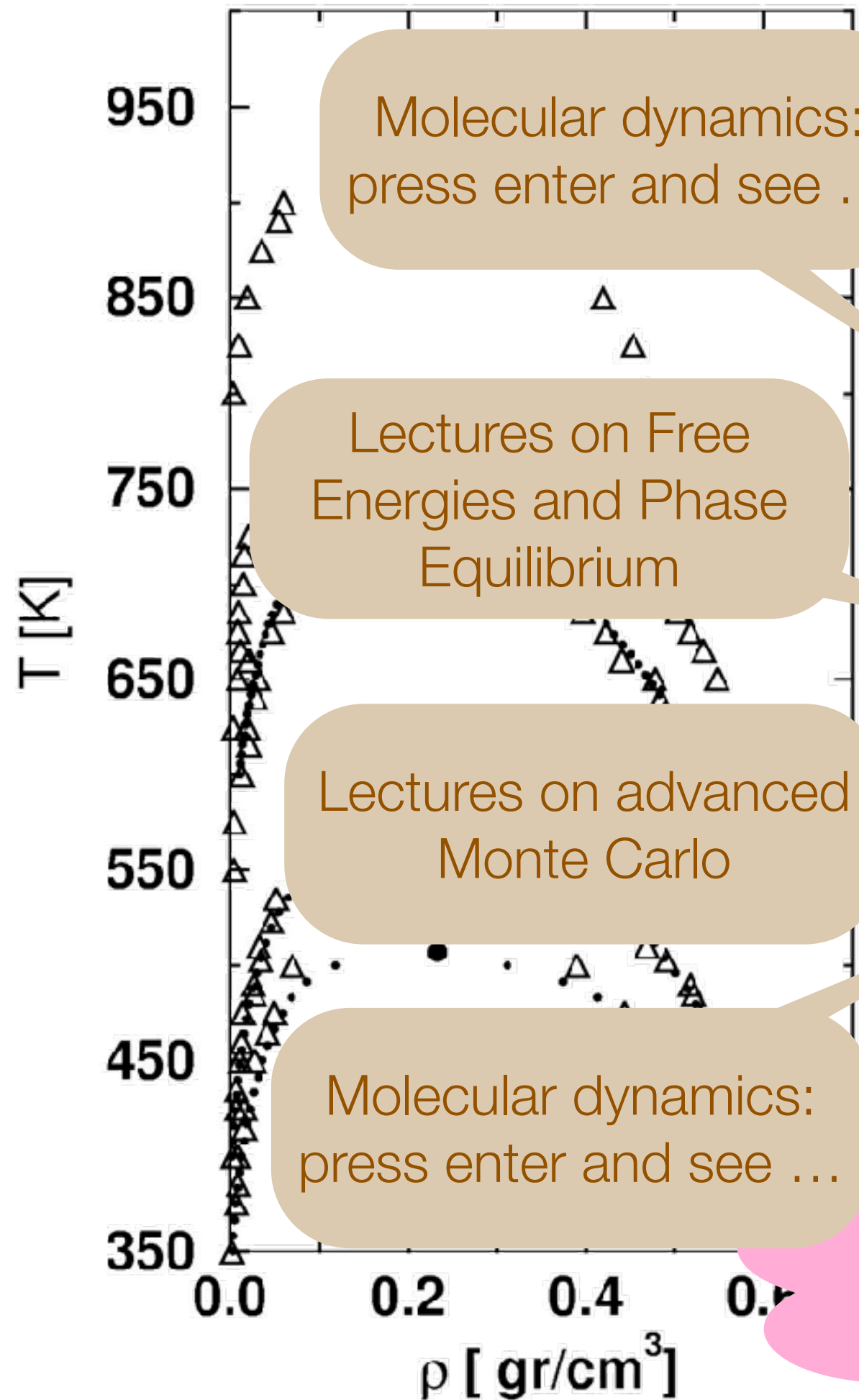
Understanding Molecular Simulation

OPLS (Jorgensen) Model

Understanding Molecular Simulation

Critical Temperature and Density

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

Understanding Molecular Simulation
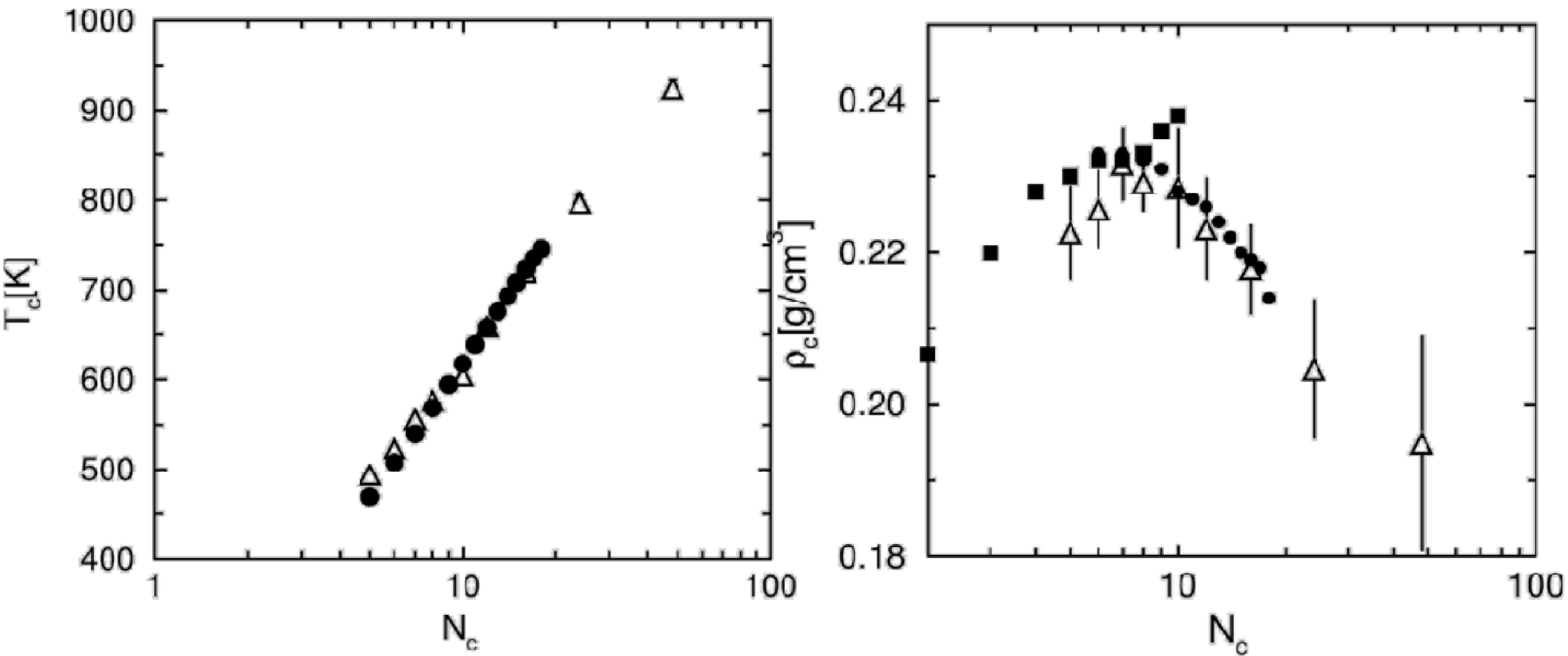
Methane storage

Methane cars: the technological obstacle

CH$_4$
1 liter

0.036 MJ

Gasoline, 1 liter

34.2 MJ

Methane versus gasoline

Volumetric Energy Density of Fuels

Legend:
- Gasoline (green)
- Liquid CH_4 (112 K) (blue)
- CH_4, 200 bar, 298 K (red)

Y-axis: Energy density (MJ/L)

X-axis labels: LNG, CNG

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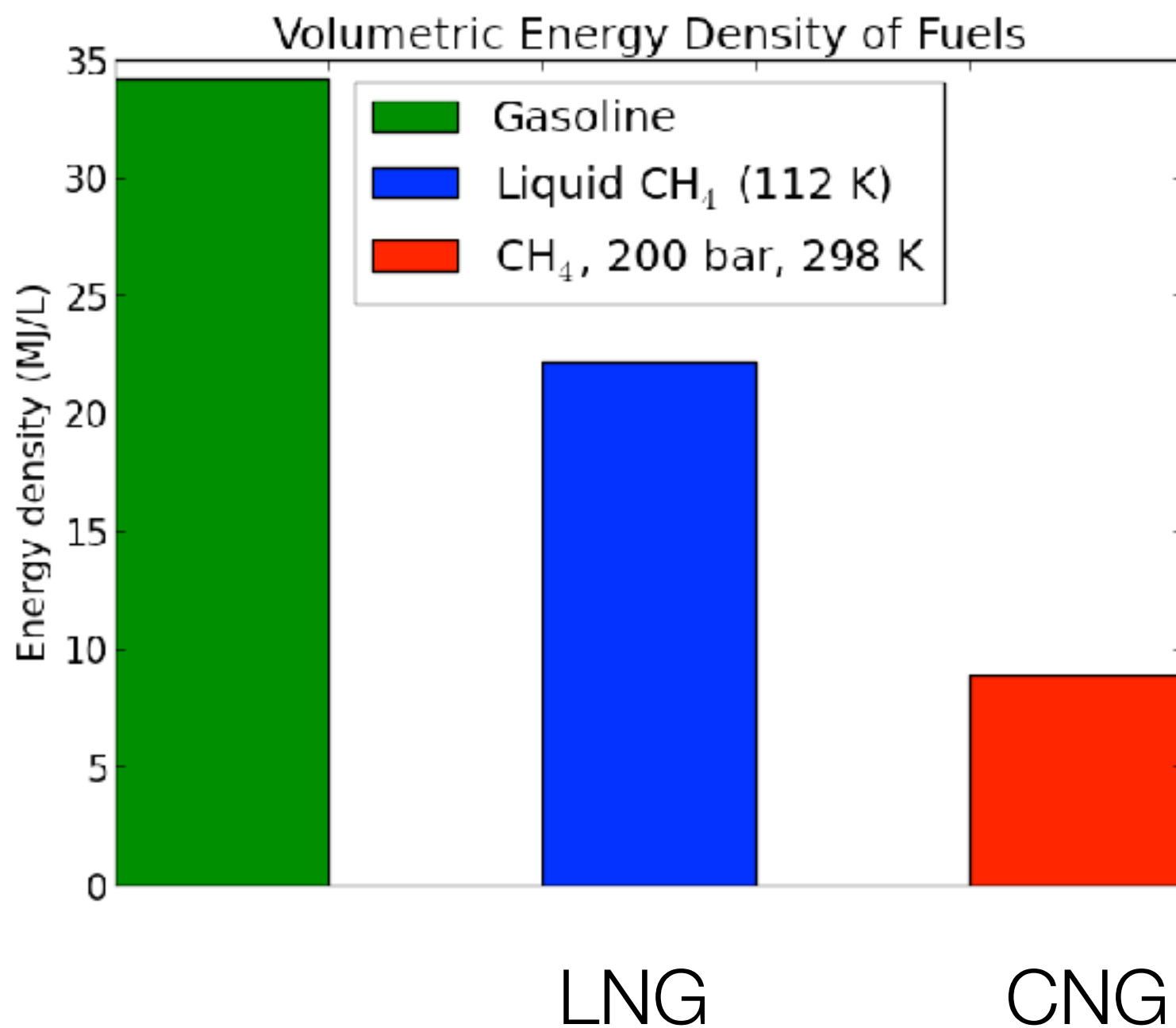
Pressure swing adsorption

65 bar
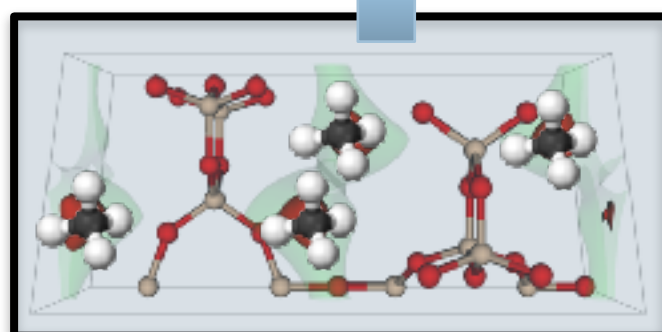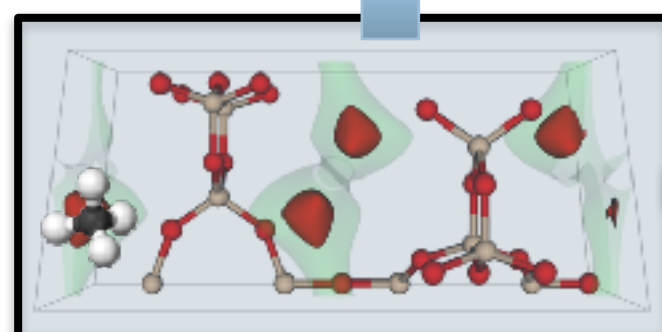
5.8 bar
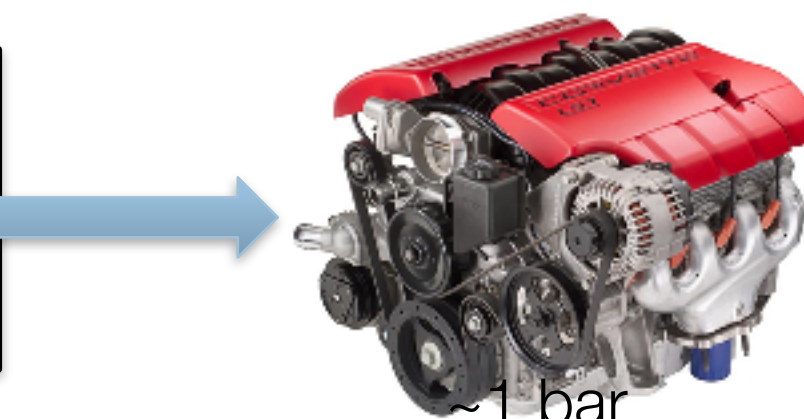
~1 bar

Insufficient
flow

$P_H = 65$ bar

$P_L = 5.8$ bar

The deliverable capacity

P_H = 65 bar

P_L = 5.8 bar
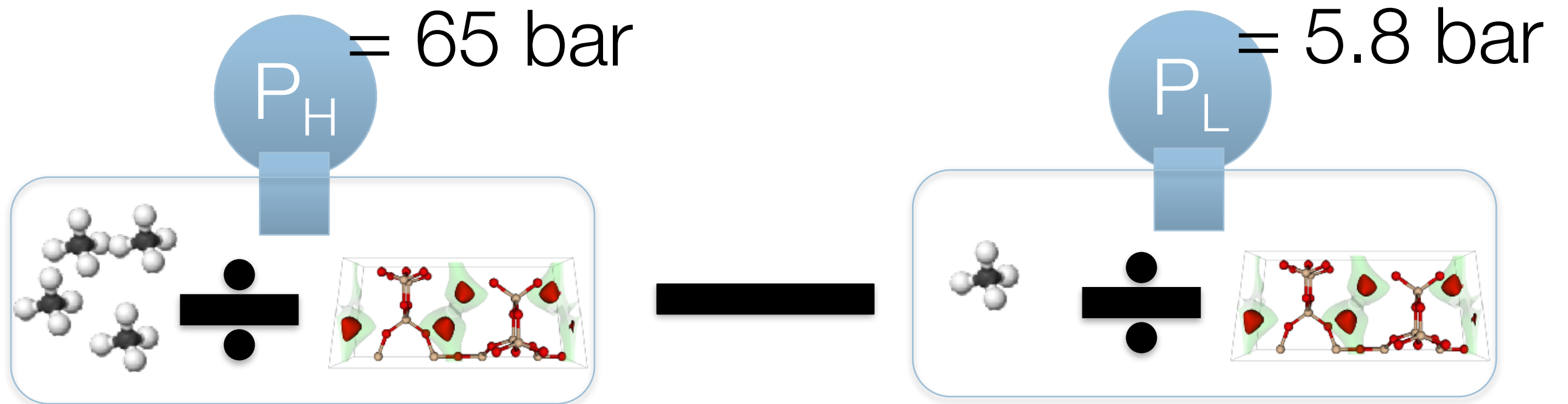
Methane adsorbed
(v STP/v)
at tank charging
pressure

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

ARPA-E (DOE) target: 315 m³ STP methane/m³ adsorbent

An optimal heat of adsorption?

Goal: maximize deliverable capacity
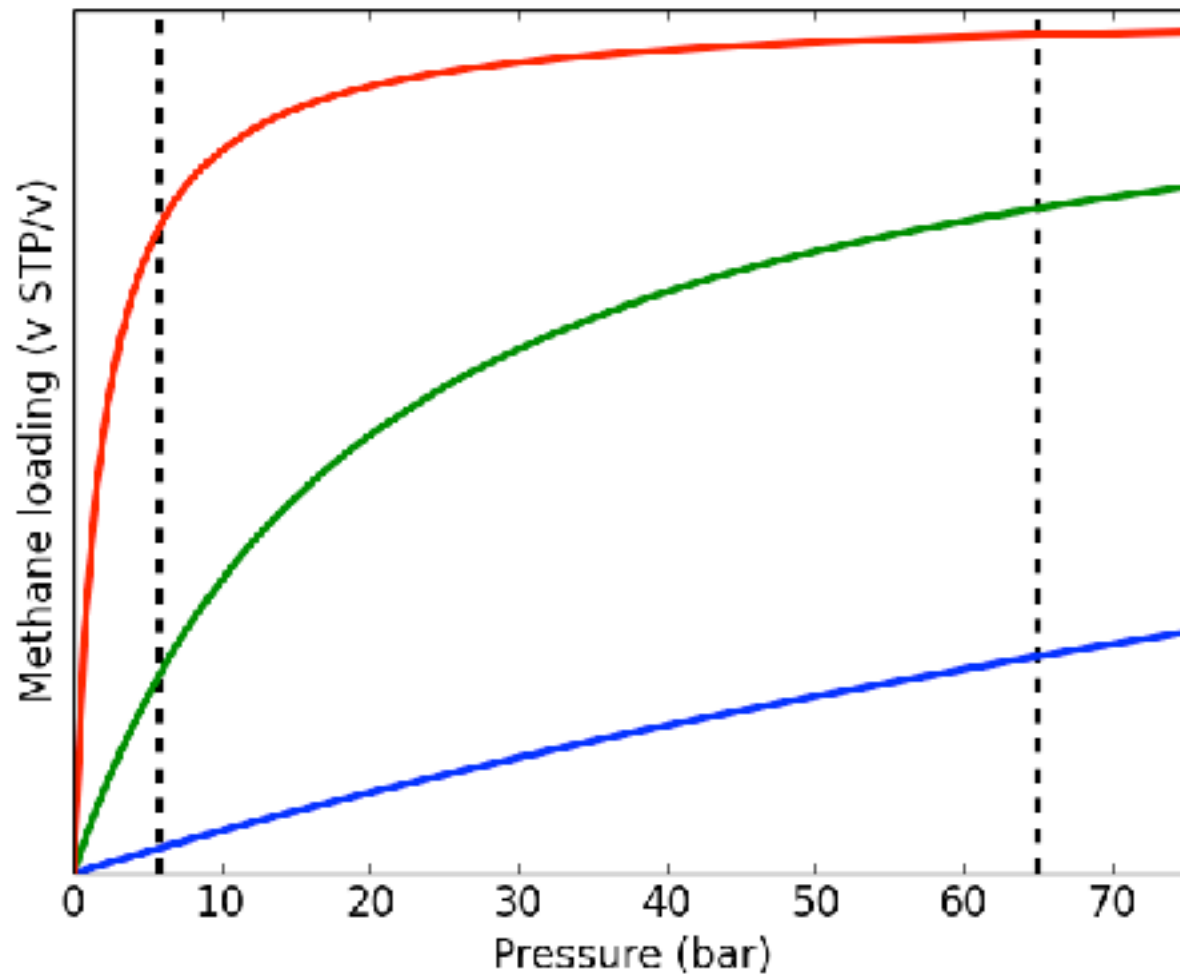
"For methane, an optimal enthalpy change of [16.2] kJ/mol is found."

Optimum Conditions for Adsorptive Storage

Suresh K. Bhatia[†]

Division of Chemical Engineering, The University of Queensland, Brisbane, QLD 4072 Australia

Alan L. Myers*

Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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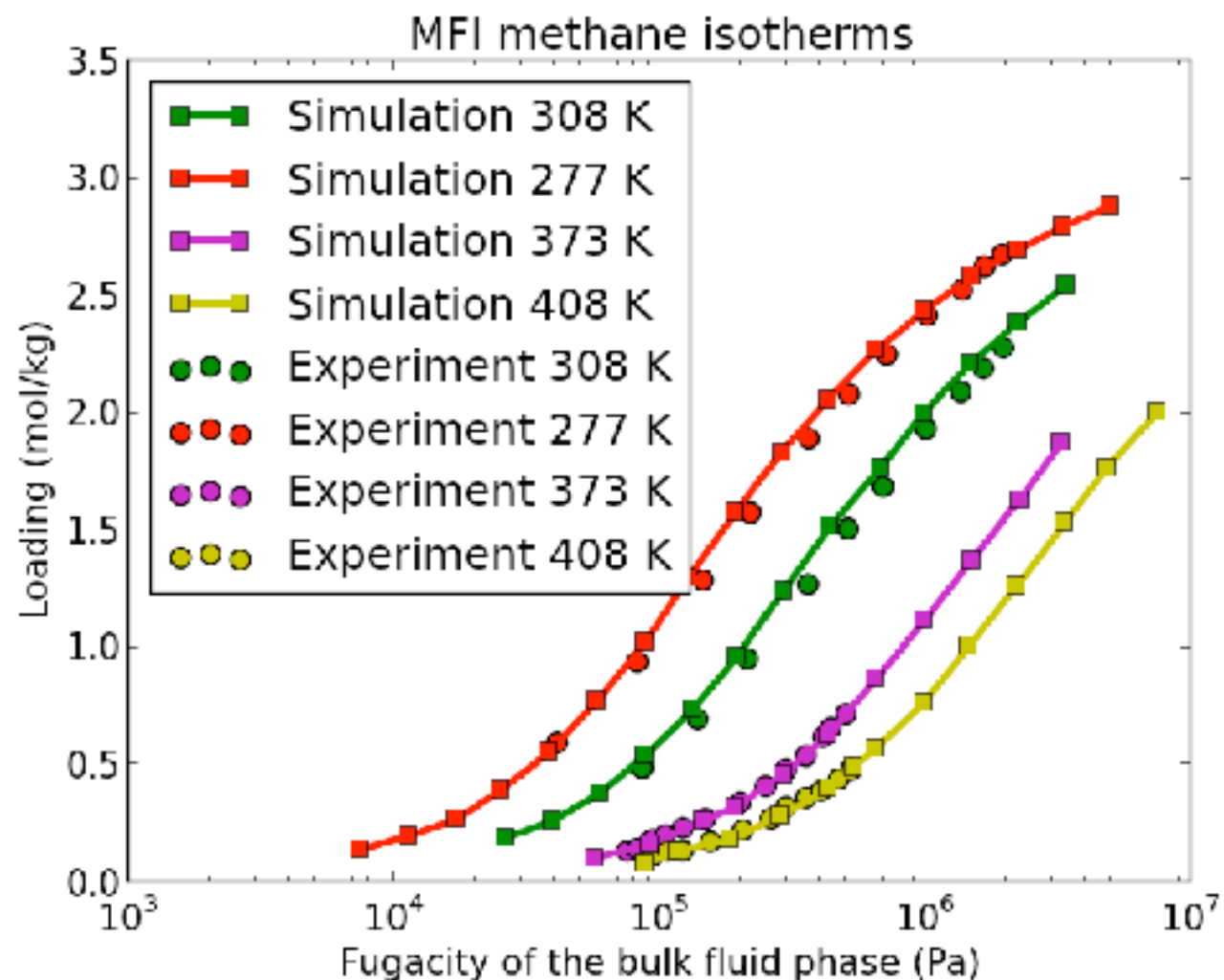
MFI expt'l data: Sun *et al.* (1998) *J. Phys. Chem. B.* 102(8), 1466-1473.
Zhu *et al.* (2000) *Phys. Chem. Chem. Phys.* 2(9), 1989-1995.
Force field: Dubbeldam *et al.* (2004) *Phys. Rev.* 93(8), 088302.

In silico screening of zeolites

Optimal ΔH_{ads} of Bhatia and Myers
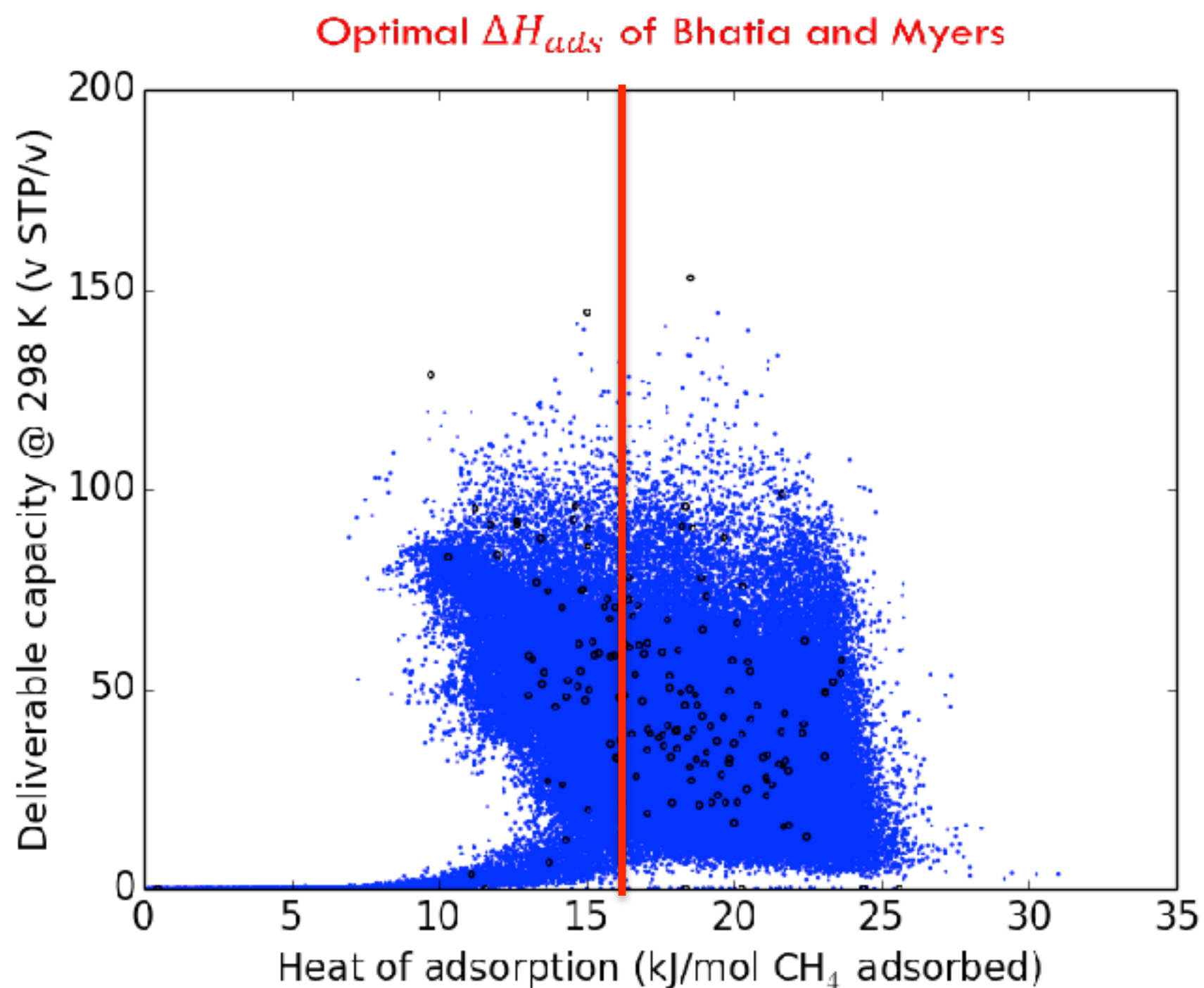
C. Simon *et al*. (2014) *Phys. Chem. Chem. Phys.* 16 (12), 5499-5513

Understanding Molecular Simulation

Enthalpy vs. entropy
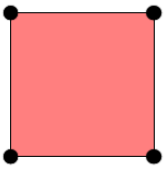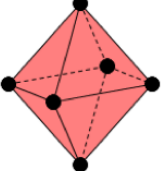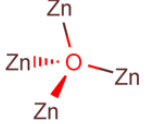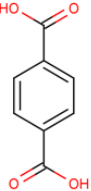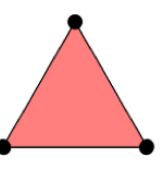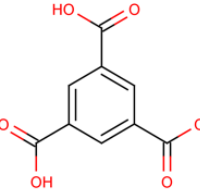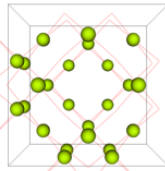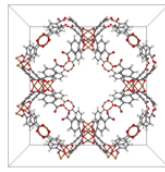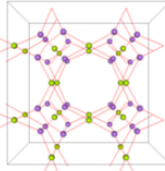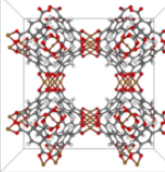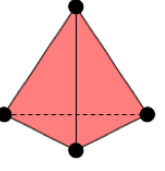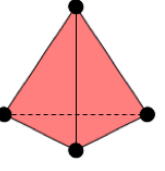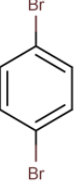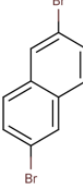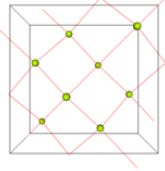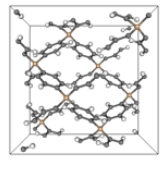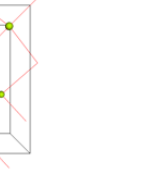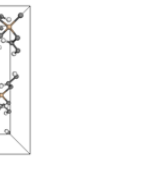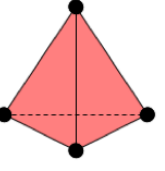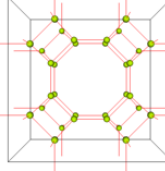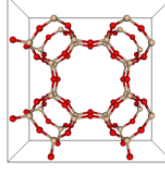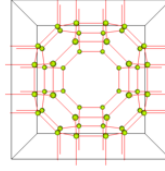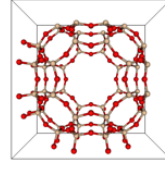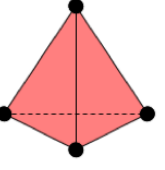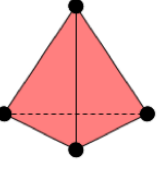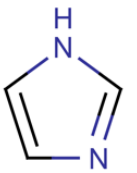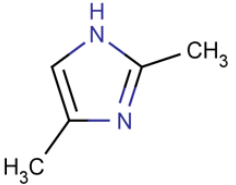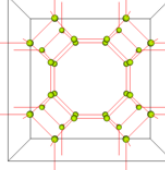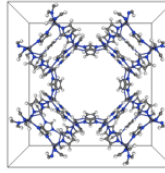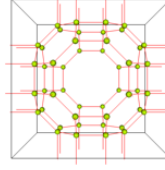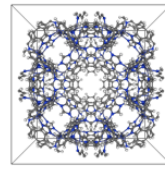
- ΔS not the same for all materials

- Wide range of ΔH that yields optimal material
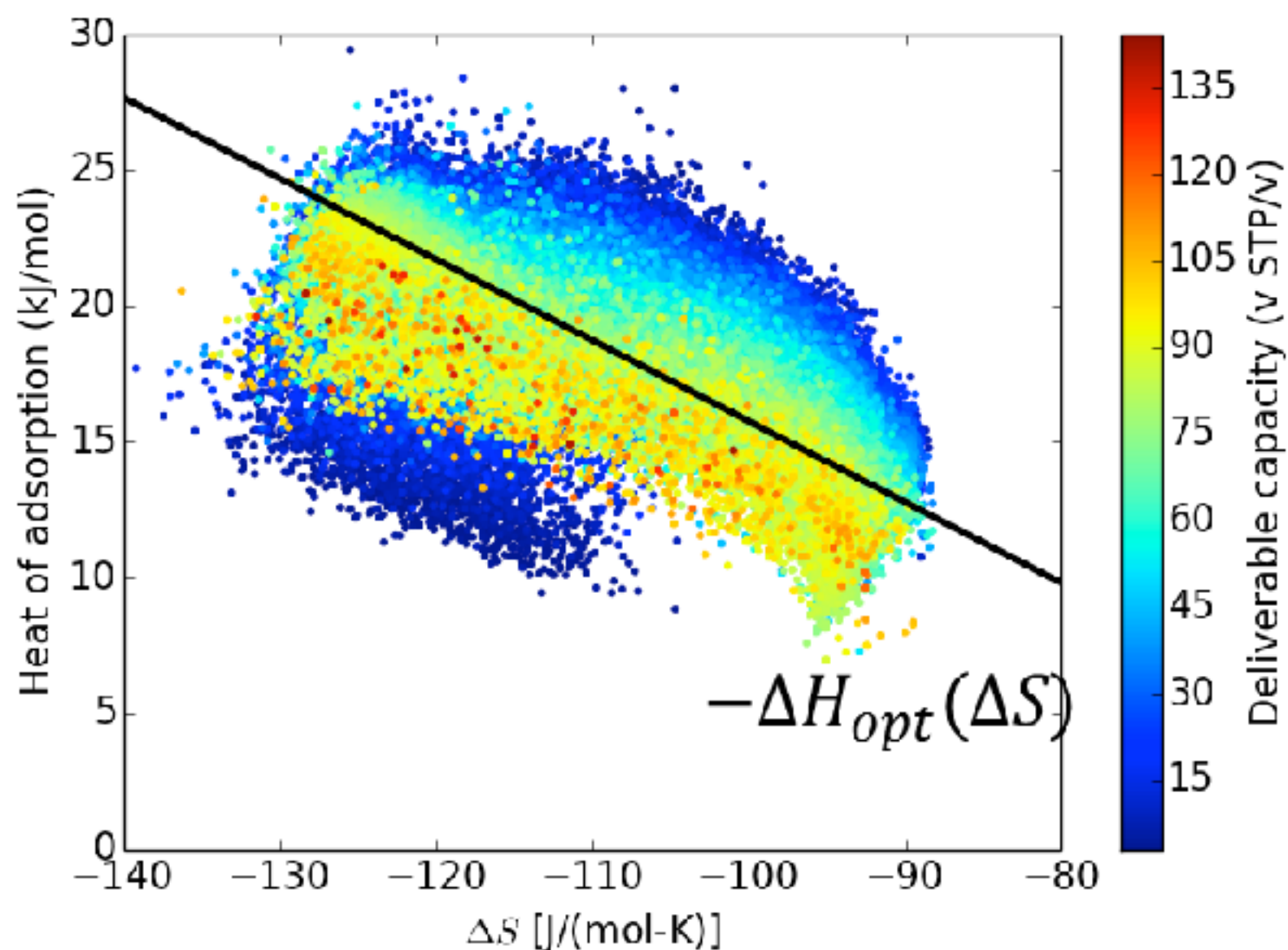
Can we find a material that meets the DOE target?

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	Zn–O–Zn (Zn, Zn, Zn)	HO–C–...–C–OH	HO–C–...–C–OH, OH		
PPNs	Si	Ge	Br–...–Br	Br–...–Br		
Zeolites	Si		O			
ZIFs	Zn	Fe	H–N imidazole	H–N 2,4-dimethylimidazole, CH₃, H₃C		

Understanding Molecular Simulation

Insight from the model

Example 3: make a model system

Question: are attractive interactions ... phase?

YES:

- Attractive forces are needed

- Theories predict this ..

BUT:

- There no molecules with *only* attractive interactions

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
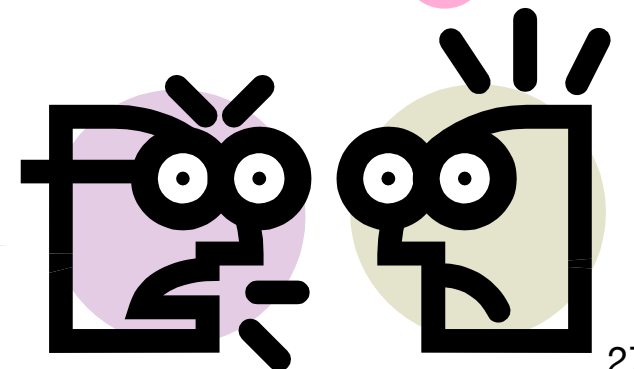
But we can simulate hard spheres ..

- 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

Understanding Molecular Simulation
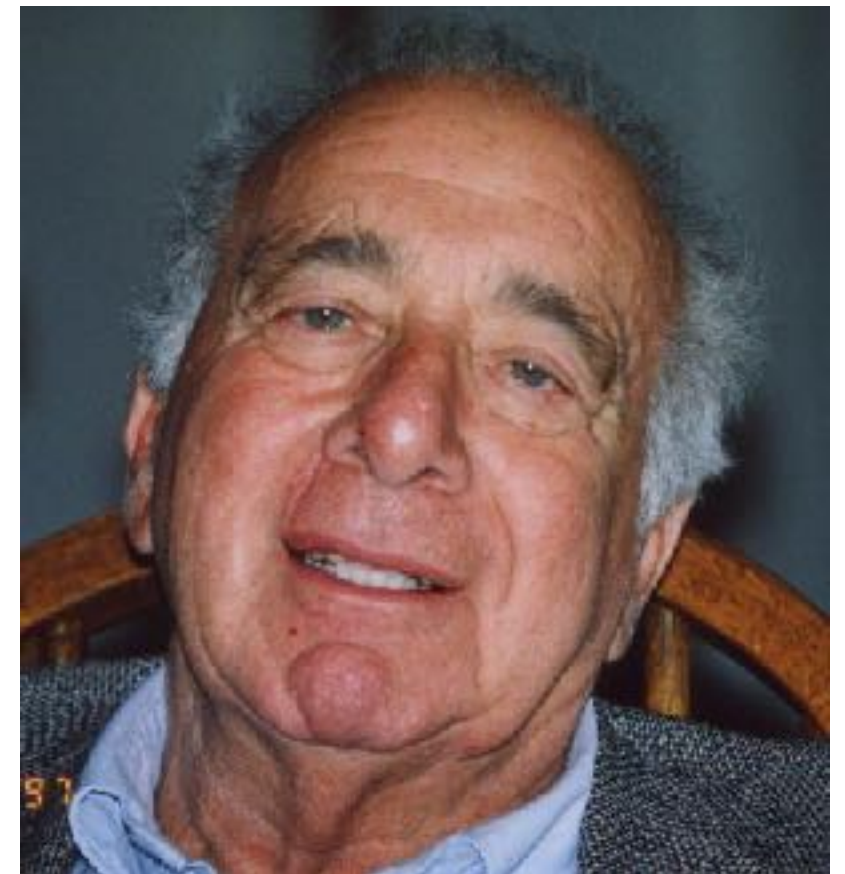
Experiments are now possible

.. But not on molecules

but on colloids:
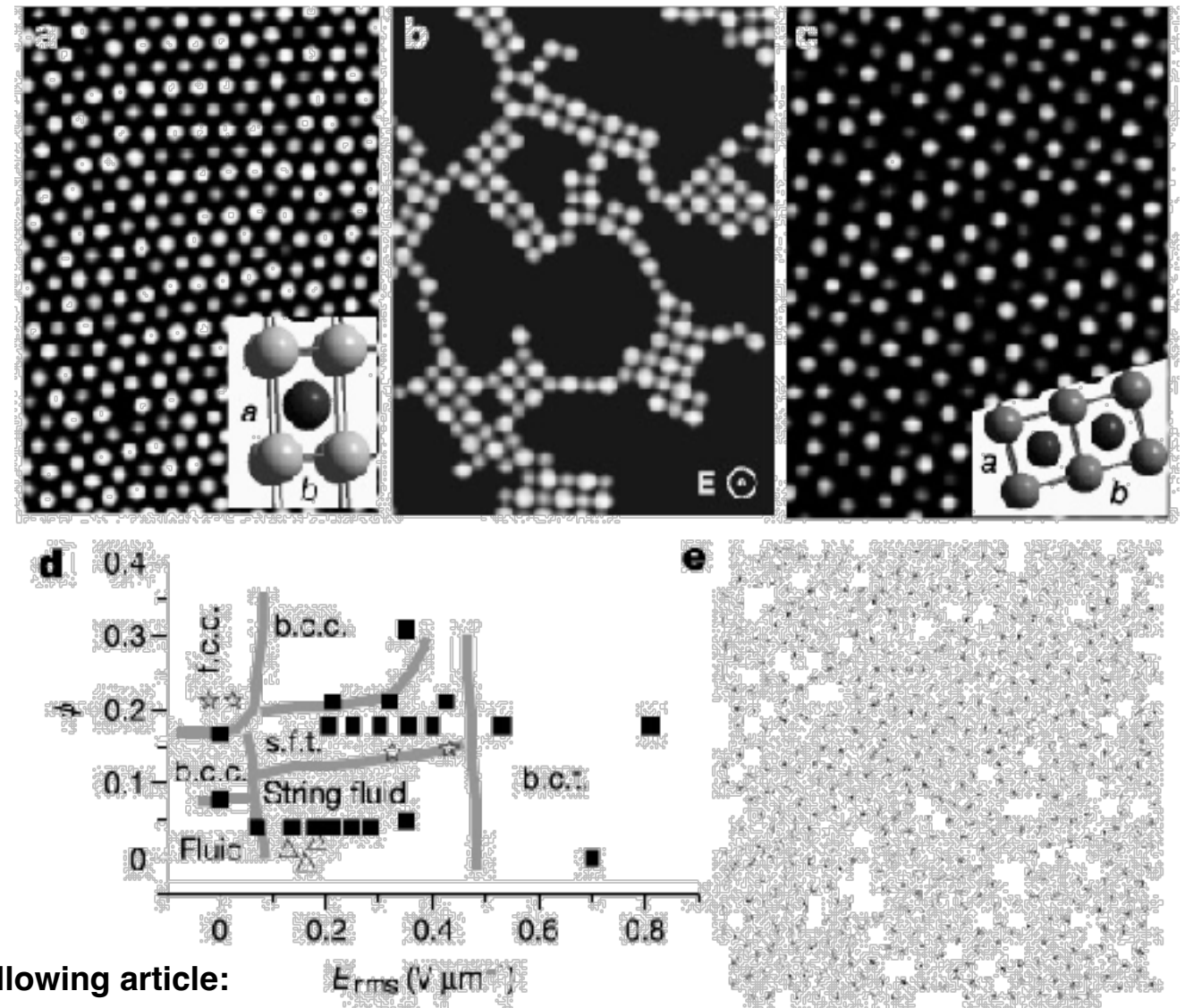
A colloidal model system with an interaction tunable from hard sphere to soft and dipolar

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

Understanding Molecular Simulation

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

r_1

r_2

r_n

Understanding Molecular Simulation
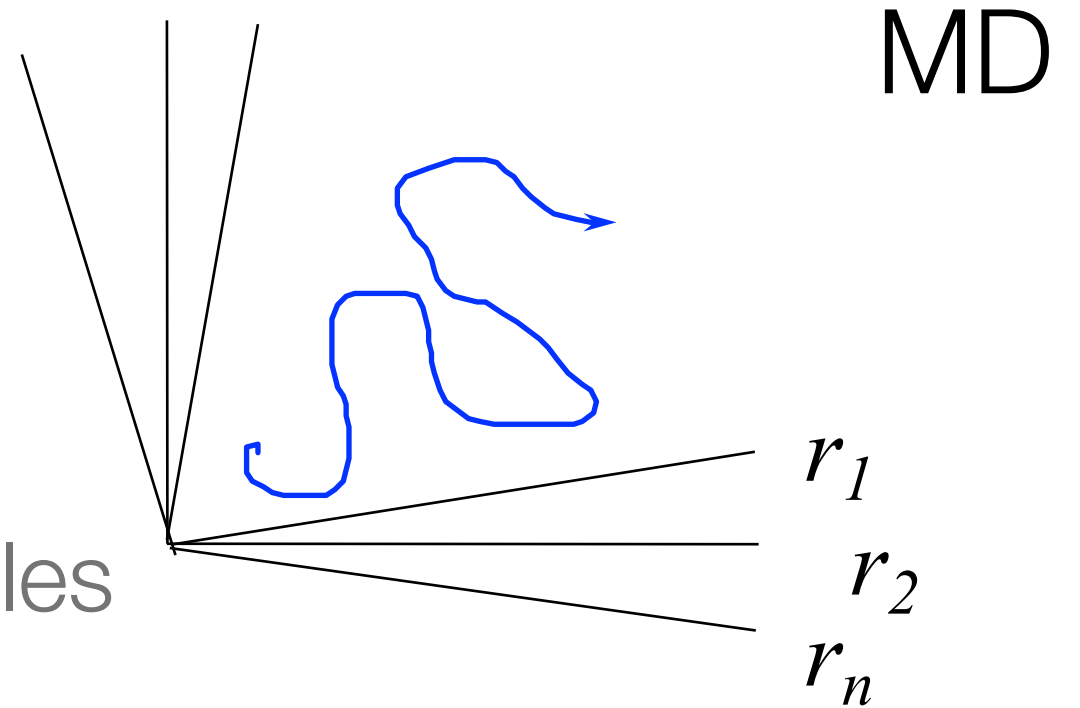
Monte Carlo

- 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?

MC

r_1

r_2

Understanding Molecular Simulation
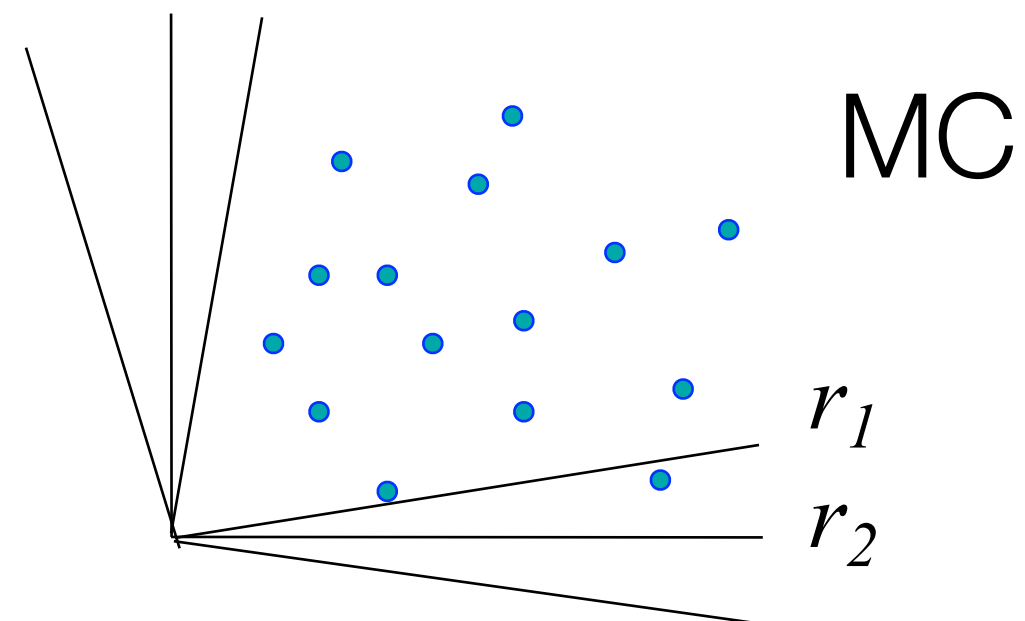
Classical and Statistical Thermodynamics

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