CHE 502 Chemical and Statistical Thermodynamics

1st semester, academic year 2019/2020 (Sept. 16 – 27, 2019)

CHE 501 Modeling of Molecules, Materials and Processes

2nd semester, academic year 2019/20 (Feb. ???????, 2019)

Syllabus / Organization / Lectures / Materials

see also part 2, supplementary material, and Examples

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Links to this and other useful files:
http://theo.ism.u-bordeaux.fr/PBopp/vistec2019.2/index.html

Our general motto

It is good enough for research driven by intellectual curiosity to expand the horizon of human knowledge, even if it does not have an immediate application

Takaaki Kajita, Nobel Prize in Physics 2015

Purpose of these classes:

– *NOT to turn you into experts in computational chemistry (especially if you are an engineer)*

– *Demonstrate the hierarchy of theoretical and computational methods available in chemistry (materials... , bio... , geo...) and their usefulness and limitations*

– *Allow you to judge scientific work (publications) in this field*

– *Give you a basis to build on if during your research work you have to do such calculations*

– *NEVER to write in a paper (or your thesis) anything like:*
”Theoretical calculations have shown .... ” 555

Other examples of 'bad'

(improper, inappropriate, misleading) language

– interaction $\neq$ "**spatial correlation**"

(*'interaction' refers to energy*)

– Something cannot be "more stable"

than something else

(*because 'stable' means 'will return to this state*

after a small perturbation')

– This ... is "more favorable" than that ...

(*What is it supposed to mean? Favorable for what?*)

We shall try to avoid such language

... even if English is difficult for you

General Organization, Syllabus:

This lecture, CHE502, and CHE501 belong together
CHE501 builds on CHI502

In CHE502 , we will deal with the basics,
which are:

– Basic concepts of Quantum Mechanics (quantum chemistry)

– Reminder of classical (Newtonian) mechanics

– Basic concept of statistical mechanics

In CHE501 , we will study how to apply the principles we have learned in CHE502 to study chemical (geo-chemical, biochemical ...) systems consiting of many interacting molecules (condensed phases)

– Molecular Dynamics (MD) computer simulations

– Monte Carlo (MC) computer simulations

– Computer Lab, take home project

In CHE502:

We will have mostly **lecture classes** and, towards the end, possibly a few exercise sessions.
We will adapt according to your level of previous knowledge and how much time we need to cover the basic ideas we want to discuss.

It will also depend on

– The number (and quality) of questions asked and the subsequent discussions

Lecture Classes: (CHE502 and, in 2019, CHE501)

- 2 1/2 to 3 hours with a short break
- since we are not very numerous, questions can **and should** be asked at any time

In CHE501 we will also have computer labs and a little take-home project to do on your own computer or on the VISTEC server.

Grades (American English) / **Marks** (British English)

CHE502 100 % Written examination, open book
CHE501 50 % written examination, open book,
50 % project

(Written examinations:
write little essays, solve small problems, give arguments
i.e. you must **understand** things, **not memorize** them!)

Textbooks

Quantum Mechanics, Phenomenological Thermodynamics:
P.W. Atkins, Physical Chemistry, *XI*th (or any other) Edition, Oxford University Press

Statistical thermodynamics
D.A. McQuarrie, Statistical Mechanics, Harper & Row
also
R.K. Pathria (and P.D. Beale in later editions)
Statistical Mechanics, Elsevier
`http://home.basu.ac.ir/~psu/Books/[Pathria_R.K.,_Beale_P.D.]_Statistical_mechanics.pdf`

Normal modes (special chapter of classical mechanics)
E. B. Wilson, J. C. Decius and P. C., Cross Molecular Vibrations
The Theory of Infrared and Raman Vibrational Spectra, Dover Books

Computer Simulations (CHE501)
M.P. Allen, D.J. Tildesley,
Computer Simulation of Liquids, Oxford Science
detailed explanations of the fundamentals, with FORTRAN codes
`http://www.ccl.net/cca/software/SOURCES/FORTRAN/allen-tildesley-book/f.00.shtml`

These books are either available in the VISTEC library
and/or can be found on the web as pdf files

More free books at:
`http://www.freebookcentre.net/Chemistry/Quantum-Chemistry-Books.html`

Among the things that you should know at the end of this class;

– Orders of magnitude of length, energy, wavelength etc. relevant for a microscopic (molecular) description of 'chemical' phenomena
– When is a description with classial mechanics appropriate, when is quantum mechanics needed?
– What are the fundamental observations that need to be described by quantum mechanics?
– What are the fundamental assumptions of classical mechanics?
– What is the purpose of statistical mechanics?
– What is of classical (phenomenological) thermodynamics; what are its fundamental assumptions?
– How is statistical mechanics related with classical thermodynamics?
–

SYLLABUS Part 1–4 = CHI502

Part 1: Phenomenological Thermodynamics

Reminder: 1st law 2nd law 3rd law ...
Reminder: Equilibria (phase equilibria chemical equilibria)

Part 2: Quantum Mechanics

Energy- and length scales
Fundamental assumptions → Schrödinger Equation
Model cases: particle in the box, harmonic oscillator, Hydrogen atom
Born-Oppenheimer approximation, Potential Energy Surface (POS)

Part 3: Basic ideas of statistical thermodynamics

leading to the **Partition functions**

Part 4: Analytical statistical thermodynamics

The canonical partition function for the ideal polyatomic gas
Equilibria, example: an isotope exchange equilibrium

SYLLABUS Part 5–8 = CHI501

Part 5: Statistical Thermodynamics via Simulations:

Basic concepts
mostly Molecular Dynamics (MD), some Monte Carlo (MC)

Part 6: Simulations
⇒ (more general) statistical mechanics

time dependent things; dynamics (kinetics), **non-equilibrium**

Part 7: Selected Examples

MD strategies, surfaces, other methods

Part 8: Computer Lab

Thermodynamics is (initially) the theory of the steam engine
(how to build one, how to make it efficient, safe, cheap, ...)

It is the time of the painter Joseph Mallord William (JMW) Turner (1775 - 1851)

Rain, Steam and Speed, The Great Western Railway
National Gallery, London

Terminology / background

(I) "chemical" / "macroscopic" / "phenomenological" **thermodynamics**:
A self-consistent mathematical representation (theory) of observations made when the states of matter (gases, liquids, solids) are modified by exposing the system to perturbations (heating, cooling, mixing, changing volume, pressure, etc. etc.)

This theory was developed in the XIX$^{\mathrm{th}}$ century;
historically, it is satisfied with the description (and prediction) of **macroscopic** observations,
it does not try to relate them to the **microscopic** properties of the constituents (molecules)
(*which were of course not known at the time*)

thermodynamics = (here) equilibrium thermodynamics
(*there is also non-equilibrium thermodynamics* → *Lars Onsager (1903-76)*)

(II) "statistical" thermodynamics
(statistical mechanics, statistical physics, many particle physics ...)

Essential ideas by Ludwig Boltzmann (1844-1906)

An attempt to obtain macroscopic properties (observables) of *chemical, biological, geological, ...* systems under given thermodynamic conditions (e.g. p and T, or V and T, or ....) from the properties ('shapes', mutual interactions ...) of the molecules

Equilibrium and non-equilibrium

Analytical solutions and numerical solutions (simulations)

Part 1

Phenomenological (chemical) thermodynamics

All this can be found in Atkins, Physical Chemistry
(pages will depend on edition)
or any other good book on Physical Chemistry

You can watch my friend Prof. Don Blake's (UC Irvine) undergraduate class (lectures 8,9, 10 ...)
`http://ps.uci.edu/content/general-chemistry-1b`

The three
'Laws' (or **'Principles'**) of phenomenological thermodynamics
(*essentially Atkins chap 2 ff,*
they can be stated in many different ways)

(I) Energy is never lost

(II) The total entropy S of an isolated system never decreases
A (cyclic) heat engine cannot convert 100% of the heat Q,
to mechanical work
`https://en.wikipedia.org/wiki/Second_law_of_thermodynamics`
....

(III) While the 'potentials' (or 'state functions*') generally have an arbitrary zero, the Entropy (S) has a physical zero (called 0 K), which can be reached only asymptotically

* has **absolutely nothing** to do with the term "state" that we will encounter in quantum mechanics (Part 2)

A few things for you to remember (symbols as usual)

Many definitions:
system, closed, isolated, adiabatic ...
equations of of state (potentials)
....

$$dU = \delta Q + \delta W_{\mathrm{expansion,external,electric,....}}$$

$$H = U + pV \quad G = H - TS \quad F(A) = U - TS \quad \mathrm{d}S = \frac{\delta Q}{T}$$

heat capacity

$$c_V = \frac{\partial U}{\partial T}, \quad c_p = \frac{\partial H}{\partial T}$$

chemical potential

$$\mu = \frac{\partial U}{\partial N} \; (\; \frac{\partial H}{\partial N} \; , \; \frac{\partial G}{\partial N} \; ... \;) \text{ depending on conditions}$$

physical understanding later

$$c_{p(V)}(T)?? \rightarrow \text{ statistical thermodynamics}$$

$$S = k_\mathrm{B}\Omega \rightarrow \text{ statistical thermodynamics}$$

van'tHoff

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta H}{RT^2}$$

Clausius Clapeyron

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta H_\mathrm{vap}}{RT^2}$$

Thermochemistry (Standard states, Haber cycles etc. etc.)

– Compute $\Delta G, \Delta H$ for reactions (possibly involving phase changes)

Equilibria ($\Delta S = 0!$), in particular phase equilibria

$$\nu_a A + \nu_b B \leftrightarrows \nu_c C + \nu_d D \ , \quad \sum_i \nu_i \mu_i = 0 \ , \quad K_{\mathrm{C}} = \frac{[A]^{\nu_a}[B]^{\nu_b}}{[C]^{\nu_c}[D]^{\nu_d}}$$

(Simplified $\mu_{\mathrm{A}} = \mu_{\mathrm{B}}$, e.g $\mu_{\mathrm{liq}} = \mu_{\mathrm{sol}}$)

Again, this **does not say anything** how, or whether, an equilibrium is established, how long it may take ......

There are more questions that phenomenological thermodynamics does not ask, e.g.

– What is the molecular origin of .....
(phenomenological thermodynamis does not know about molecules)

– What is the evolution of ....
(phenomenological thermodynamis does not know "time"
even though it is called "dynamics",
but there is something like non-equilibrium thermodynamics)

–

$\Longrightarrow$ statistical mechanics, simulations

Part 2

Quantum Mechanics (QM)

You should already know about quantum mechanics
(*Certainly if you are a chemist, or a chemical engineer from Kasetsart*)

In this section we will
– either just brush up your knowledge or
– try to establish the very basic ideas underlying this approach

Use any textbook of quantum mechanics (e.g. I.R. Levine)
or quantum chemistry (e.g. Aj. Vudhichai's booklet)
or Aj. Chachiyo's free book (in Thai!)
`https://docs.google.com/viewer?a=v&pid=sites&srcid=ZGVmYXVsdGRvbWFpbnxzaWFtcGh5c2ljc3xneDoyOWZhMTYwNzRmYjYxOGIx)`

Why do wee need QM?

- rationalize, find (consistent, mathematical) expressions for many new
  (experiments (around 1900-1920)
  black body radiation, atomic spectra, Franck-Hertz experiment,
  photoelectric effect, ... , Stern-Gerlach experiment, ...)
  Heisenberg uncertainty principle

Consequence: need a new description (theory)

Postulates of QM, Eigenvalues and Eigenfunctions

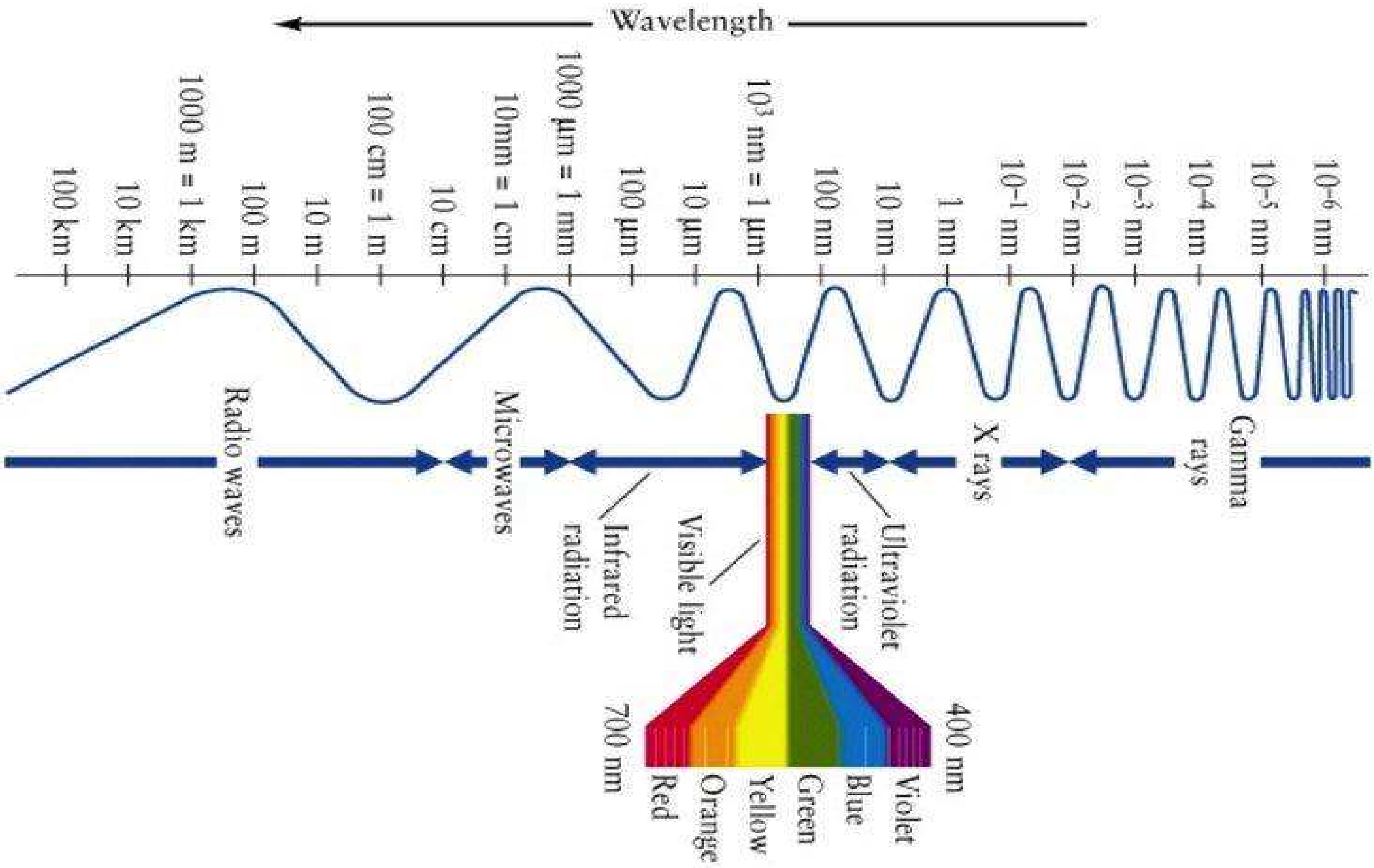
http://vergil.chemistry.gatech.edu/notes/quantrev/node20.html

→ two mathematically equivalent formulations:
Heisenberg , Schrödinger

→ Heisenberg: matrices / operators

→ Schrödinger: time dependent differential equation
(Schrödinger Equation)

Length and energy scale



Length and energy scale

Typical energy to compare with in chemistry:

thermal energy at T= 300 K:

$$E^{\mathrm{thermal}} = k_{\mathrm{B}} \cdot 300 \text{ K} \;,\;\; k_{\mathrm{B}} : \text{Boltzmann's constant}$$

$$= 25.86 \text{ mev} = 0.5959 \text{ kcal/mol} \;, \text{ or } 208.5 \text{ cm}^{-1}$$

corresponding wavelength: $1/208.5$ cm

$$i\hbar\frac{\partial}{\partial t}\Psi(R,t) = \hat{H}\Psi(R,t)$$

roughly equivalent to Newton's Equation $m\frac{\partial^2 r}{\partial t^2} = f = m{\cdot}a$

Impose **steady state**:
$\rightarrow$ time independent Schrödinger Equation

$$\hat{H}\psi_j(R) = E_j \cdot \psi_j(R) \quad \text{(eigenvalue eigenvector(function) equation)}$$

$\hbar$ is Planck's universal constant h divided by $2\cdot\pi$;
i is the imaginary unit ($\sqrt{-1}$);
Ψ_j are the wave functions (or state functions or eigenfunctions),
R refers to all variables (degrees of freedom) of the particles (electrons, nuclei, ...) involved;
$\hat{H}$ is the Hamiltonian (Heisenberg: Hamilton operator) which describes the system;
E_j are the accessible energies (energy levels, eigenvalues ...);
j (or many js), the quantum numbers,
which count the eigenfunctions and eigenvalues

$$\boxed{\hat{H}\psi_i = E_i \cdot \psi_i}$$

Everything we know about the system of interest

is in the operator $\hat{H}$, the Hamiltonian

It describes the system completely

- The system described by the Hamiltonian can then exist (forever) in a state ψ_i (Eigenvector, Eigenfunction, State) with an energy E_i (Eigenvalue)
- The counting number(s) (here i) is/are then called "quantum number(s)"
- It is convenient to use different counting schemes for different systems, see below

- simple model systems

model Hamiltonian	Eigenvalues	Eigenfunctions
particle in box	$E_n = h^2/(8mL^2) \cdot n^2, n = 1, 2, 3...$	Cosine
harmonic oscillator	$E_v = \hbar\omega(v + 1/2) \quad , v = 0, 1, 2, ..$	Hermite·Gaussian
rigid rotor	$E_l = \hbar^2/(2I)l(l + 1), l = 0, 1, 2...$	spherical harmonics (l, m)
hydrogenoid	$E_n = -\mathcal{R} \cdot 1/n^2, n = 1, 2, 3...$	*
....	......	...

Notes: The frequency ω can be computed by classical mechanics, see normal modes

* this is what you have almost exclusively studied (→ QC)
3 (4 with spin) quantum numbers ....

These models can be used to study various problems:

'particle in box': π-electron systems, rings, confined particles, translational motions of molecules

'harmonic oscillator': molecular vibrations, solids, much used in statistical mechanics

'rigid rotor': molecular rotations

'hydrogenoids', atoms (with approximations (Slater) also polyelectronic), basis of LCAO methods ...

i.e. with very different masses and lengths !
→ Compare the typical energies

- relation of QM to classical (Newton's) mechanics
  the larger the mass, the higher the temperature, the more 'classical',
  see "de Broglie (thermal) wavelength":

$$\lambda = \frac{h}{p} \ , \quad \text{with } p \text{ from } \ < E_{\text{kin}} >: \ \lambda = \frac{h}{\sqrt{2\pi m k_{\text{B}} T}}$$

$$\lambda < \text{particle dimension} : \ '\text{classical}' \text{ behavior} : \ (\text{trajectory}, \ \text{no interference})$$

$$\lambda > \text{particle dimension} : \ '\text{quantum}' \text{ behavior} : \ (\text{uncertainty principle}, \ \text{interferences})$$

for you to remember

Some of the approximations and abbreviations when quantum mechanics (QM) is used to study the electrons in atoms and molecules
i.e. for quantum chemistry (QC) (*in no particular oder*):

- Born-Oppenheimer approximation
- Mean-field approximation
- Orbitals
- LCAO
- Hartree Fock
- Basis set
- SCF
- Møller-Plesset perturbation
- Configuration Interaction (CI)
- DFT
- ...
- Variational principle

- Born Oppenheimer **approximation**

Let's look at a molecule.
Its Hamiltonian $\hat{H}$ will depend on the positions of the nuclei $\mathcal{R}$ and electrons r, and so will the Eigenvalues (energies) and Eigenfunctions (states), e.g $\Psi(\mathcal{R}, r]$

Exercise:
Write down the Hamiltonian (total energy $=$ kinetic $+$ potential energy; the only potential energy is electrostatic, we neglect anything else (which would be what?))

In the Born-Oppenheimer (B-O) approximation, the Schrödinger equation for $\Psi(\mathcal{R}, r]$ with the Hamiltonian that you have written down, can be separated into two Schrödinger equations, one for the nuclei $\mathcal{R}$ and one for the electrons r.

The one for the **nuclei** can in many cases (but not always!) be replaced by classical mechanics (MD)

Solving the equations for the **electrons**, at fixed positions of the nuclei (which appear in the Hamiltonian of the electronic equation (via the PES) is the topic of quantum chemistry

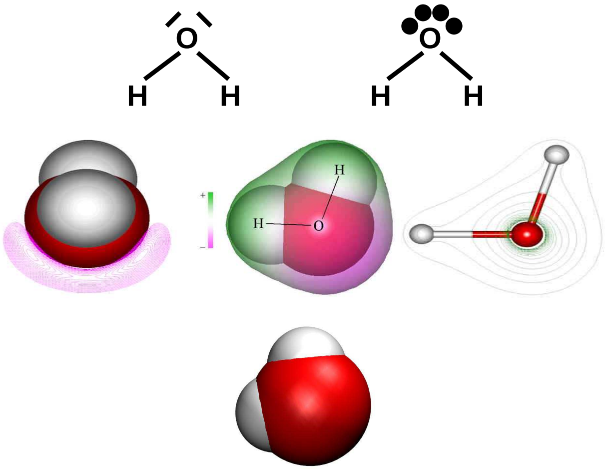
Keywords (which you should remember) for the solution of the Schrödinger equation for the electrons at fixed positions of he nuclei:

- Orbital **approximation**: We write the wavefunction of an atom as a product (with suitable symmetry) of one-electron functions
- We consider the spin functions independently of the other degrees of freedom
- LCAO: we write the molecular wave function as a product (Slater determinant) of atomic functions
- We expand the wavefunction in terms of some (orthonormal) basis (e.g.Gaussians)
- We make use of the (linear, the L in LCAO) variational principle to find the lowest energy

- Mean field **approximation** (Hartree-Fock (HF)), i.e. independent electrons
- Configuration interaction (electrons 'see' each other individually, not just as a 'mean field' made by the other $n-1$ electrons)

These methods are really **ab-initio**,
i.e. "from the very beginning", "from scratch",
the variational principle* guarantees that (within the approximations made)
the results can always be improved.

Density Functional Theory (DFT) does not qualify as 'ab-initio' since it contains a lot of 'empirical' information in the chosen functional.
So you 'must know what you do', and there is no systematic way to improve results



Remember that these are just **representations**, and
nothing more

* Excursion: The variational principle

Expand a trial function Φ in terms of the (orthonormal)
Eigenfunctions ψ_i of your problem:

$$\Phi = \sum_i c_i \cdot \psi_i \quad , \quad \hat{H}\psi_j = E_j \cdot \psi_j \quad , \quad \int \psi_i \psi_j \, \mathrm{d}\tau = \delta_{ij}$$

Assume Φ to be real,
compute energy of system in trial state Φ:

$$E_\Phi = \langle \Phi | \hat{H} | \Phi \rangle = \frac{\int \Phi \; \hat{H}\Phi \; \mathrm{d}\tau}{\int \Phi\Phi \; \mathrm{d}\tau} = \frac{\sum_{ij} c_i \; c_j \int \psi_i \; \hat{H}\psi_j \; \mathrm{d}\tau}{\sum_{ij} c_i \; c_j \int \psi_i \psi_j \; \mathrm{d}\tau}$$

Subtract the lowest (ground state) energy E_0 of your system:

$$E_\Phi - E_0 = \frac{\sum_{ij} c_i \; c_j \; E_j \int \psi_i \psi_j \; \mathrm{d}\tau}{\sum_{ij} c_i \; c_j \int \psi_i \psi_j \; \mathrm{d}\tau} - E_0 = \frac{\sum_i c_i \; c_i \; E_i}{\sum_i c_i \; c_i} - E_0$$

$$E_\Phi - E_0 = \frac{\sum_i c_i\ c_i\ E_i}{\sum_i c_i\ c_i} - \frac{\sum_i c_i\ c_i\ E_0}{\sum_i c_i\ c_i} = \frac{\sum_i c_i\ c_i\ (E_i - E_0)}{\sum_i c_i\ c_i} > 0$$

because **all** $E_i - E_0 > 0$ (since E_0 is the lowest energy)

So any energy E_Φ is larger than E_0.

How to vary the cs so that to find the best possible Φ
is a different question.

Since we have written Φ as a **linear** function of the ψ,
the optimum set of cs can be found by matrix operations.
But it can also be done differently by other methods to find minima.

Part 3

Basic ideas of statistical thermodynamics

Some of this can be found in Mc.Quarrie, Statistical Mechanics
and in Pathria, Statistical Mechanics

– What is **the purpose** of statistical mechanics ?
(also called statistical thermodynamics, statistical physics, ...)

– What is it good for? Why should you study it?

Have you ever asked yourself:
→ Why is warm water a better solvent than cold water?
→ Why am I healthy if my body temperature is T ≈37°C
and dead if it is T ≈47°C ?

You know e.g. that an equilibrium constant K may be
temperature dependent
pressure (density) dependent
may depend on the solvent
......

The properties on chemical systems (materials, whatever) depend strongly on temperature (and other circumstances)
Just knowing e.g. the energy at $T = 0$ K is not sufficient

First (this part)

– Conceptual and (some) technical/mathematical/computational background

Then (next part)

- **Molecular simulations** are one way to do statistical mechanics
  - Molecular Dynamics or MD
  - Monte Carlo or MC

We observe: people say: "The spectrum is the fingerprint of a molecule"

Is this true?

Always?

Under which conditions?

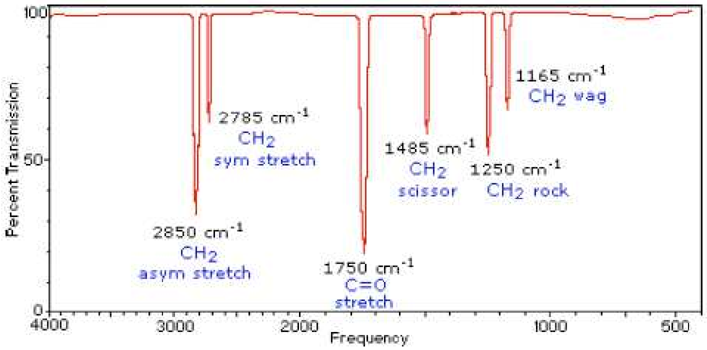
---

microscopic interpretation

MACROSCOPIC spectrum
(on a screen or a piece of paper)

CH_2 sym. stretching vibration
CH_2 asym. stretching vibration
C=O stretch
...
...
How can they know that?

IR absorption spectrum of formaldehyde in gas phase



Formaldehyde gas phase IR spectrum

$H_2C=0$, so 12-6 normal modes

1 molecule

some $\mathbf{10}^{17}$ molecules (10^{-6} N_A)

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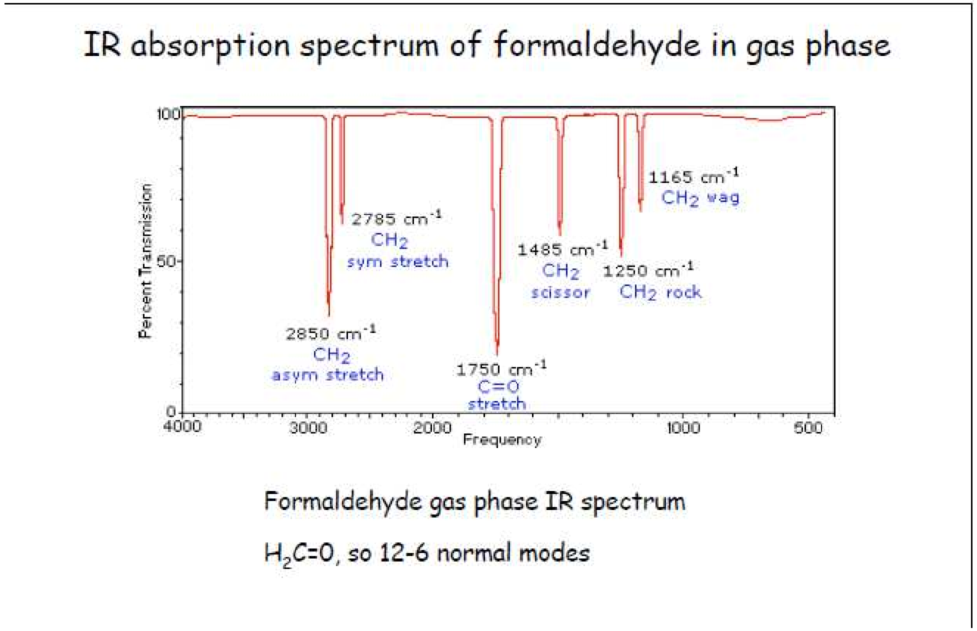
IR absorption spectrum of formaldehyde in gas phase

Formaldehyde gas phase IR spectrum

$H_2C=0$, so 12-6 normal modes

1 molecule

some **10^{17}** molecules (10^{-6} N_A)

They know it based on **assumptions** such as:

– All H_2CO molecules 'do the same thing' (vibrate, rotate, ...)

– They do it **independently** of each other
(i.e the vibration of molecule i does not change whether or not another molecule j is nearby)

'independent' means that the molecules do not interact, or, better,
that their interactions can be **neglected**
because (e.g.) the interaction energies involved are (very) **small compared to** some other
energies of interest,

e.g. the thermal energy $k_{\mathrm{B}}T$, k_{B} is Boltzmann's constant.

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What happens if these assumptions are not valid any more?

More things to think about:

– Think e.g. of a typical property of a liquid like 'viscosity'. One molecule does not have a viscosity, two molecules don't have a viscosity, ... , and you could actually ask yourself:
How many molecules does it take so that something like viscosity arises?

– So we need a technique to treat many (enough) molecules.
(*If we are after something like "viscosity" (only an example!) we need not only to know 'on the average' where the molecules are (the 'structure', thermodynamics), but also how they move (the 'dynamics').*
We shall not deal much with this aspect here.

– And last but not least:
Nothing occurs at $T = 0$ K. We need also to understand the effect of **temperature**.

In other words

– The properties of matter (e.g. its structure, (e.g. phases in solids, but also in liquids), internal energy, viscosity, diffusion, ...)
cannot be related to the properties of a single molecule alone.
Such properties are properties of ensembles of many (how many?) molecules.
Such properties depend on the conditions e.g.:
temperatures T, density ρ, pressure p, ...

– Most methods in theoretical chemistry consider only the (potential) energies at T $=$ 0 K an thus neglect the influence of the kinetic energy (entropy).

– This is sufficient in many cases, e.g. when energy differences between educt and product in chemical reactions are large.

However, many reactions, e.g. in biology, are so fine-tuned that e.g. **temperature becomes a very important factor**

The solution
– Ludwig Boltzmann (1844-1906) and **statistical mechanics**

Statistical mechanics ≈ statistical thermodynamics
≈ statistical physics ≈ many particle physics ≈

– **Analytical work**
Very simple models, gas phase ((almost) independent molecules),
some crystalline solids (→ phonons]

– **Molecular simulations**
allow to go beyond simple (e.g. harmonic potentials)
and 'academic' cases, liquids, interfaces, inhomogeneous systems, ...

Here we shall briefly look at the **"partition function"**
and then study one simulation method: **Molecular Dynamics (MD)**
the other important one is (Metropolis) Monte Carlo (**MC**),
and there are several others (to be discussed if we have time)

Historic remark:

Numerical work (e.g. MD, MC) was not possible before computers became generally available (1970ies with some precursors (Edward Teller, Bernie Alder ...) since the 1940ies (Manhattan Project))

Theoreticians were used to search for 'analytical solutions' (i.e. finding mathematical solutions of (usually differential or integral) equations)

Simulations required a different way of thinking, they were thus often called **computer experiments**

$\Longrightarrow$ So we can say:

Statistical mechanics is a method to deal with systems of many **interacting molecules** at **finite temperatures**.

microscopic

MACROSCOPIC

⇒ **Ludwig Boltzmann** and **Statistical Mechanics**

1844 -1906

Note: Ludwig Boltzmann probably knew nothing about quantum theory.
Max Planck's famous seminar
(introducing the 'quantum', Planck's constant (h or $\hbar$))
in Berlin was on Dec. 14, 1900.

WIKIPEDIA says it all:

It (i.e. statistical mechanics) provides a framework for relating the **microscopic** properties of individual atoms and molecules to the **macroscopic** or bulk properties of materials that can be observed in everyday life

The basic tenet of statistical mechanics:

microscopic		**MACROSCOPIC**
microstates	$\Longleftrightarrow$	**MACROSTATE**
atoms, molecules		pressure, temperature , viscosity, ...
$\hat{H}\psi = E\psi$		$p, V, T, Q, \Delta U, S, ...$
$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}$		observables
Schrödinger equation		thermodynamics,
$\rightarrow$ need to simplify (coarse grain)		classical theories

The problem is:

Under “normal“ conditions (i.e. at $T > 0$) there are, for any (physical/chemical) system*,

NOT ONLY ONE,
but **very, very, very many**
microscopic states (microstates)
that are **compatible with**

ONE given MACROSTATE of that system.

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* System: E.g. some **condensed phase**: A liquid, a supercritical fluid (vapor), a solution, a mixture, ...

Example

Take 1 mole of water.
Gibbs' rule (remember?) says you can specify (e.g.)
N (1 mole), the pressure (e.g. p =1 bar), and the temperature (e.g. T =298 K).
When you have specified these 3 quantities,
you **cannot** specify any 4th one (e.g. some volume ($V = n$ cm^3))
with these given values for N, p, T
the system will just 'have' the volume it wants.

This is one **MACROSTATE** of this system
and you can do classical (or phenomenological) thermodynamics
($\Delta U, \Delta G, \Delta S, c_p, c_V$, ... see part 2)

Example (in principle only, in reality it's much more complicated)

1	2	3	4	
vJn	v’J’n’	v’’J’’n’’		microstate 1
vJn	v’J’n’	v’’J’’n’’		microstate 2
vJn	v’J’n’	v’’J’’n’’		microstate 3

(*different colors mean different values*)

All these (and many more) microstates can lead (be compatible with) the same MACROSTATE (N, p, T)
(→ principle of equal 'a-priori' probability)

Very important

At the conditions in chemistry ($T \approx 200, 300, 400...$ K,
and for 'heavy enough' molecules ($m > m_{\mathrm{H}_2}$))
the translational/rotational/(vibrational) microstates can be described by
classical (Newtonian) mechanics
instead of quantum mechanics (Quantum numbers → positions and velocities)

(remember the 'de Broglie wavelength' $\lambda = h/p = h/(mv)$, p momentum, v velocity)

$\Longrightarrow$ Assuming that there is no electronic excitation
(we stay in the electronic ground state)
we can do classical (Boltzmann) statistical mechanics.

This also implies that we have many more **microstates** than particles, so
we can neglect spin (Pauli principle)
If not: → quantum statistics:
Fermi statistics (fermions), Bose-Einstein statistics (bosons)
example: electrons in metals (Fermi)

Summary of the introduction to stat.mech.

A MACROSTATE is completely described by only very few macroscopic variables, e.g. N_i, V, p, ... (→ Mr. Gibbs)

We can never (**really never never ever!)** hope to know all* microstates $\mathcal{P}_j$

Using, as just argued, classical mechanics, we can call:

$$\mathcal{P}_j = \{\vec{r}_1, \vec{r}_2, \vec{r}_3, ..., \vec{r}_{N_A}, \vec{v}_1, \vec{v}_2, \vec{v}_3, ..., \vec{v}_{N_A} \text{ at (say) some time } t_j\}$$

one (of many) **microstate**s of a chemical system compatible with one MACROSTATE.

* Roughly: There are more microstates in a glass of water than stars (possibly atoms) in the universe!

Summarize the Simplifications

(**i**)(If the temperature is sufficiently high and/or the particles sufficiently heavy (i.e. the de Broglie wavelength $\lambda = h/p$ is small compared to the dimension of the particles) the atoms/molecules can be considered as 'classical' particles, subject to Newton's equation $M_i \cdot \frac{\partial^2 \vec{r}_i}{\partial t^2} = \vec{F}_i(........) \quad i = 1, ..., N$.
→ Exit Schrödinger's equation **(for the nuclei ONLY!)**

(**ii**) We can in some way 'pre-calculate' the interactions between the molecules and use these pre-calculated interactions (**the model**) in our study.
This 'removes' the electrons (which are at the origin of the interactions) from the problem (**The Born-Oppenheimer approximation**)

What to do about all this?

level of description of microstate		What can be done?
everything quantum mechanical	⇒	almost impossible except in very simple cases
classical mechanics highly simplified problems e.g. particle in the box, rigid rotor harmonic oscillator	⇒	analytical theory →**partition function** **Part 4**
classical mechanics, Born-Oppenheimer interaction models	⇒	**Computer simulations** MD or MC **Parts 5,6**
(some) electrons QM nuclei classical	⇒	special simulations

Part 4

Statistical thermodynamics, a few analytical results

This is entirely taken from Mc.Quarrie, Statistical Mechanics
see Wilson, Decius & Cross for Normal Modes

We start from the assumptions just described (classical mechanics, forget about spin) and introduce Boltzmann's basic concepts (with a minimum of math, see textbooks for a rigorous treatment).

At the end, we will see that QM sneaks in again
– isotope exchange equilibria
– ortho-para hydrogen problem

Philosophy gets on my nerves. If we analyze the ultimate ground of everything, then everything finally falls into nothingness. But I have decided to resume my lectures again and look the Hydra of doubt straight into the eye, (Ludwig Boltzmann (1844-1906))

Boltzmann ($\dagger 1906$) did not know about quantum mechanics,
but firmly believed in the existence of 'molecules'

So the arguments leading to the correct
statistical mechanical expressions,
(essentially the '**partition functions**',
called $\Omega, Q = Z, \Xi$ ... , as the case may be)
where much more difficult for him (i.e. using classical mechanics)
than for us (since we **can** define **'state'**).

The basis idea is that there are an extremely large number of micro- (quantum-) states that all lead to the same macroscopic state, characterized e.g. by a certain number of molecules N in a certain volume V having a certain total energy E (thus (NVE))
(or (NpT) or (NVT) or (μpT) or $(N_1 N_2, V, E)$ or ...(Gibbs phase rule))

If one knows (or knows how to construct for a model)
all possible micro-states
one can (try to) compute the so-called '**partition function**'
(*German* **Zustandssumme = sum over states**)
by summing (integrating) over all (supposedly known) states compatible with the given conditions (e.g. NpT).

If one has this partition function (Ω, Q (Z) as the case (i.e. the external conditions) may be)
thermodynamic averages, i.e. the average value of observables under the given conditions, can be obtained.

under conditions of N, V, E constant,
the partition function is call **microcanonical** Ω (capital ω, o-mega)

under conditions of N, V, T constant,
the partition function is call **canonical** Q or Z
(*this is the one mostly used*)

under conditions of μ, V, T constant,
the partition function is call **grand canonical** Ξ (capital ξ, xi)

under conditions of .... constant,
the partition function is called **.......**

We shall deal, very little, only with Ω and Q

From the partition function $Q\ (Z, \Omega, ...)$ one can compute thermodynamic quantities like entropy, free energy, ..

From Ω

$$S = k_{\mathrm{B}} \ln \Omega \ \ (\textit{the most famous equation})$$

It says W, from German 'Wahrscheinlichkeit' (probability), because that is really what it is (as we shall shortly see)

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \text{ etc. etc.}$$

From Q, the canonical partition function

$$Q = \sum_{\textbf{all states } i} \exp(\frac{-E_i(N,V,T)}{k_\mathrm{B}T})$$

$$S = k_\mathrm{B}T\ (\frac{\partial \ln Q}{\partial T})_{N,V} + k_\mathrm{B} \ln Q$$

$$\langle E \rangle = k_\mathrm{B}T^2\ \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

For an equilibrium

$$\nu_a A\ +\ \nu_b B\ \rightleftharpoons\ \nu_c C\ +\ \nu_d D$$

$$\mu_A = -k_\mathrm{B}T\ \left(\frac{\partial \ln Q}{\partial N_A}\right)_{N,V,T} \approx -k_\mathrm{B}T\ \ln \frac{q_A(V,T)}{N_A}$$

q is the **molecular partition function** (see later)

The average value $\langle ... \rangle$ of any quantity (observable) A over the given ensemble (NVE, NVT , etc.) is given by (just two examples):

From Q (NVT)

$$\langle A \rangle_T = \frac{1}{Q} \int_{\text{all } p,q} A(p,q) \cdot \exp \frac{E(p,q)}{k_{\mathrm{B}}T} \, \mathrm{d}p \, \mathrm{d}q \tag{AvQ}$$

From Ω (NVE)

$$\langle A \rangle_E = \frac{1}{\Omega} \int_{\text{all } p,q} A(p,q) \cdot \delta(E(p,q) - E_0) \, \mathrm{d}p \, \mathrm{d}q \tag{AvΩ}$$

where q stands for all positions variables $(x_1, y_1, z_1, x_2.y_2, ..., z_N)$
and p for all velocity variables $(vx_1, vy_1, ..., vz_N)$

So the integrals are $6N$-fold integrals ($\int \int \int ...... \int$) over the (q,p)-space, which is called **phase space**

$\Rightarrow$ not really doable (except in some very simple cases)!

We will look only at one case: "the diatomic ideal gas"
(see McQuarrie for details)
under NVT conditions → canonical partition function Q (Z)

Even though we will use classical statistical mechanics, it is simpler to argue with QM

The wavefunction for one molecule is assumed to be

$$\Psi = \psi_{\text{trans}} \cdot \psi_{\text{rot}} \cdot \psi_{\text{vib}} \cdot \psi_{\text{elect}}$$

(this is not always possible, nuclear spin is neglected)

We will use the following approximations:
ψ_{trans}: particle in box states, continuum
ψ_{rot}: rigid rotor states, almost classical
ψ_{trans}: harmonic oscillator states, can be summed analytically
ψ_{elect}: whatever you have computed quantum mechanically, ground state only

We can then compute a 'molecular partition function' q

$$q = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \cdot q_{\text{elect}}$$

and since the molecules are assumed **not to interact** (ideal gas):

$$Q = \frac{q^N}{N!}$$

(It is with these approximations that most quantum chemistry programs propose values for such quantities)

All this is not easy, it takes one semester to derive the expressions,
and we have no time to do it here

$$q_{\text{molec}} = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \cdot q_{\text{elect}}$$

Approximations:

q_{elect}: Only electronic ground state

q_{trans}: Particle in box states
q_{rot}: Rigid rotor states
q_{vib} : Harmonic oscillator (normal mode) states

Remember?

Hamiltonian	Eigenvalues	Eigenfunctions
particle in box	$E_n = h^2/(8mL^2) \cdot n^2, n = 1, 2, 3...$	
harmonic oscillator	$E_v = \hbar\omega(v + 1/2) \quad , v = 0, 1, 2, ..$	
rigid rotor	$E_l = \hbar^2/(2I)l(l + 1), l = 0, 1, 2...$	

So, basically, we have to do sums like:

$$q_{\text{trans}} = \sum_{n=1}^{\infty} \exp \frac{-\mathcal{C}n^2}{k_{\text{B}}T} \quad \text{for the } x, y \text{ and } z \text{ directions}$$

$$q_{\text{rot}} = \sum_{l=1}^{\infty} \exp \frac{-\mathcal{D}l(l+1)}{k_{\text{B}}T} \quad \text{for the 3 axes of rotation (moments of inertia)}$$

$$q_{\text{vib}_\text{i}} = \sum_{v_i=0}^{\infty} \exp \frac{-\mathcal{E}_i(v_i+1/2)}{k_{\text{B}}T} \quad \text{for each mode } i \text{ (only 1 here)}$$

with $\mathcal{C}, \mathcal{D}, \mathcal{E}_i$ constants, see previous page

This can be done (maths), we'll only quickly look at the vibrational part

– The infinite sums can be carried out either exactly or to a very good approximation (see textbook)

– So we need to find
the $\mathcal{C}$s, $\mathcal{D}$s and $\mathcal{E}$s

– For a molecule, (except for constants),
$\mathcal{C}$ contains the masses m,
$\mathcal{D}$ contains the moments of inertia I (from the masses and the geometry)
and $\mathcal{E}$ contains the vibrational frequencies

– This data is available in (from) quantum chemical programs (GAUSSIAN and such), so thermodynamic quantities can be computed with these approximations
(non-interacting molecules, rigid rotor, harmonic frequencies)

Example: Equilibria (see McQuarrie's book p.143)

$$\text{from the equilibrium condition : at } T, V = \text{const. :} \quad \sum_i \nu_i \mu_i = 0$$

$$\nu_i = \frac{N_i}{\sum_i N_i} \quad \text{mole fraction}$$

$$A + B \rightleftarrows 2AB \quad , \quad K = \frac{N_{AB}^2}{N_A \cdot N_B} \quad = \quad ..... \quad = \quad \frac{q_{AB}^2}{q_A \cdot q_B}$$

So we need to find the individual qs for the molecules A, B and AB, combine them to get the Qs
(*which will be simple and only the* q*s survive, see above*),
and compute from them the ...., see equation .... above

In most chemical reactions, the main contribution to K comes from the q_{electr}-parts of the partition functions

Let's test this in a particular case:

$$\text{experimentally:} \quad \mathrm{H_2 + D_2 \rightleftarrows 2HD} \quad , \quad \mathrm{K} \neq \frac{2^2}{1 \cdot 1} = 4$$

K becomes $= 4$ only when $T \to \infty$. Why this?

It cannot be the q_{electr} since the electronic energies are **the same** for H_2, D_2 and HD (**Born-Oppenheimer approximation**)
So what is it?

Equilibrium constant, see e.g.
http://www4.ncsu.edu/~franzen/public_html/CH795N/lecture/XV/XV.html

---

We note in passing: The partition function contains no information about how the system gets from one state to the other, no time
(*like when you consider equilibria (say chemical potentials μ), you do not worry how you got there, how long it took to reach equilibrium*)

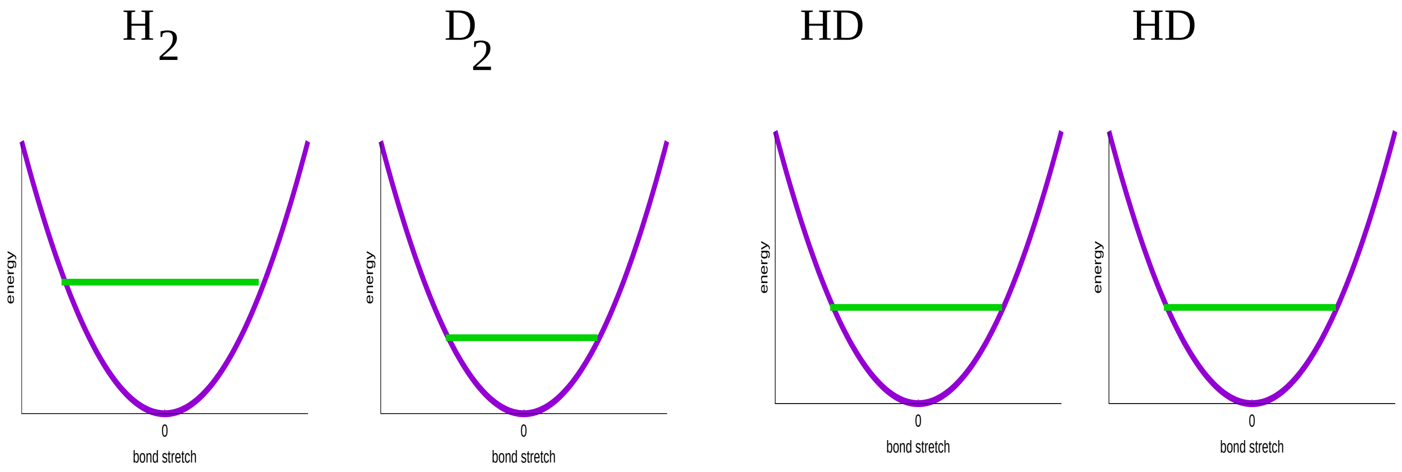
$$\mathrm{H_2 + D_2 \rightleftarrows 2HD} \quad , \quad \mathrm{K} \neq \frac{2^2}{1 \cdot 1} = 4$$

– q_{elect} is the same for H_2, D_2, HD

– One can check (not done here) that q_{rot} also does not contribute (even though the Is are not the same)

– this leaves q_{vib}
We go to a sufficiently low temperatures* so that the sum in q_{vib} can be approximated by the first term, $i = 0$, i.e. the zero point energy, ZPE

* but not too low, otherwise, in Hydrogen, other quantum effects (ortho- vs. para-hydrogen) have to be considered



$$\text{ZPE} = \frac{\hbar\omega}{2} = \frac{\hbar\sqrt{\frac{k}{\mu}}}{2} \quad , \quad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad , \quad \text{we set } m_{\text{H}} = 1\,,\ m_{\text{D}} = 2\,,\ k = 1\,,$$

$$\hbar = 1 \qquad \Rightarrow \mu_{\text{H}_2} = \frac{1}{2}\,,\ \mu_{\text{D}_2} = 1\,,\ \mu_{\text{HD}} = \frac{2}{3}$$

$$\text{ZPE}_{\text{H}_2} = \frac{\sqrt{2}}{2} \quad + \quad \text{ZPE}_{\text{D}_2} = \frac{1}{2} \qquad\qquad \text{ZPE}_{\text{HD}} = \frac{\sqrt{\frac{3}{2}}}{2} \quad (\cdot 2)$$

Energy balance : 1.207 $<$ 1.225

So the energy is a bit lower on the left hand side,
the partition function $(\exp(-....)$ thus a bit higher,
and K thus less than 4

Of course, the deviation of K from 4 will depend on temperature:
the higher T, the smaller the deviation
(as befits a quantum effect: when all vibrational levels become populated,
the effect goes away)

Excursion: Normal Modes (spectroscopy, computing simlified partition functions, ...)

In some cases, Newton's coupled differential equations:

$$m_i \frac{\partial^2 r_i}{\partial t^2} = \vec{\mathrm{grad}}_i V = \vec{F}_i \quad , \quad i = 1, N$$

do have an analytical solution.

The most famous case are 'normal modes'
(*physicists talk about 'group coordinates'*),
which exist ONLY if the right hand side
(rhs, i.e. the potential V and forces $\vec{F}$)
have a very special form* and the motions are 'infinitesimally small' around an extremum (usually minimum, however, → transition states).

Normal modes are a generalization of the well-know
harmonic oscillator problem

* Otherwise, the equations cannot be solved analytically (Henri Poincaré)
$\Rightarrow$ numerical solutions = simulations

Reminder:

$$\omega = \sqrt{\frac{k}{m}} \quad , \quad E_v = \hbar\, \omega\ (v + \frac{1}{2})$$

m: the mass; k: the force constant (2nd derivative of potential)
ω: frequency, v **vibrational quantum number**

(Note again the the frequency computed from classical mechanics is used in the expression for the quantum energies)

Classical solution:

$$\Delta x(t) = A \cdot \cos(\omega t) + B \cdot \sin(\omega t) = C \cdot \cos(\omega t + \delta)$$

$\Delta x(t) = x(t) - x_0$: a displacement with respect to an equilibrium position
A, B, C, δ from the initial conditions

for two masses m and M (and one 'spring') on has:

$$\omega = \sqrt{\frac{k}{\mu}} \quad , \quad \frac{1}{\mu} = \frac{1}{m} + \frac{1}{M} \quad , \quad \text{and } E_v = \hbar\, \omega\, (v + \frac{1}{2})$$

Spring: Hooke's law $V(x) = k \cdot (x - x_0)^2$
(often written as $V(x) = k/2 \cdot (x - x_0)^2$

For more masses and 'springs', we generalize the springs as:

$$V = \sum_{ij} k_{ij} \rho_i \rho_j \;\; (which\ can\ be\ expanded\ as\ V = \sum_{kl} c_{kl}\, u_k^{x,y,z} u_l^{x,y,z} \;\;)$$

k_{ij} are (generalized) force constants (force field),
ρ internal (Wilson) coordinates (stretch, bend, torsion ...)
$u_k^{x,y,z}$ are (infinitesimally) small displacements
of particle k in x, y or z direction

Such a 'harmonic' potential can be obtained by expanding any potential around an extremum (minimum)
This is what the quantum chemistry codes do.

With this potential (bilinear form) Newton's equations of motion can be solved analytically
(*see Wilson, Decius and Cross*)
and one gets for the motions of particle i:

$$\vec{r}_i(t) - \vec{r}_i^{\,0} = \sum_{J=1}^{\mathcal{N}} A_J \cdot \vec{Q}_i^{J} \cdot \cos\left(\Omega_J \cdot t + \delta_J\right)$$

There are (if ....) $\mathcal{N} = 3N - 6$ normal modes for a system (molecule) of N masses, $\mathcal{N} = 3N - 5$ for linear systems (molecules)

A_j and δ_J are arbitrary amplitude and phase factors
(which depend on the initial conditions)

$\vec{Q}_i^{J}$ are vectors (the normal modes) describing the relative motion of atom i under mode J.

Properties of normal modes, look at the equation:

- All atoms i in a normal mode J move 'in phase' (or anti-phase), the A and δ depend only on J, not on i

- Normal modes are 'orthogonal' (or adiabatic) to each other,
this means a mode J will not transfer vibrational energy to another mode
(*you know that e.g. in molecules this is not entirely true*)

- Normal modes are the main tool to assign and interpret
vibrational spectra (IR, Raman)
the symmetry of the normal modes is related to the selection rules

We can uses the frequencies Ω from the classical normal mode calculations to obtain the QM energy levels
The quantum energies are, since the modes are independent:

$$E_{v_1,v_2,v_3,\ldots,v_{\mathcal{N}}} = \hbar\Big(\Omega_1(v_1+\frac{1}{2})+\Omega_2(v_2+\frac{1}{2})+\Omega_3(v_3+\frac{1}{2})+\ldots+\Omega_{\mathcal{N}}(v_{\mathcal{N}}+\frac{1}{2})\Big)$$

$$(\ \mathcal{N}\ \text{independent modes} \quad \Rightarrow \quad \mathcal{N}\ \text{quantum numbers}\ \nu\ )$$

Some words of caution:

Since normal modes are independent, i.e. do not exchange energy, a normal mode system will not evolve toward thermodynamic equilibrium!

Refer to:

→ Your spectroscopy class (IR, Raman)

→ Statistical mechanics (the Ωs for the vibrational partition function)

4: Summary

What have we missed up to now? Mostly intermolecular interactions
(real gas, fluids, liquid, solid ... condensed phases)

Let's go back to Ludwig Boltzmann
(who could not know quantum mechanics)

–He thought about N classical particles (beads) interacting in some way through potentials.
–He would then get the 'states' by solving Newton's equations for the N particles (numerically or otherwise)
and write down the positions and velocities at regular time intervals.
The total energy would stay constant due to the properties of these equations (see above).
–Summing over the so-defined 'states'
(and there is a difficulty here that only quantum mechanics could resolve)
he got a slightly different partition function (called microcanonical, Ω)

Reminder:

Statistics where the spin contributions can be neglected (e.g. molecules) are called **'Boltzmann statistics'**
If the spin cannot be neglected
(symmetry of wave function, Pauli principle)
we have either **'Fermi statistics'**
(e.g. 'free' electrons in solids, spin $= 1/2$, fermions)
or **'Bose.Einstein statistics'** (spin 1,2,3, ..., bosons)

'Fermi statistics': electrons in solids, Fermi surface,
Fermi energy (which is usually $>> k_{\mathrm{B}}T$), ...

'Bose statistics', e.g.: ^{3}He-^{4}He mixtures below 4 K

Part 5

Statistical thermodynamics via simulations

Allen & Tildesley, with FORTRAN programs
and many other books

Molecular Simulation:
Use the computer to construct a **representative sample** of microstates
(The 'Gallup Poll approach' to statistical mechanics)

In **MD**, we construct the sample assuming that the molecules move according to **Newton's law**.

In **MC** we construct the $\{\vec{r}\}$-part of the sample by a **'random walk'**.

In both cases we use the sample to do **'statistical' mechanics**.

MD constructs a sample of phase space $\mathcal{P}$ (see below)
MC constructs a sample of configuration space $\mathcal{C}$ (only the rs)

'State' (the thing Boltzmann was not sure about)
we skip over some difficulties here:

$$\mathcal{P}_j = \{\vec{r}_1, \vec{r}_2, \vec{r}_3, ..., \vec{r}_{N_A}, \vec{v}_1, \vec{v}_2, \vec{v}_3, ..., \vec{v}_{N_A} \text{ at some time } t_j,\ j = 1, 2, 3, ..\}$$

(The difficulty: t is continuous, 'state' is discrete,
we'll see that we can work around this)

In MD (and MC) simulations we construct 'states'
since we know that **it is impossible to construct all states**,
we will construct (only) **a representative sample, e.g.**:

$$
\begin{array}{rlll}
\mathrm{Sample}_{\mathrm{MD}} = \{ & & r_1, r_2, r_3, ...r_N,\ v_1, v_2, v_3, ..., v_N & t = 0 \\
& , & r_1, r_2, r_3, ...r_N,\ v_1, v_2, v_3, ..., v_N & t = 1 \\
& , & r_1, r_2, r_3, ...r_N,\ v_1, v_2, v_3, ..., v_N & t = 2 \\
& , & r_1, r_2, r_3, ...r_N,\ v_1, v_2, v_3, ..., v_N & t = 3 \\
& , & \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots & t = \ldots \\
& , & r_1, r_2, r_3, ...r_N,\ v_1, v_2, v_3, ..., v_N & t = M \quad \} \\
\subset & \mathcal{P} & &
\end{array}
$$

In the language of differential equations,
this is (a part of) the **system trajectory**
(which meanders through (i.e. samples) **phase space**)
we also call this the **configurations**, or the **history**

On the computer: several Mb or Gb of data

Statistical mechanics: compute thermodynamics averages from the partition function, (see equations AvQ and AVΩ above)

From Q (NVT)

$$\langle A \rangle_T = \frac{1}{Q} \int_{\text{all } p,q} A(p,q) \cdot \exp \frac{E(p,q)}{k_\text{B}T} \, \text{d}p \, \text{d}q$$

From Ω (NVE)

$$\langle A \rangle_E = \frac{1}{\Omega} \int_{\text{all } p,q} A(p,q) \cdot \delta(E(p,q) - E_0) \, \text{d}p \, \text{d}q$$

where q stands for all positions variables $(x_1, y_1, z_1, x_2.y_2, ..., z_N)$
and p for all velocity variables $(vx_1, vy_1, ..., vz_N)$

So the integrals are $6N$-fold integrals ($\int \int \int ...... \int$) over the (q,p)-space, which is called **phase space**

Thermodynamic average from simulations (**much simpler!**)

$$\mathrm{MD}: \quad \langle A \rangle_E = \frac{1}{N}\sum_{i=1}^{N} A(\mathcal{P}_i)$$

$$\mathrm{MC}: \quad \langle A \rangle_T = \frac{1}{N}\sum_{i=1}^{N} A(\mathcal{C}_i)$$

where $\mathcal{P}_i$ is the ith configuration from the sample in phase space and $\mathcal{C}_i$ is the ith configuration from the sample in **configuration** space (which contains only the positions, as we saw)

Note:
Boltzmann's problem how to define a 'state' from classical mechanics (how much should the continuous variables change so that one has a 'new' state) thus goes away.
This is why you find $\hbar$ in expressions for the classical(!) partition functions

Thus:

If we have the sample,
and the sample is 'representative' of the **'ensemble' of all microstates** compatible with one **MACROSTATE**
(*e.g.: so and so many moles of substance* XYZ *at some temperature* T *K and some density* ρ *g cm*$^{-3}$)
we are interested in, we can compute the value $\mathcal{A}_j$
(*such as the pressure, the internal energy, the X-ray scattering signal, ...*)
for each microstate j in the sample and get the correct 'thermodynamic' average at the system at temperature T and density ρ:

$$\langle\ \mathcal{A}\ \rangle_{T,\rho} = \frac{1}{M}\sum_{j=1}^{M}\mathcal{A}_j$$

Note: Sums ($\sum$) in simulations instead of integrals ($\int \mathrm{d}q\ \mathrm{d}p$) with partition functions

In a little more detail:

$$\langle\, \mathcal{A}\, \rangle^{\text{MD}}_{\text{conditions}} \quad = \quad \frac{1}{M}\sum_{j=1}^{M} \mathcal{A}_j$$

$$= \quad \frac{1}{M}\sum_{j=1}^{M} \mathcal{A}(\vec{r}^{\,j}_1, \vec{r}^{\,j}_2, \vec{r}^{\,j}_3, \ldots \vec{v}^{\,j}_1, \vec{v}^{\,j}_2, \vec{v}^{\,j}_3, \ldots) = \frac{1}{M} \sum_{\substack{\{\mathbf{p},\mathbf{q}\} \\ \text{from simulation}}}^{M} \mathcal{A}(\mathbf{p},\mathbf{q})$$

compare with what you have learned above:

$$\langle\, \mathcal{A}\, \rangle_{N,V,E_0} = \frac{1}{\Omega} \cdot \mathop{\sum\!\!\!\!\!\!\int}_{\text{all }\mathbf{p},\mathbf{q}} \mathcal{A}(\mathbf{p},\mathbf{q})\ \delta(E(\mathbf{p},\mathbf{q}) - E_0) \quad \text{(microcanonical)}$$

$$\langle\, \mathcal{A}\, \rangle_{N,V,T} = \frac{1}{Q} \cdot \mathop{\sum\!\!\!\!\!\!\int}_{\text{all }\mathbf{p},\mathbf{q}} \mathcal{A}(\mathbf{p},\mathbf{q})\ e^{(-\beta E(\mathbf{p},\mathbf{q}))} \qquad \text{(canonical)}$$

$$\beta = \frac{1}{k_{\text{B}}} T$$

The conventional approach

Model 1 $\Longleftrightarrow$ Observable $\mathcal{A}$

Model 2 $\Longleftrightarrow$ Observable $\mathcal{B}$

Model 3 $\Longleftrightarrow$ Observable $\mathcal{C}$

The conventional approach

Model 1 $\Longleftrightarrow$ Observable $\mathcal{A}$

Model 2 $\Longleftrightarrow$ Observable $\mathcal{B}$

Model 3 $\Longleftrightarrow$ Observable $\mathcal{C}$

The simulation approach

$$\textbf{One}\ \text{model} \quad \left\{ \begin{array}{ll} \Longleftrightarrow & \text{Observable } \mathcal{A} \\ \\ \Longleftrightarrow & \text{Observable } \mathcal{B} \\ \\ \Longleftrightarrow & \text{Observable } \mathcal{C} \end{array} \right.$$

Being able to perform such consistency checks is one of the main advancements brought about by molecular simulations

Consistent Coarse Graining

$$\left\{\begin{array}{l}\Longleftrightarrow \quad \text{Observable } \mathcal{A}\\[2ex] \Longleftrightarrow \quad \text{Observable } \mathcal{B}\\[2ex] \Longleftrightarrow \quad \text{Observable } \mathcal{C}\end{array}\right.$$

One model

$\Downarrow$

$\Downarrow$

Coarse graining procedure

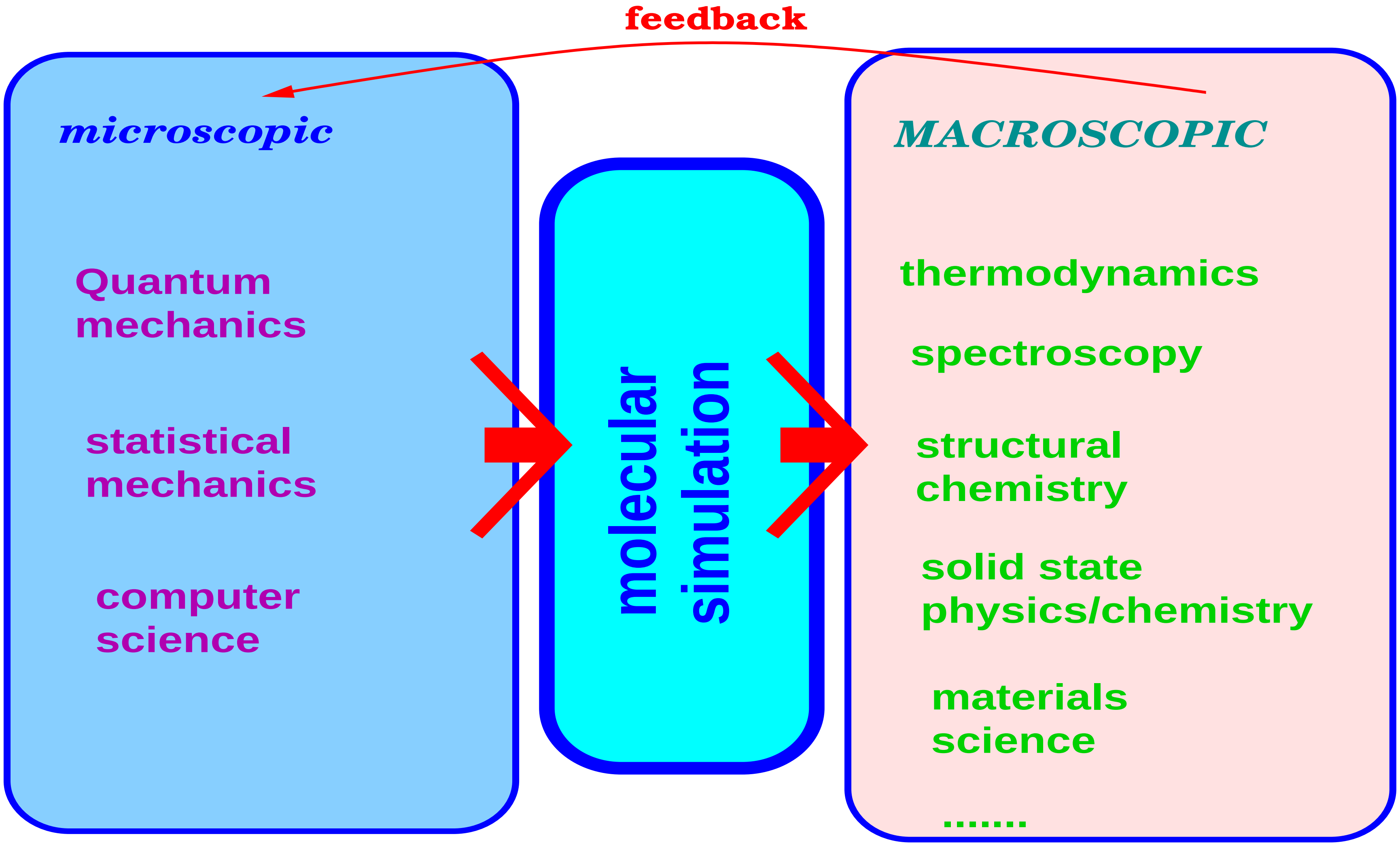
$\Downarrow$

$\Downarrow$

Coarse grained model

$$\left\{\begin{array}{l}\Longleftrightarrow \quad \text{Observable } \mathcal{D}\\[2ex] \Longleftrightarrow \quad \text{Observable } \mathcal{E}\\[2ex] \Longleftrightarrow \quad \text{Observable } \mathcal{F}\end{array}\right.$$

The Principle of Molecular Simulations



feedback

microscopic

Quantum mechanics

statistical mechanics

computer science

molecular simulation

MACROSCOPIC

thermodynamics

spectroscopy

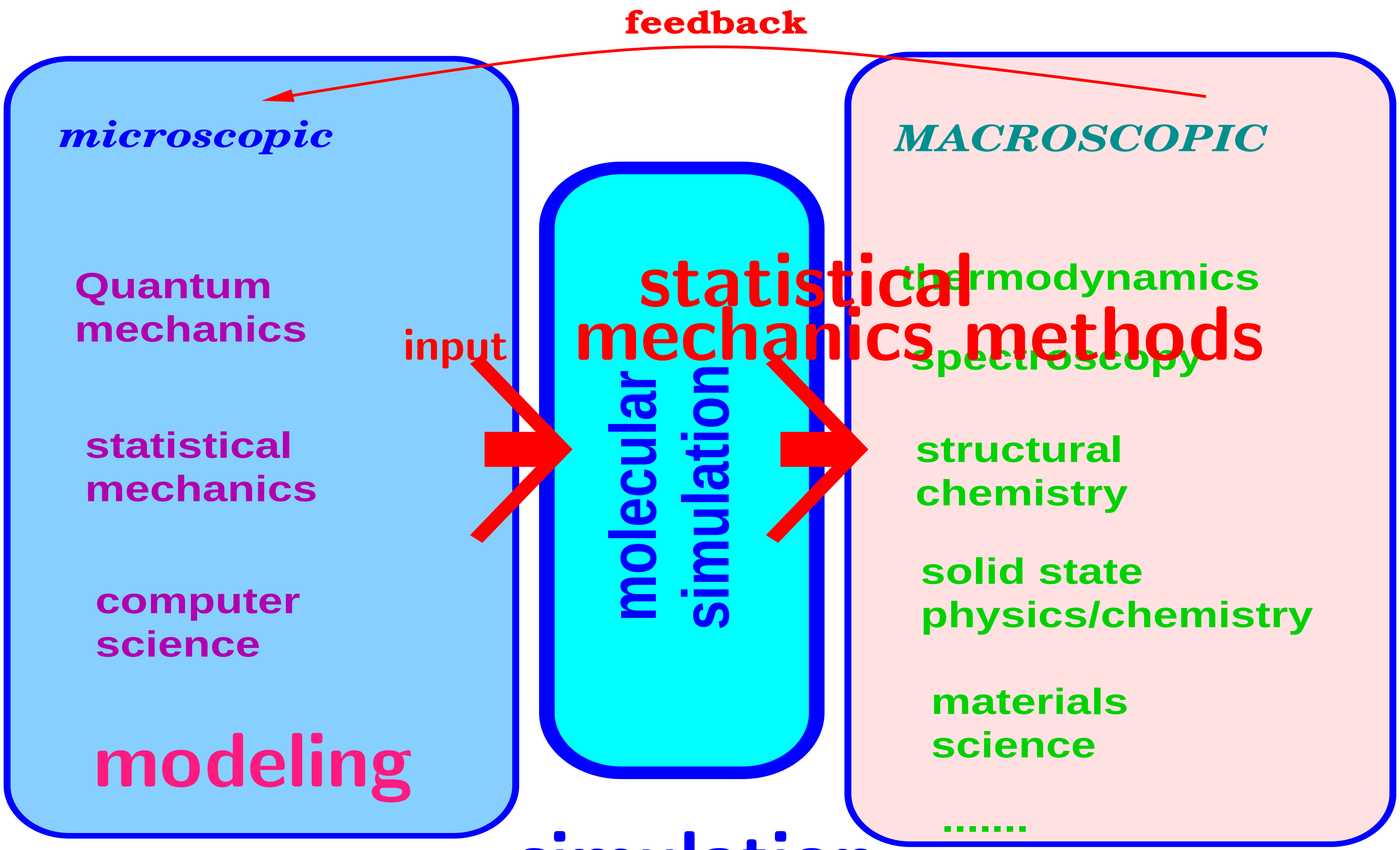
structural chemistry

solid state physics/chemistry

materials science

....

The Principle of Molecular Simulations



feedback

microscopic

Quantum mechanics

statistical mechanics

computer science

modeling

input

molecular simulation

statistical mechanics methods

MACROSCOPIC

thermodynamics

spectroscopy

structural chemistry

solid state physics/chemistry

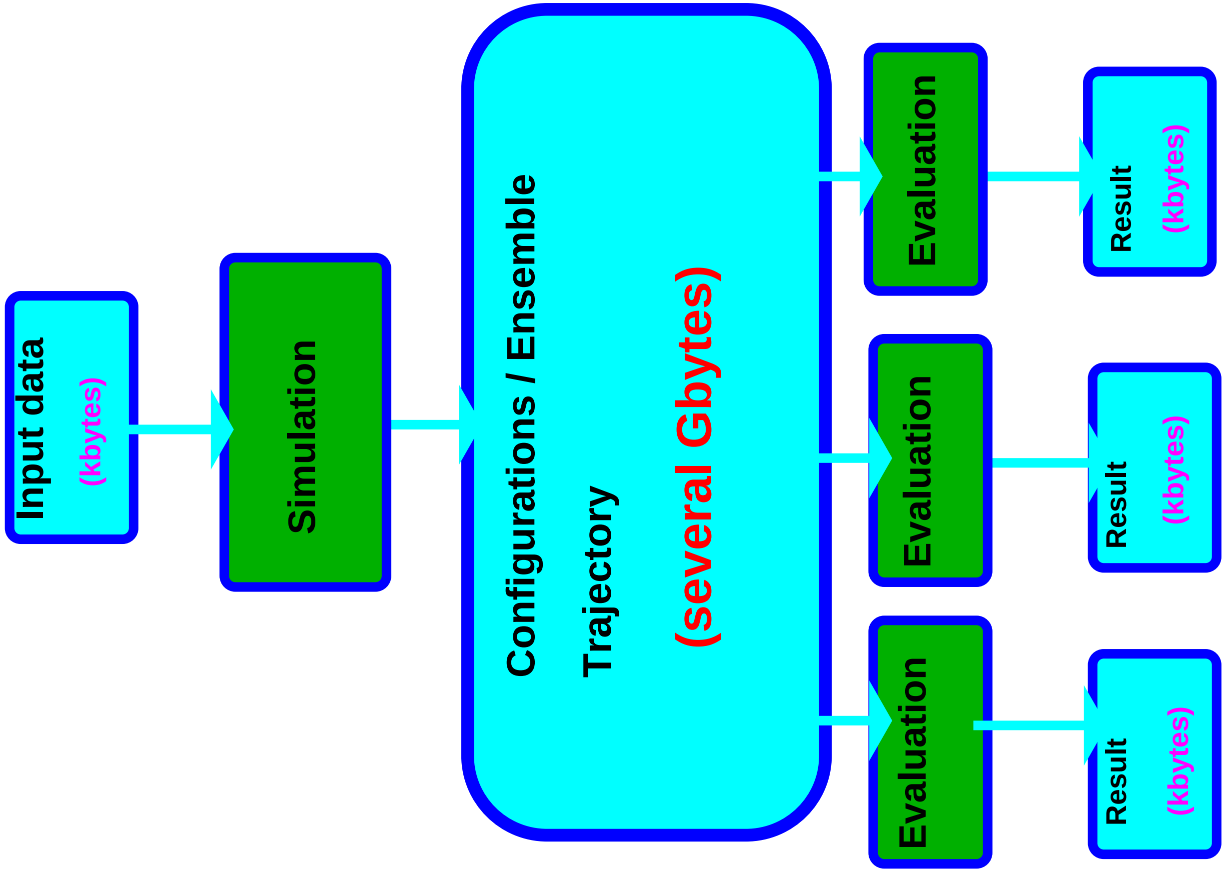
materials science

....

simulation

From input to output through a huge amount of intermediate data

Typical Data Flow



= statistical mechanics

A few remarks

–Some people have questioned whether first generating such a huge amount of data and then whittling them down to a few 'observables' qualifies as 'simple'

–Others have called simulation methods 'brute force'

–There is indeed no systematic way to 'improve' (what does it mean?) results (unlike e.g. the variational principle)

–However, simulations usually need fewer, and weaker, assumptions than analytical methods

–In their philosophy, they are akin to experiments
- computer experiments -
and thus often allow 'trial and error' approaches

Some more **problems** (which have bothered people a lot):

The solution of differential equations (see harmonic oscillator)
depend on the initial conditions

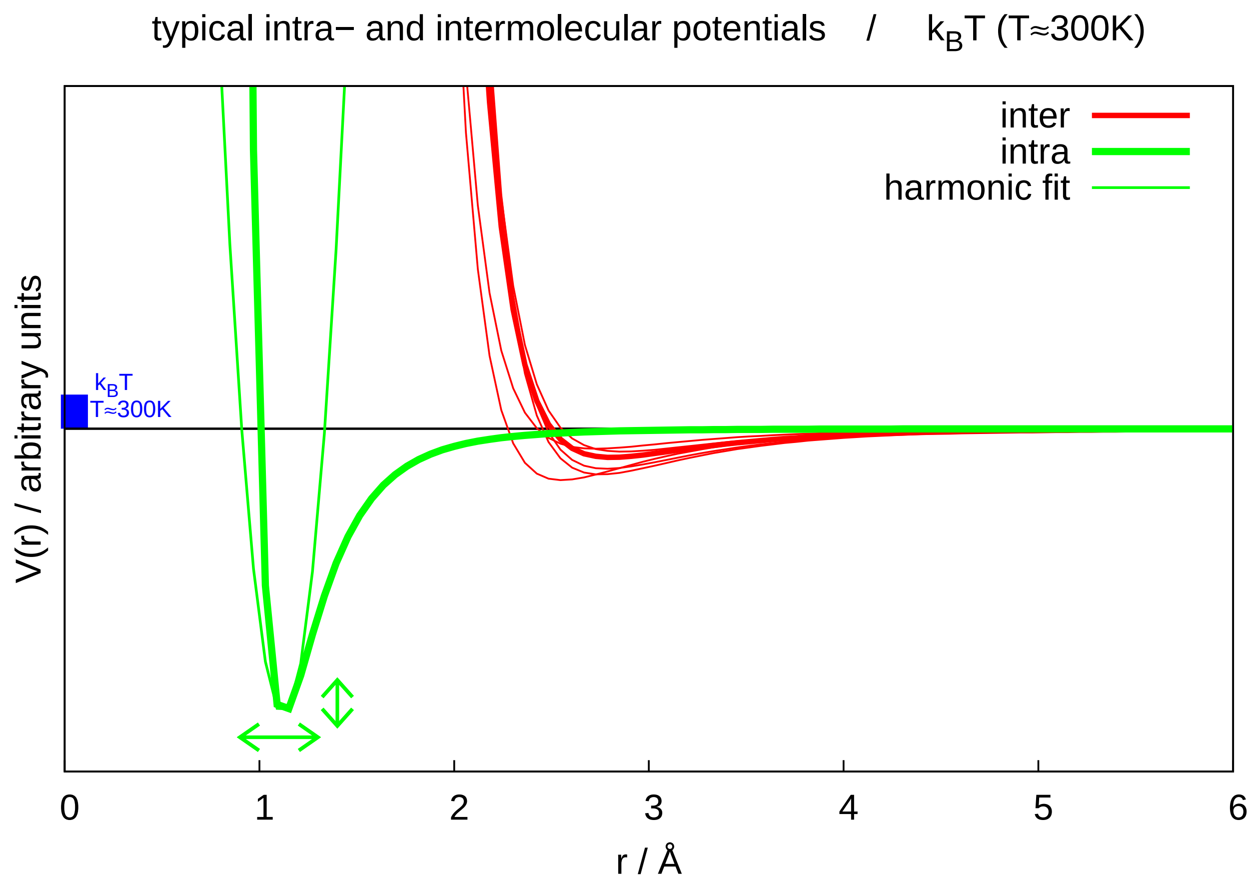
So MD results will depend on initial conditions

– Is this good? Do we want this?
– Are there cases where we want this and others where we do not?
– What can we do to avoid it if we do not like it?

⇒ This can be in some cases a **Big Problem**

⇒ Some Discussion later

Interaction models (or simply **models**)



Note: the (average) thermal energy, $k_\mathrm{B}T$, $T = \ldots$ K, is **the** reference energy with which, in thrmodynamics, other energies should be compared

In molecular simulations, you must at least know (assume that you know) how the molecules interact with each other

There are many ways to express this 'knowledge', e.g.

– potentials from quantum mechanical (ab-initio, DFT) calculations of the electronic ground state... $\Longrightarrow$ Simulations

– from some model assumptions, e.g. Lennard-Jones (LJ) potential **model**, Morse potentials, ...
$\Longrightarrow$ Simulations

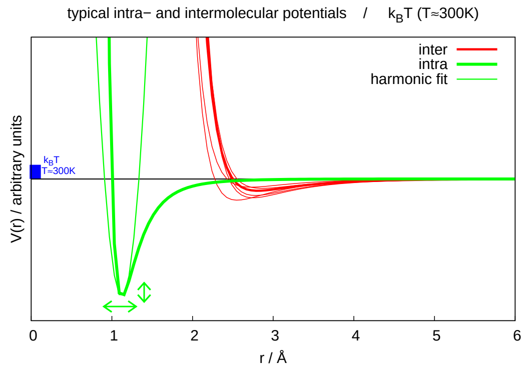
– ....

– simple harmonic oscillators, rigid rotors, particle in the box
$\Longrightarrow$ Simulations or compute Partition Function

Interaction Models

One usually writes a sum of
inter– *(between)* and intra– *(inside)* molecular interactions

$$V^{\text{total}} = V^{\text{inter}} + V^{\text{intra}} \qquad \uwave{+ \qquad V^{\text{inter}-\text{intra}} \quad ?}$$



Frequent assumptions

– Intermolecular:

Pairwise additive (or simply **pair**) potentials: $V = \sum \text{terms}(r_{ij}),\ r_{ij}\text{a distance}$

Many-body potentials, polarizabilities and polarization

– Intramolecular:

Internal coordinates (bond-**stretch**, angle-**bend**, **torsion** ...)

"bonded" and **"non-bonded"** (like intermolecular) interactions

– Coupling potential:

usually neglected

So if we have a system of $i = 1, ..., N$ interacting particles (via a given potential energy function V
(*which describes, as you will remember, the changing QM electronic ground state energies, see B.O. approximation*)

$$m_i \, \frac{\partial^2 r_i}{\partial t^2} = \vec{\mathrm{grad}}_i V = \vec{F}_i \quad , \; i = 1, N$$

However, such general systems of coupled differential equations
(because $\vec{F}_i$ depends in general not only on $\vec{r}_i$ but also on all other $\vec{r}_j$s,
$2N$ first order vector equations or
$6N$ (x, y, z) first order scalar equations)
do not have **'analytical'** solutions* (Henri Poincaré)

(*There are exceptions* $\Rightarrow$ *'harmonic' problems, normal modes, remember?*)

But there are **numerical** solutions
This is what we will do in MD simulations

*Systems which have analytical solutions (i.e. mathematical expressions, like sin(..), cos(...), exp(..), ...) are called 'regular' systems, the others are 'irregular' or 'chaotic'

Thus:

If the potential V (or forces $\vec{F}$) in Newton's equation depend ONLY on the positions ($\vec{r}$s) (and not on some 'external' variables) the total energy of this system will remain constant (conservation of total energy).

These quantities which remain constant (total energy E, momenta p_x, p_y, p_z) are called 'integrals' of the system

So if we solve Newton's equations for the N particles, the resulting trajectory will be a sample of the NVE ensemble
(microcanonic ensemble with additionally $\vec{p}$=const)

Reminder concerning the nuclear motions

For all masses larger than Hydrogen and
temperatures $\geq$ room temperature
classical mechanics (Newton's equation) is a good approximation.

Hydrogen is 'borderline' (de Broglie wavelength $\approx$ particle dimension)

Remember that in the harmonic case, the classical frequencies Ω
(multiplied by $\hbar$!) are the same as the QM $n \to n \pm 1$ transition energies

Thus, if the potential is 'narrow' (i.e. well approximated by a parabola)
(which also means that Δx small in the uncertainty relation)
the frequencies Ω can still be obtained classically and used to compute the 'quantum' energies.

Examples of thermodynamic averages routinely computed from MD-simulations

the average kinetic energy/particle (= temperature)
the distribution (Maxwell-Boltzmann) of these temperatures
the equipartition of the kinetic energies

$$\frac{3}{2}\,k_{\mathrm{B}}T = \frac{3}{2}\,m\,\left(\frac{1}{N}\sum_{i=1}^{N} v_i^2\,\right) = \frac{3}{2}\,m\langle v^2\rangle_N$$

We can compute this for all particles,
– for selected particles (to check e.g. whether the system is in equilibrium),
– for selected degrees of freedom (e.g. using only the v_xs, v_θs, $v_{....}$s), also combinations thereof,
– or we can comput histograms

An important technique for such analyses is **binning** (histograms)

Here one does several averages at the same time:

$$\langle n(\mathcal{A}(x+\Delta x)\rangle_E \propto \sum_{\text{all configurations}} \delta(\mathcal{A}_i \text{ between } \mathcal{A}(x) \text{ and } \mathcal{A}(x+\Delta x))$$

i.e. a 1 is added to the counter $n(\mathcal{A}(x+\Delta x)$ every time a value of $\mathcal{A}_i$ between $\mathcal{A}(x)$ and $\mathcal{A}(x+\Delta x)$ is found in the configurations

We decide on a value for Δx (the resolution) and study $\langle n_{\mathcal{A}}(x)\rangle$, which, suitably normalized*, is the probability distribution (of $\mathcal{A}$): $p_{\mathcal{A}}(x)$

* for a **probability** distribution $p(x)$ it is required:

$$\int_{\text{all } x} p(x) \, \mathrm{d}x = 1$$

How to code this:

```
REAL A
INTEGER INDEX
REAL or INTEGER histogram(....), total_number_of_A

A = ..........
index = convert_to_integer ( A / resolution + shift)
histogram(index) = histogram(index) + 1
total_number_of_A = total_number_of_A + 1
```

You have to make sure that your histogram does not overflow, i.e. that no index larger or smaller than the array boundaries of `histogram` appears during the computations (Compilers can generate code to do this automatically, but then it runs much more slowly)

You can then normalize the histogram to one:

```
LOOP OVER index
histogram(index) = histogram(index) / total_number_of_A
```

5: averages

Studying the velocities in the equilibrium system:

If we bin the $\vec{v}_x$, we get a Gaussian
(the width depending on the mass and the temperature)

If we bin the v^2, we get the Maxwell-Boltzmann (almost) distribution
(if our system is in equilibrium)

If we do that for interparticle distances $r_{\alpha\beta}(= r_{\beta\alpha})$ (r scalar, not vector!)
and normalize correctly
we get the so-called radial pair distribution functions (rdf, $g(r)$),
which are important in many statistical mechanics theories,
(more about this later)
and can also be obtained (not so easily, but still)
from X-ray scattering, neutron scattering, electron scattering ....

Note about $g(r)$:

$$n_{\alpha\beta}(R_{\alpha\beta}) = 4\pi \cdot \frac{N_\beta}{V} \cdot \int_0^{R_{\alpha\beta}} r_{\alpha\beta}^2 \; g_{\alpha\beta}(r_{\alpha\beta}) \; \mathrm{d}r_{\alpha\beta}$$

is the average number of neighbors of type β around a particle of type α in a sphere of radius $R_{\alpha\beta}$ (upper limit of integral).

$$\textbf{Thus}: \quad g_{\alpha\beta} = g_{\beta\alpha} \quad \text{(from the definition)}\;, \;\; \text{but} \quad n_{\alpha\beta} \neq n_{\beta\alpha}$$

So often it is more instructive to plot the n rather than the g.
Example:
The average number of water molecules around an ion is meaningful (the hydration number)
The average number of ions around a water molecule is much less intuitive

As an aside

The $g(r)$s are so important
(many properties e.g. of liquids can be approximated
'in the 2-body approximation' if one knows them)

People have tried, and in many cases succeeded,
in computing $g(r)$s without taking the detour through the
huge simulation ensemble (see above)

On thus tries to go straight from the pair potentials to the $g(r)$s

These methods are usually called 'integral equation theory'
(more later may be)
they can be classified more as analytical methods
but the very complex equations can be solved only with a computer

Note furthermore

The g-functions are related through Fourier transforms (FT) to the experimental X-ray–, neutron– (elastic), electron–scattering functions:

$$S(Q) \propto \sum x_\alpha x_\beta \; f_\alpha \; f_\beta \; \left(\mathrm{FT}(g_{\alpha,\beta}(r) - 1)\right)$$

Q scattering vector, also often called k
α, β types of atom in the system
x mole fractions
f factors that depend on the type of scattering and type of atom

As we have seen, when we use **MD**
(i.e. numerical solutions of Newton's equations)
to construct (a sample of) the 'microcanonical (NVE)' ensemble,
we get, quasi 'for free', information about
the **time evolution** of the system.

This can be studied 'in equilibrium'* and 'out of equilibrium'

The way to explore the evolution of things in the **equilibrium ensemble***
is to compute **time-correlation functions**

* Equilibrium does not mean that 'nothing moves',
it is just that for macroscopic observables one has $\frac{\partial}{\partial t} = 0$

With **MD** we can thus go beyond computing simple averages
(since the sample (trajectory) contains the time evolution of the system)

→ Time correlation functions
relate to infrared/Raman/NMR signals, viscosity, self-diffucion, ...

Even if your system is at equilibrium, it does not mean that nothing moves!, see e.g. Brownian motion, self-diffusion

and generally Molecular or collective motions of all kinds

Example
Chemical equilibrium: A $\underset{K}{\rightleftharpoons}$ B means: A $\underset{k_1}{\rightharpoonup}$ B and B $\underset{k_2}{\rightharpoonup}$ A all the time

and

$$k_1[A] = k_2[B] \quad , \text{ thus } K = \frac{[B]}{[A]} = \frac{k_1}{k_2} \quad , \quad \text{remember?}$$

In more detail:

$$\langle\ \mathcal{A}\ \rangle = \frac{1}{M} \sum_{j=1}^{M} \mathcal{A}_j$$

does **not** depend on the order in which you compute the $\mathcal{A}_j$,

in MD we do have the microstates (configurations) ordered according to time:

$$\mathcal{P}(t_1), \mathcal{P}(t_2), \mathcal{P}(t_3), \mathcal{P}(t_4), ..., \mathcal{P}(t_M)$$

$\Rightarrow$ To take advantage of this, one computes
"time correlation functions", their Fourier transforms (spectra),
and their integrals (transport coefficients)

(*if we have time, we'll deal with this in the next slides*
$\Longrightarrow$ *study "time dependent" properties*)

For this purpose, we extend the equation (*known by now*)

$$\langle \mathcal{A} \rangle_E = \frac{1}{N} \sum_{i=1}^{N} \mathcal{A}(\mathcal{P}_i)$$

to become

$$\langle \mathcal{A}(0)\mathcal{A}(t) \rangle_E = \frac{1}{M_j}\frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{M_j} \mathcal{A}(\mathcal{P}(t_j)_i) \otimes \mathcal{A}(\mathcal{P}(t_j + t)_i) = c_{\mathcal{A}\mathcal{A}}(t)$$

the <u>auto</u>correlation function of $\mathcal{A}$, or more generally

$$\langle \mathcal{A}(0)\mathcal{B}(t) \rangle_E = \frac{1}{M_j}\frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{M_j} \mathcal{A}(\mathcal{P}(t_j)_i) \otimes \mathcal{B}(\mathcal{P}(t_j + t)_i) = c_{\mathcal{A}\mathcal{B}}(t)$$

the $\mathcal{A}\mathcal{B}$-<u>cross</u>correlation
$\otimes$ is some operation, often a scalar product.
Like previously, the i-sum can be over all or only over selected particles

Example: the **velocity autocorrelation function** $C_{vv}(t)$

$\mathcal{A}(t_j)$ is a big vector (for all particles i) $\mathcal{V}$ for the time t_j:

$$\begin{aligned}\mathcal{V}(t_j) \quad = \quad & (\ vx_1(t_j), vy_1(t_j), vz_1(t_j),\ vx_2(t_j), vy_2(t_j), vz_2(t_j),\ vx_3(t_j), \\ & vy_3(t_j), vz_3(t_j), ..., vx_N(t_j), vy_N(t_j), vz_N(t_j)\ )\end{aligned}$$

a big $3N$-dimensional vector,

$\otimes$ is the normal scalar product

and one gets

$$\langle v(0)v(t)\rangle_E = \frac{1}{M_j}\sum_{j=1}^{M_j} (\mathcal{V}(t_j)) \cdot (\mathcal{V}(t_j + t)) = c_{vv}(t)$$

(the i-sum is already in the scalar product)

6: more MD

The Fourier Transforms (FT) of correlation functions are called 'spectra':

$$c_{vv}(\omega) = f \cdot \int_0^\infty c_{vv}(t) \cdot \cos(\omega\ t)\ \mathrm{d}t = \mathrm{FT}(c_{vv}(t))$$

(It is enough to take the cosine since the (classical) correlation function is even in time: $c_{vv}(t) = c_{vv}(-t)$)
f is some factor that people chose differently.

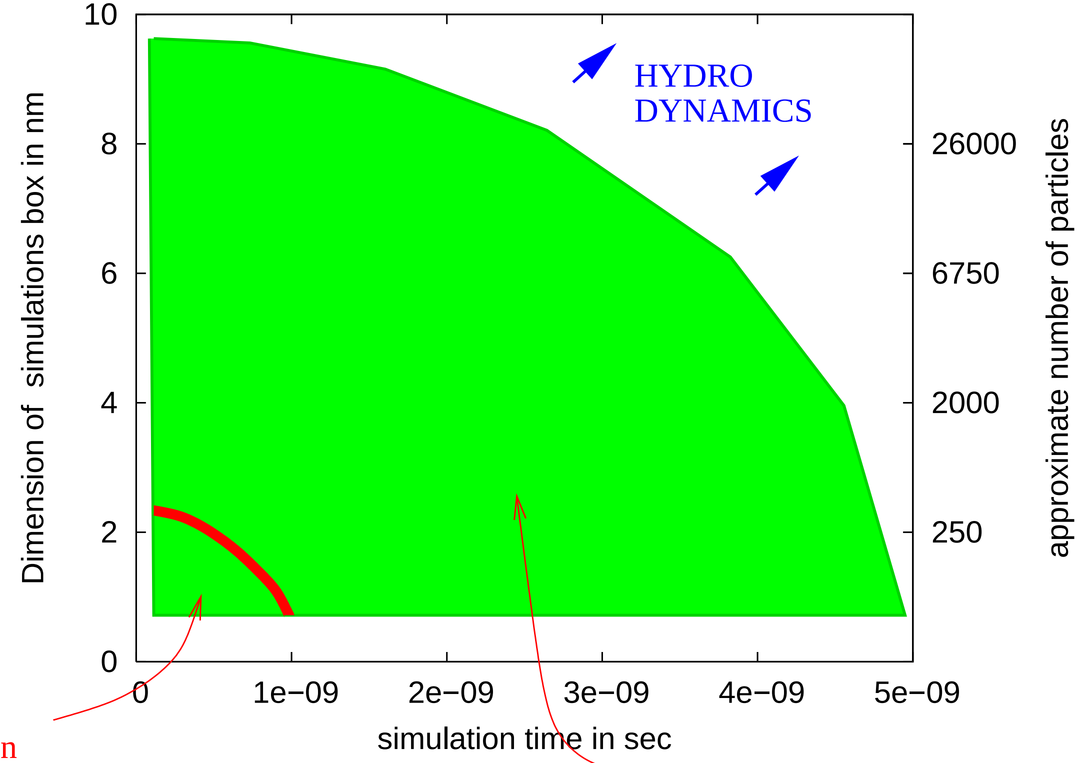
A time-correlation function (time domain)
and a spectrum (frequency domain)
thus contain exactly the same information
(*experimentally one may be much harder to get than the other*)

Details of MD- (and in many instances also MC-) simulations
that we shall **not** discuss in detail here:
(*they are very important nevertheless if you want to work with these methods*)

- periodic boundary conditions (PBC) with
  minimum distance convention
- internal displacement (Wilson's) coordinates,
  "bonded" and "non-bonded" interactions
- truncations and corrections
- long-ranged (i.e. essentially electrostatic (Coulomb)) interactions
- integration methods
- random walks
- time steps and displacements
- equilibration, thermalization
  problem of initial conditions
- estimation of uncertainties (quite difficult)
-

Space-time window

accessible to MD simulations



IR
Raman
NMR relaxations
....

slower relaxations
dielectrics
accoustics
...

i.e. today a few 100 or 1000 molecules (depending on complexity) and a few 100 or 1000 picoseconds

We take advantage of the fact that when we compute averages

$$< \mathcal{A} >= \frac{1}{N}\sum_{j}^{N} \mathcal{A}_j$$

the $\mathcal{A}_j$ can be in any order.

So instead of using Newton's equation to construct the **microstates**, we use a **random walk**

7: Examples

Examples

Three strategies in Computational Chemistry to go beyond studies the 0 K energies

(A) The (mostly) 'standard' way of **MD** simulations

(B) **Non**equilibrium **MD (NEMD)** simulations

(C) Taking into account the **quantum** nature of molecular vibrations

Mostly strategies and approaches shall be discussed here
One result is given for each case as an example
For details see the several seminar presentations

There are hundreds of different approaches, combinations of methods, new methods etc. etc.
This is the interesting part for your research

7: Examples

(A) *Water Dynamics in Chabazite*,

R. Chanajaree, Ph. A. Bopp, J. Kärger, and S. Fritzsche,
Microporous & Mesoporous Materials 146, 106-118 (2011)

In a nutshell

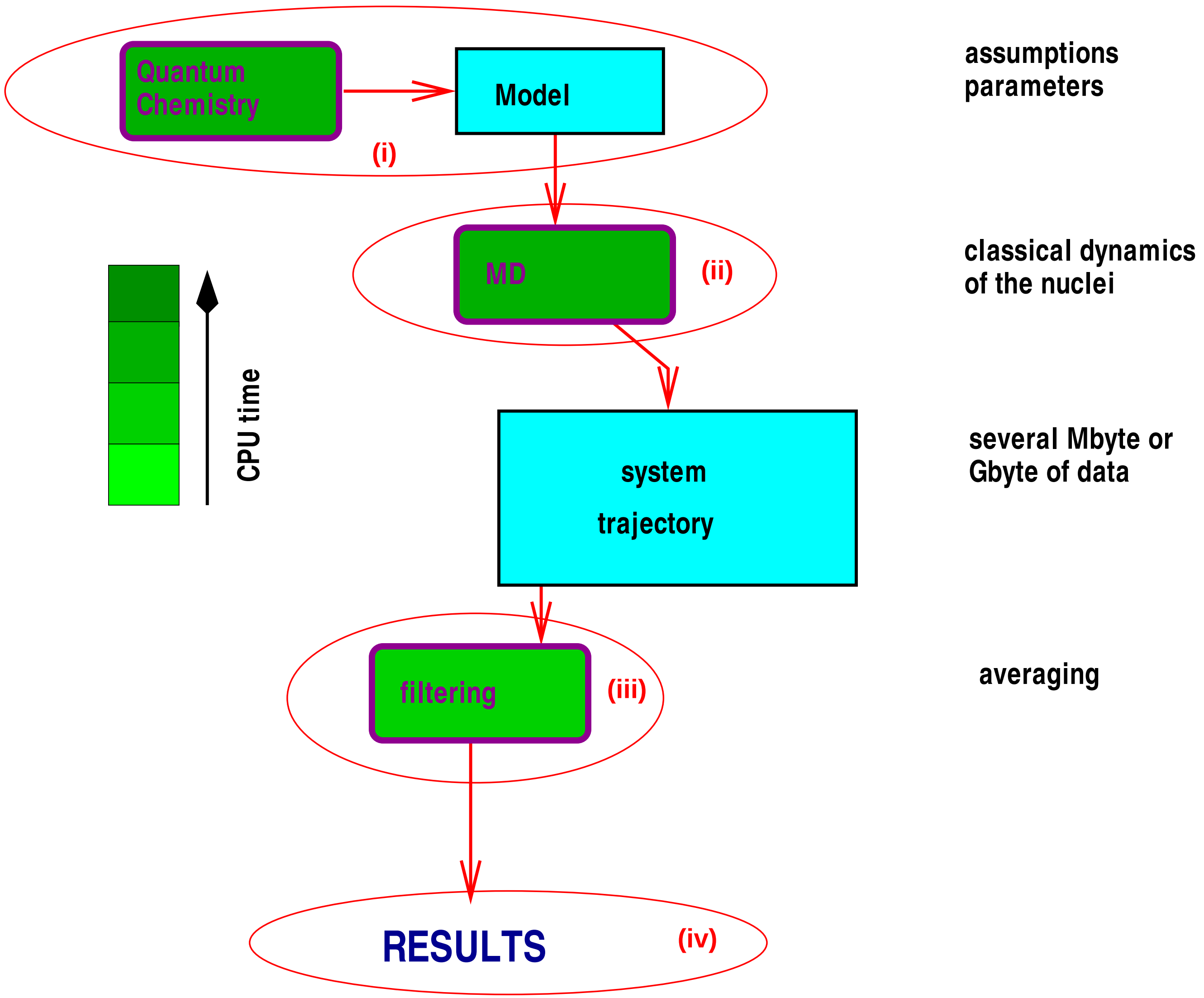
Chabazite: A porous hydrated calcium aluminosilicate
used e.g. in industry for removing cations from solutions
Anisotropic internal structure → **anisotropy of motions**

Course of action:

(i) Model development: (zeolite lattice, guest molecules (mostly from literature))
(ii) **Simulations** (**MD**)
(iii) Velocity-, angular velocity, ... autocorrelation functions → **spectra**
(iv) Comparison with experiment: Self-diffusion-anisotropy,
molecular reorientations (NMR)

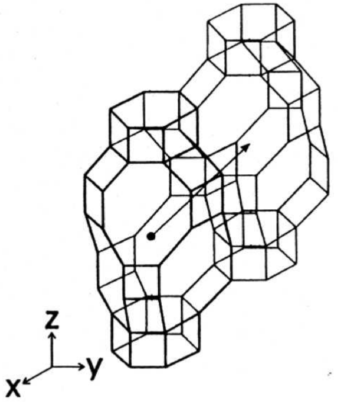
7: Examples

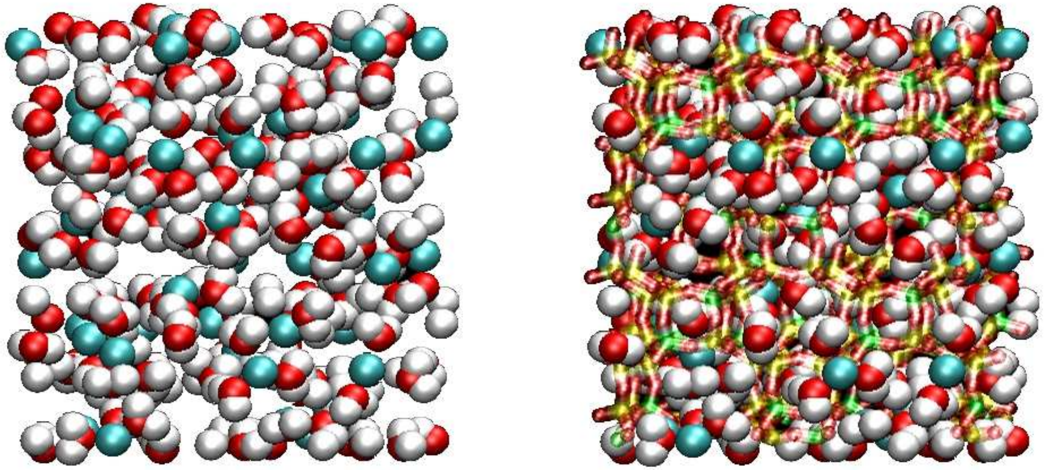
(A)


Quantum Chemistry
Model
(i)
MD
(ii)
CPU time
system trajectory
filtering
(iii)
RESULTS
(iv)
assumptions parameters
classical dynamics of the nuclei
several Mbyte or Gbyte of data
averaging

(A)

Zeolite Chabazite





→ Experimental (NMR) self-diffusion coefficients $D_{x,y} \neq D_z$: $\alpha = \frac{D_z}{D_{x,y}}$

Simulation box (26.4 × 22.863 × 30.2 $Å^3$, periodicity of zeolite)
contains 864 lattice atoms for 24 cages.

Two calcium cations per cavity are randomly distributed
(i.e. 48 Ca^{2+} per simulation box)

2 to 13 water molecules par cavity (loading) (i.e. 48 to 312 water molecules in toto)

(A) Anisotropy of Self-diffusion Coefficients in Hydration and Bulk Water

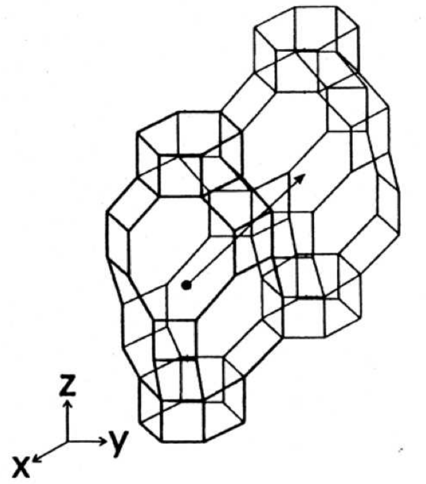
$\frac{D_z}{D_{x,y}} = 0.8$ N.K. Bär, J.Kärger, H.Pfeifer, H. Schäfer, W.Schmitz

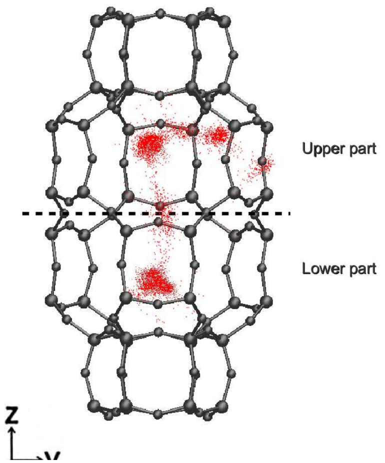
Microporous & Mesoporous Materials 22, 289 (1998)

(geometric considerations) old

$\frac{D_z}{D_{x,y}} = 0.4 \pm 0.1$ NMR single-crystal and powder new

$\frac{D_z}{D_{x,y}} \approx 0.3$ present MD work new





H_2O molecules mostly do not go straight from lower to upper part of cavity

(B) *MD Simulations of the Soret Effect in Simple Partially Miscible Binary Biphasic Mixtures*,

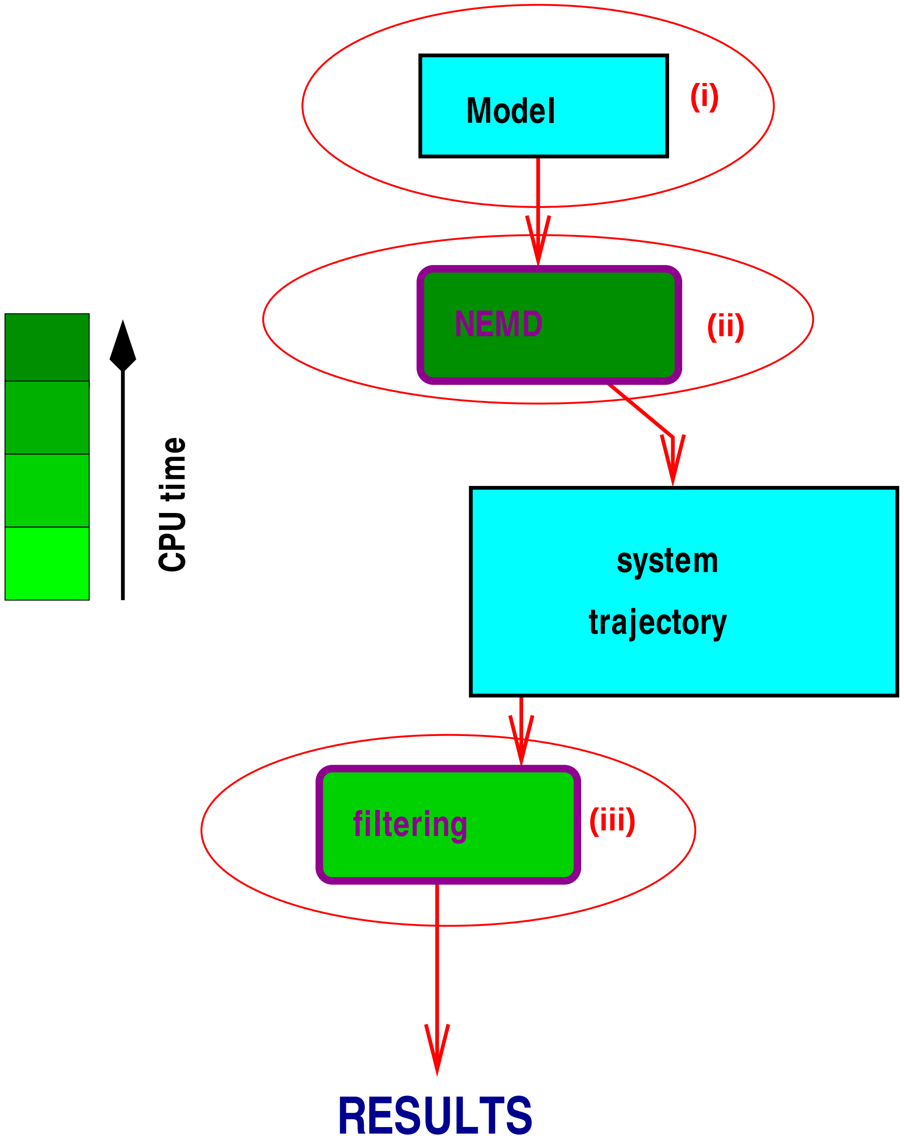
MD Simulations of the Soret Effect in Simple Partially Miscible Binary Biphasic Mixtures
H. A. Maier, M. J. Hampe, and Ph. A. Bopp, Chem.Phys.Let. 518, 55-60 (2011);

Non-Equilibrium Molecular Dynamics Simulation of the Thermocapillary Effect,
H. A. Maier, Ph. A. Bopp, and M. J. Hampe, Can.J.Chem.Eng. 90, 833 (2012)

In a nutshell
In a binary $(A - B)$ partly miscible two phase system, so-called **Marangoni convections** occur in the vicinity of the liquid-liquid interfaces if they are subject to a temperature gradient

Course of action:
(i) Extremely simplified (generic) interaction model: Lennard-Jones
(ii) **Stationary state non-equilibrium MD simulations**
(iii) Thermodynamic data (Soret coefficient),
collective dynamics (Marangoni convection)

(B)



Model (i)

assumptions
parameters

NEMD (ii)

classical dynamics
of the nuclei
out of equilibrium

CPU time

system
trajectory

several Mbyte or
Gbyte of data

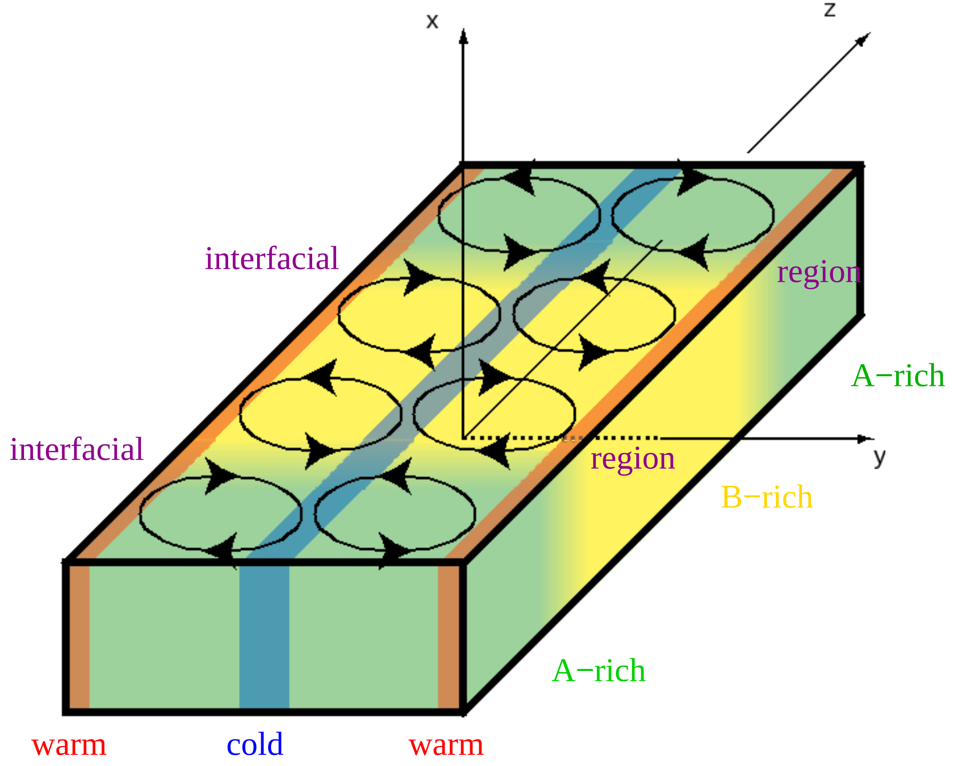
filtering (iii)

averaging

RESULTS

(B)

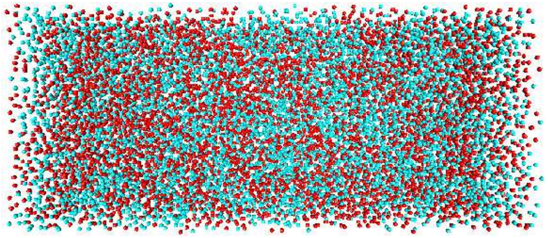
system infinitely periodic in all 3 directions



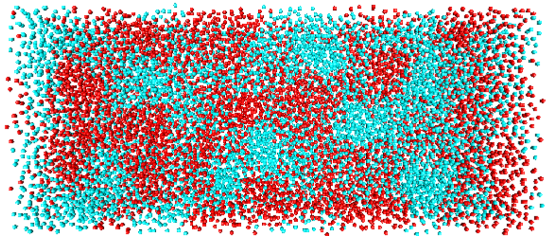
Mixture of simple LJ-particles, composition $x_\mathrm{A} \approx x_\mathrm{B} \approx 0.5$
(roughly in the middle of the miscibility gap)
Systems with several 1,000 to 10,000 particles

(B) Demixing 'experiment' (under NVT-conditions)

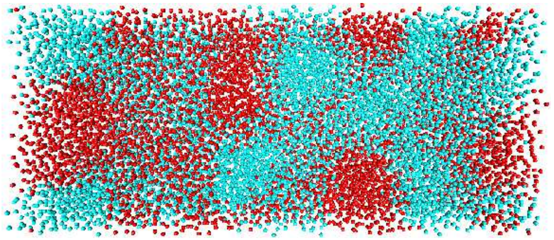
$t = 0$ ns



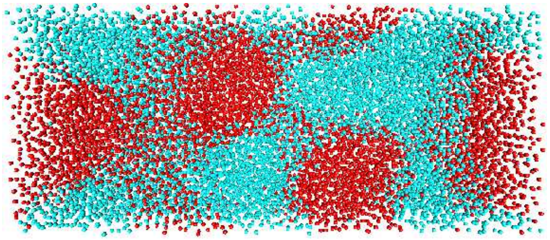
$t = 0.16$ ns



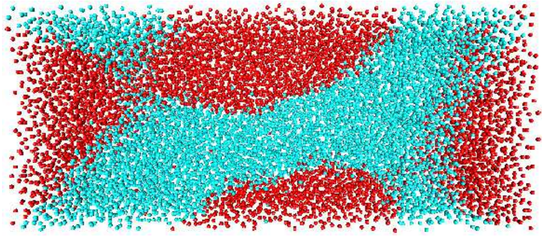
$t = 0.36$ ns



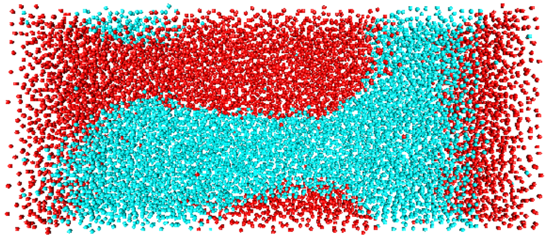
$t = 0.6$ ns



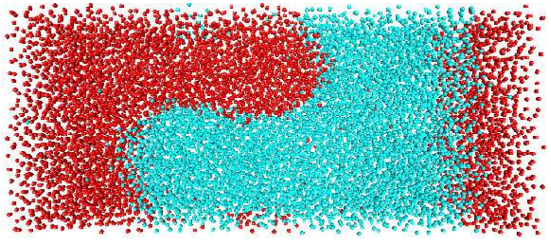
$t = 1.0$ ns



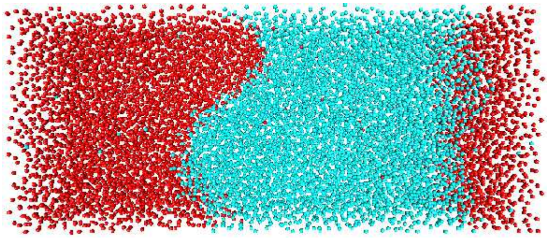
$t = 1.36$ ns



$t = 2.4$ ns

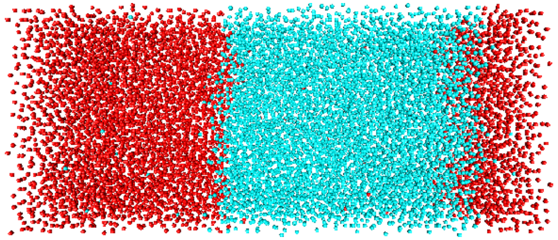


$t = 2.8$ ns



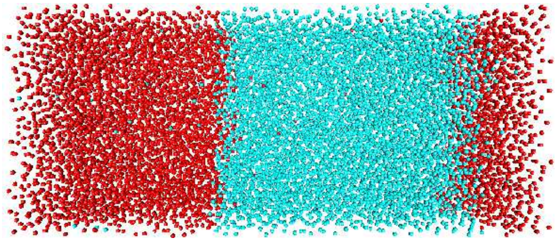
↑ interface ↑

$t = 3.0$ ns



↑ interface↑

$t = 5.0$ ns



exactly like any phys.chem. textbook says it should be

(C) *The vibrating hydroxide ion in water,*

K. Hermansson, Ph. A. Bopp, D. Spångberg, L. Pejov, I. Bakó, and P. D. Mitev,
Chem.Phys.Let. 514(1-3), 1-15 (2011)

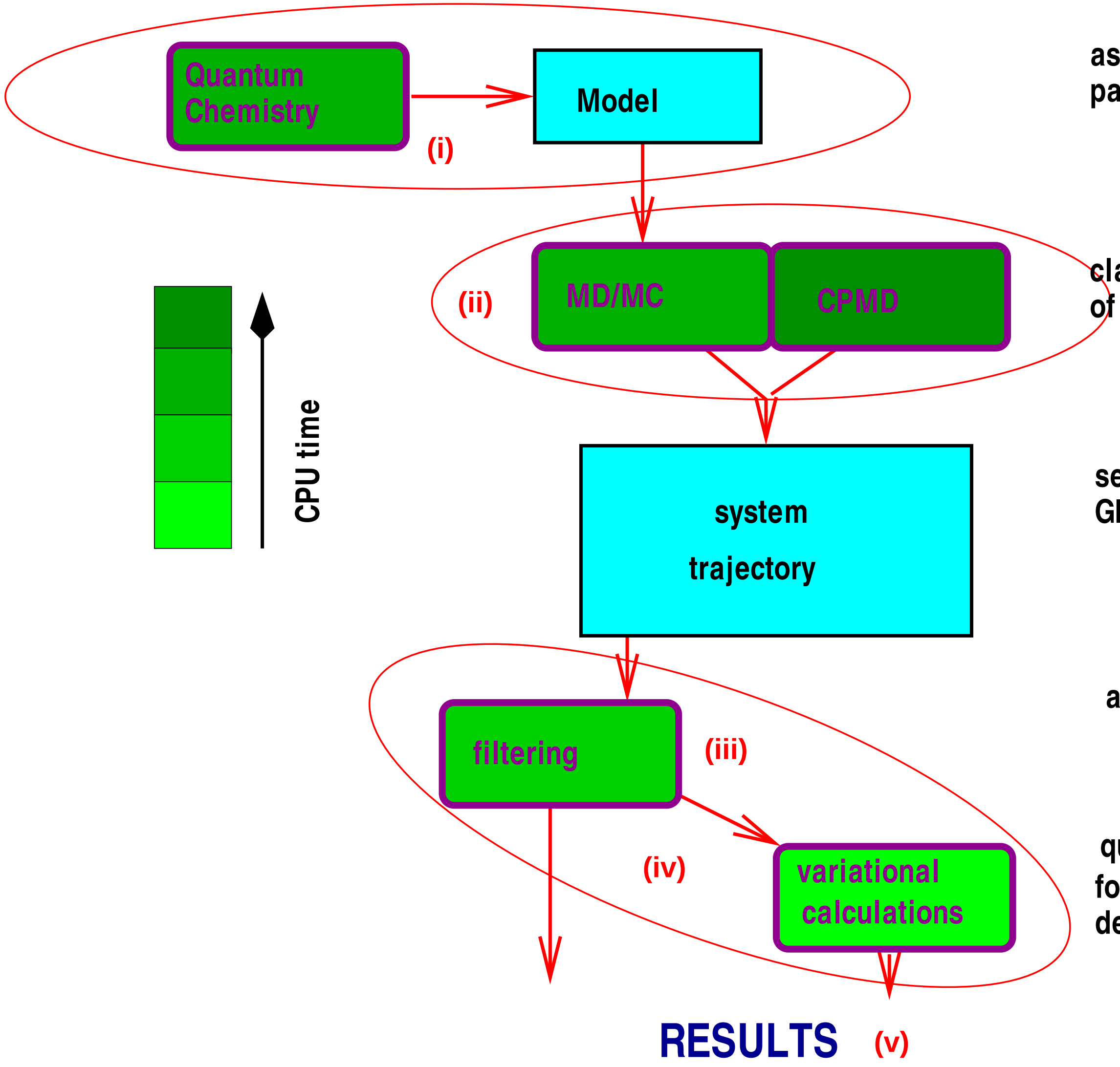
In a nutshell

The vibrational band (IR, Raman) of the OH^--ion, which is narrow in the gas phase, shifts and broadens in aqueous solution. Try to understand this.

Course of action:

(i) Model development
(ii) **Molecular simulations** (CPMD, MC) of the environment of the OH^--ion in water at ambient temperature and pressure
(iii) Quantum mechanical determination of the intramolecular Potential Energy Surface (PES) perturbed by the environment
(iv) Determination of the distribution of the (exact **anharmonic**) vibrational frequencies of OH^-
(v) Comparison with experiment (Raman, Infrared)
(→ temperature effect?)

(C)



assumptions
parameters

classical dynamics
of the nuclei

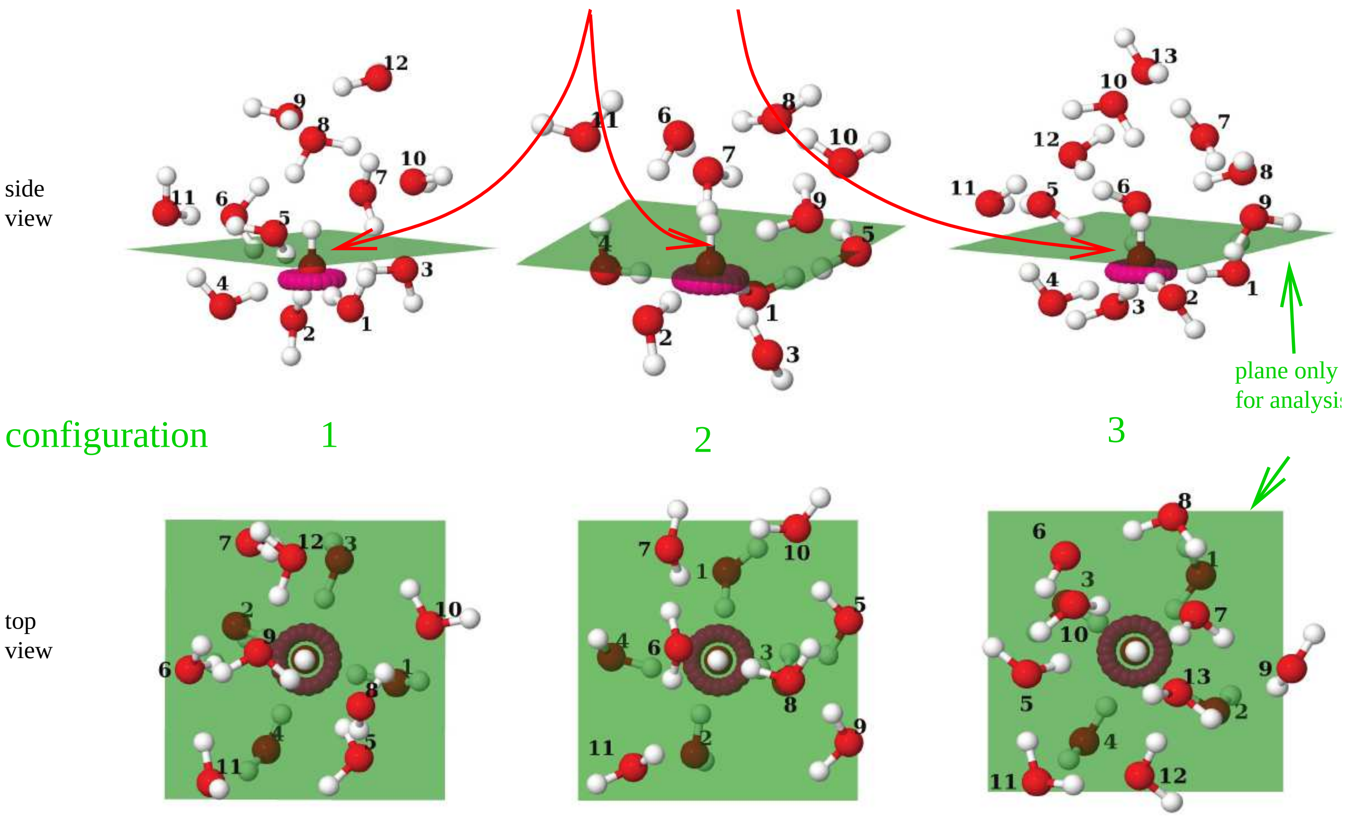
several Mbyte or
Gbyte of data

averaging

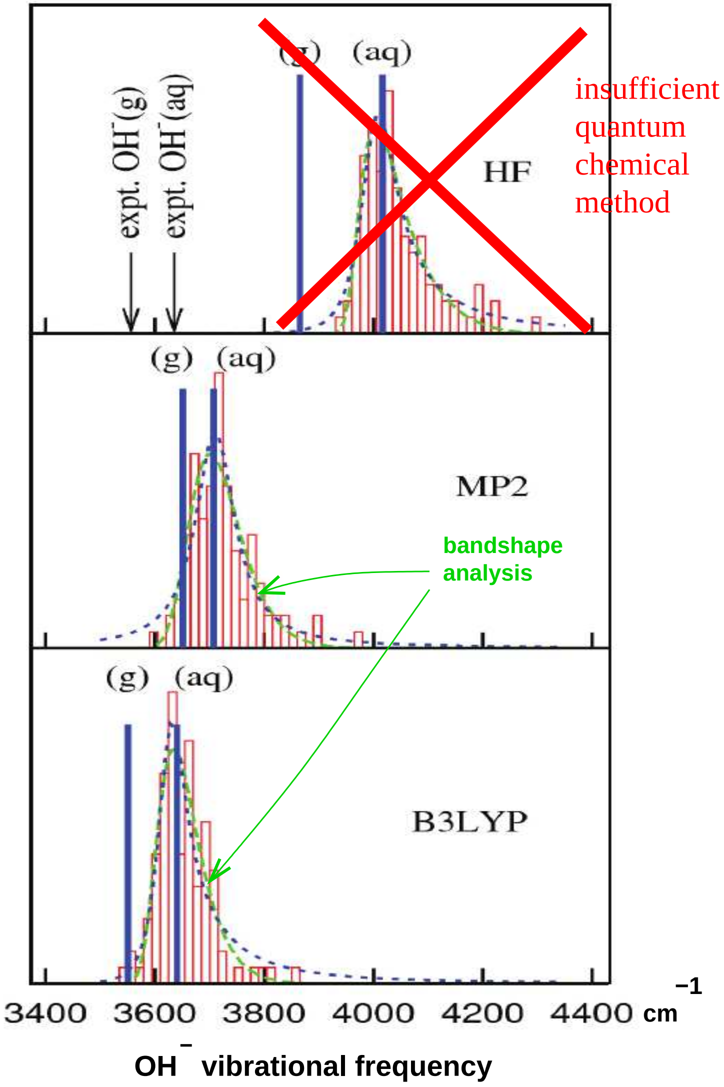
quantum mechanics
for selected nuclear
degrees of freedom

7: Examples

(C)



Histogram of vibrational frequencies



Sometimes molecular simulations (MD, MC) either

- provide much more information than we need

- cannot be carried out meaningfully because of
  - lack of information (model)
  - lack of computational resources
  - costs (industry)
  - .....

What alternatives do we have?

7: Alternate

This can be addressed by:

- Applying different levels of theory to different parts of the problem
  e.g. in QM/MM approaches
  by coupling to 'cheaper' methods
  (normal modes, field equations on grids,....)

- Coarse graining
  e.g. by removing (integrating over) the solvent
  and treating only the solute

- Some times: computing (with approximations) **only** certain quantities,
  e.g. rdfs in integral theory approaches

We'll look briefly at these things in the reverse order

(I) Let's start with the basic ideas of **integral equation theory**

We define a 'total' pair **correlation** function as:

$$h(r_{ij}) = g(r_{ij}) - 1$$

which goes to 0 for r large, as a correlation function should

which we divide up into a 'direct' and and 'indirect' part:

$$h(r_{13}) = c(r_{12}) + \rho \cdot \int_{\text{all particles 3}} c(r_{13}) \cdot h(r_{23})\, \mathrm{d}r_3$$

where the integral describes the 'indirect' influence of particle 1 on particle 2 via particle 3.
(The g_{12}-function results not only from the interaction of 1 with 2, but also from **all** interactions between 1 and 3, and 3 and 2)

This is called the Ornstein Zernike (OZ) equation

$c(r_{ij})$ is called the 'direct correlation' (ρ is the density)

Since we know neither h nor c
we need one more equation for any attempt to solve this.

This additional equation, an approximation, is called
the **closure relation**

There are several in the literature, among which:
the Percus Yevick approximation
the Hypernetted-chain equation

This is a very specialized field of statistical mechanics, and we shall not dwell much on this here.

See the Wikipedia articles on these topics

See also prof. Wim Briels lecture:
http://cbp.tnw.utwente.nl/PolymeerDictaat/index.html

7: Alternate

The relation with the pair potential is made in the closure relation, e,g, in HNC via the 'potential of mean force' (PMF, $\mathcal{W}$)

If one thinks of $g(r)$ as a probability (distribution), one can write some sort of 'Boltzmann factor' $(N_1/N_2 = \exp(-\Delta E/(k_\mathrm{B}T))$

$$g_{ij}(r_{ij}) = \exp(\frac{-\mathcal{W}_{ij}(r_{ij})}{k_\mathrm{B}T})$$

We note in passing
The PMF is often used in other contexts too.
When one has the g-functions, like in MD, it is simply
(beware the error bars)
computed by taking the logarithm of $g(r)$
Several thermodynamic quantities can be computed from $\mathcal{W}$

7: Alternate

We assume (see above, no ijs written))

$$c = g^{\text{total}} - g^{\text{indirect}} = \exp(\frac{-\mathcal{W}}{k_{\text{B}}T}) - \exp(\frac{-(\mathcal{W} - V)}{k_{\text{B}}T})$$

and V is the pair potential

Fourier transform techniques are used to solve this
ONE DIMENSIONAL integral
$\rightarrow$ So even if the math is complicted,
at the end it is fast on the computer
(i.e. get g-functions in minutes, not hours)

(II) 'Removing' the solvent: **Brownian** (and similar) **Dynamics**

This is of interest if we are interested in some *'big'* solute
(i.e. much bulkier, much heavier than the solvent molecules)
in a solutions

In this case, we are often not interested in the (fast) motions of the
'little' solvent molecules
and it would thus be nice if they could somehow be removed from
the simulation
(there are usually many more solvent than solute molecules)

Idea:
Solve equations of motion only for the solute particles,
describe the influence of the solvent by:
– and 'effective' solute-solute potential (cf. PMF $\mathcal{W}(r)$)
– a friction term in the equations of motion
– an additional (stochastic, random)- force that balances the friction

7: Alternate

So the equation of motion becomes for a solute particle i

$$M_i \cdot \frac{\partial^2 r_i}{\partial t^2} + \gamma \cdot \frac{\partial r_i}{\partial t} = -\mathrm{grad}_i\ \mathcal{V} + \mathcal{F}_i$$

In red the new terms:
– velocity dependent: friction
– additonal force $\mathcal{F}$ to compensate the friction

The various methods
(Brownian Dynamics (BD), Dissipative Particle Dynamics (DPD) etc.)
differ in what they postulate for $\mathcal{V}$, the friction and the compensating forces.

$\mathcal{V}$ is a suitable solute-solute effective potential
(e.g. the PMF obtained from MD or MC simulations)

If the $\mathcal{V}$, γ and $\mathcal{F}$ are taken from molecular simulations,
this would be real 'coarse graining'

(III) **Hybrid methods**

See e.g.
Hybrid Particle-Continuum Methods in Computational Materials Physics
edited by M.H. Müser, G. Sutmann, and R.G. Winkler
Publication Series of the John von Neumann Institute for Computing NIC
Series Volume 46
available for free on the internet

From the preface:
,,, It [*the book*] covers subjects from modelling of hydrodynamic interactions between particles in complex fluids or environments, through coarse-grained descriptions of biological systems, to the coupling of atomically represented regions with various continuum-based theories for fluids and solids. Special aspects are long-time-scale properties of systems with slow collective dynamics, ...

Example:

Molecular Dynamics Meets Finite Elements:
An Approach for Coupled Simulations of Nanocomposites
S.Pfaller, G.Possart, P.Steinmann, M.Rahimi , M.C. Böhm, F. Müller-Plathe

Hybrid techniques bring together the **advantages** of particle-based and continuum- based tools by coupling the different domains. In our approach, we aim to combine the efficiency of continuum mechanics with the accuracy of MD simulations by applying the particle-based approach only in regions of interest, e.g. in the vicinity of solid-polymer interfaces. The remaining parts are treated by continuum mechanics at a much coarser resolution. Thus, a spatial decomposition into a particle region and into a continuum is necessary.

However as Hans Ågren (Stockholm) famously said:

QM-MM methods combine the **disadvantages** of QM
with the **disadvantages** of MM

In the 'hybrid' methods, where one uses a spatial decomposition,
e.g. QM 'inside' and MM (i.e. mainly MD) 'outside' (as in QM-MM),
or
MD 'inside' and continuum mechanics (e,g Navier-Stokes)) 'outside',
or
MD 'inside' and BD 'outside',
the main problems arise in the intermediate region:

How to couple the 'inside' with the 'outside'

This is an active area of current research

In guise of a summary

– Thermodynamis describes the effect of the external conditions (temperature, presure, density, ...) on chemical systems

– Phenomenological (or chemical) thermodynamics writes self-consistent equations that describe observable quantities (heat, pressure, derivatives thereof (heat capacity, compressibility ..) ...)
Systems are described by assumed 'equations of state (e.g. van der Waals)

– Statistical thermodynamics attempts to derive thermodynamic (and other, e.g. spectroscopic) observables form microscopic (molecular) interactions (which can themselves be studied by quantum mechanics)
The interactions are usually described by 'models'

– Statistcial mechanics can be studies by analytical and numerical approaches, and combinations thereof

– Molecular simulations allow to link molecular properties with macroscopic observables at **finite temperatures**
In most cases this cannot be treated by conventional theory
(i.e. analytical methods)

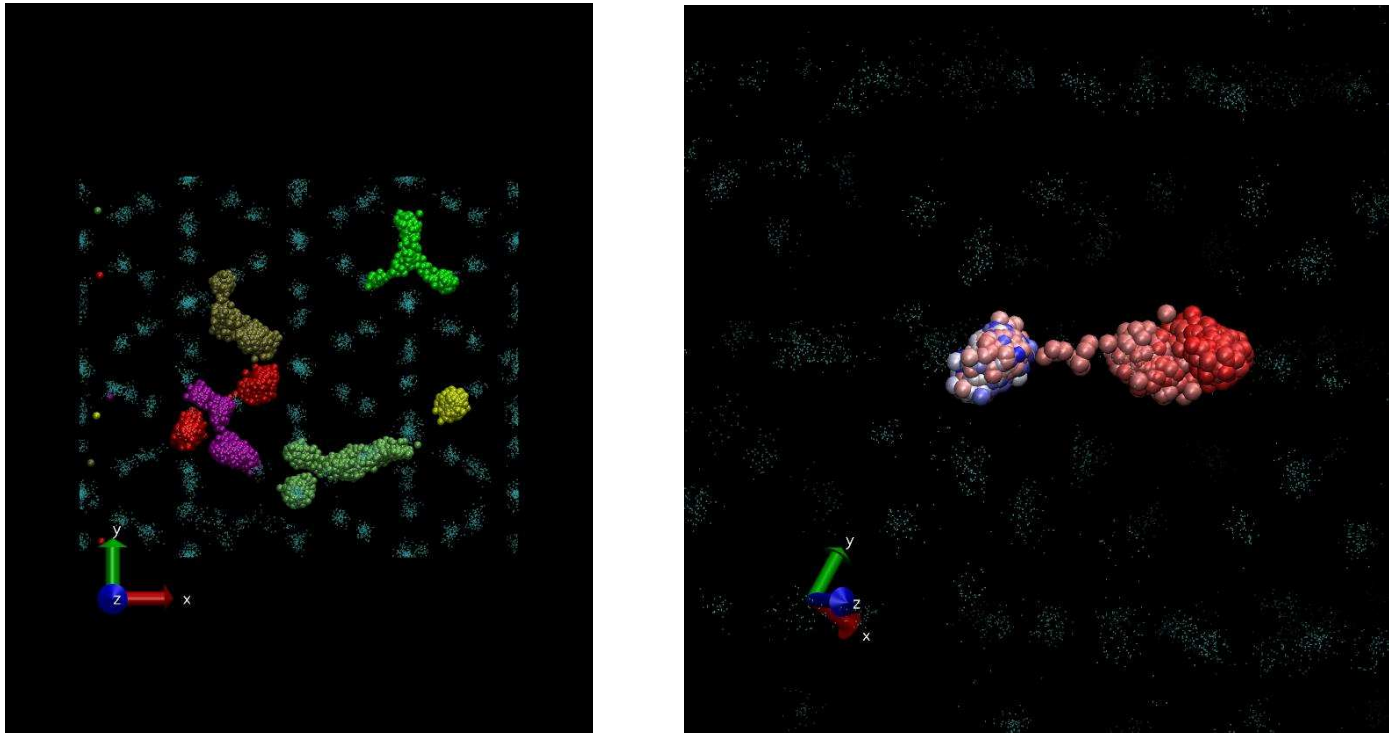
– Molecular simulations allow the **consistent** determination of many observables from from one model

– Molecular simulations are part of a well defined hierarchy of methods, making thus **coarse graining** possible (if not easy!)

– Limitations are the **space** (MC and MD) and **time** (MD) **domains** that can be explored.

– Computer time (and storage) still is, and always will be, a limitation
$\Longrightarrow$ **pure brute force does not work, smart approaches are required**

General remark 1



Motions of CH_4 molecules in a MOF framework during a few 10 ns
→ All are 'different', none looks like 'the average'
→ In many cases it is not sufficient to study the average, one must at least study the distributions
The example on the right is e.g. typical of 'jump diffusion'

`data by Pooneh Pilvar and Siegfried Fritzsche, Leipzig`

General remark 2

analytical vs. predictive usage of simulations

A referee recently stressed in a comment:

".. the importance of carefully validating models before their applications .."

However, this is more easily said than done:

– using simulations as an analytical tool → possible (*and often done*)

– using simulations as a predictive tool → difficult at best
(if you do not want your result just
to reflect your prejudice)

General remark 3

When you make, or listen to, an argument, always make very clear
to yourself whether this argument is based on:

– equilibrium considerations ((free or other) energies, partition functions, etc.)
or on
– the time evolution of the system (kinetics)
(how long it takes for the system to reach equilibrium,
if it does! Some systems (e.g. glasses) take forever to reach equilibrium, (i.e. they never reach it))

– The question how long it takes to reach equilibrium is also important if you want to prepare an equilibrium system for simulations.

General remark 4

Examples of questions (for the exam?):

Explain why some reactions work well in the liquid phase
and not so well in the gas phase?

– what could favor reactions in the liquid phase?
– what could hamper, or slow down, reactions in the liquid phase?
(*see also next question*)

What computations could I do to study this?

A particle B with mass m$_B$ a kinetic energy of $E_{\text{kin}} = 0.1$ (in some units) approaches a particle A with mass M$_A$ and no kinetic energy, initially at a very large distances r_{AB}.

A and B interact via an interaction potential which has a depth of 0.15 units

→ Will they react to form an AB molecule
with an energy of ≈ -0.25 units?
or some other energy ?
What will be the final state of this system?

→ Can things trun out differently if there are other molecules $C, D, E, \ldots$ around that interact both with A and B?

8: .. & Exam

Which term in the partition function ratio dominates in the equilibrium constants of the following equilibria:

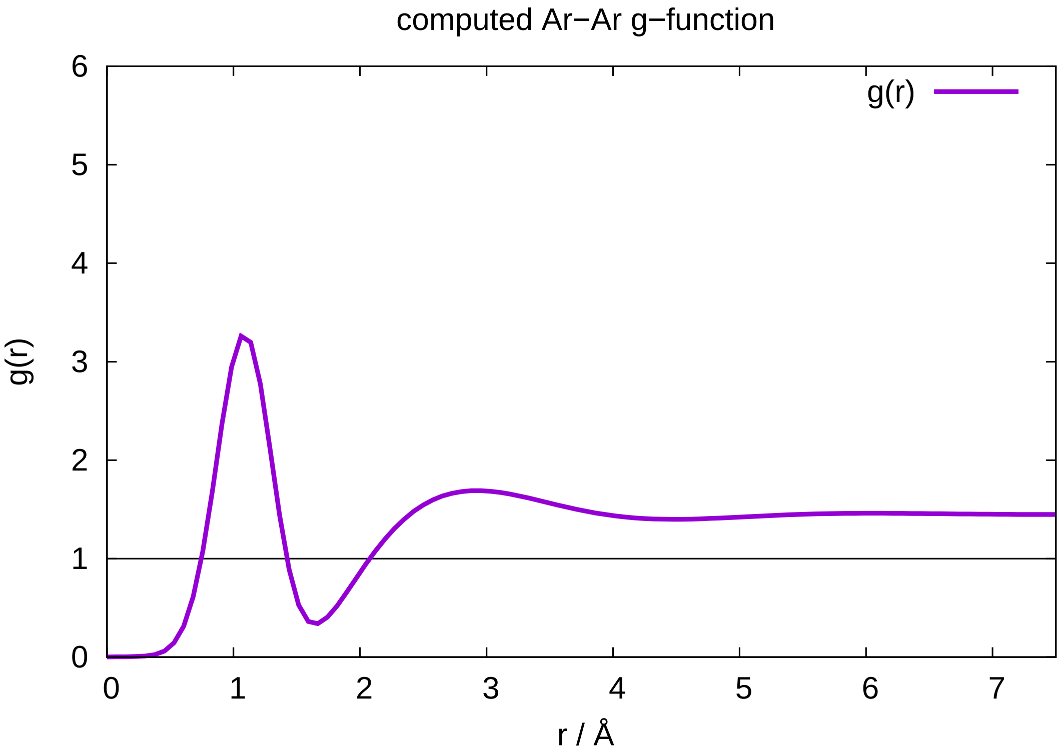
$$\mathrm{H_2} + \mathrm{Cl_2} \leftrightharpoons 2\mathrm{HCl}$$

$$\mathrm{H_2O} + \mathrm{D_2O} \leftrightharpoons 2\mathrm{HDO}$$

$$\mathrm{Ar} + \mathrm{Ar} \leftrightharpoons \mathrm{Ar_2}$$

Explain your reasoning,
make a comment about the temperatures

How do I know that something is wrong in my MD (or MC) simulation of liquid Argon at 65 K if the computed Ar-Ar $g(r)$-function looks like this (several reasons)



The depth of the Ar-Ar interaction (pair) potential is about $\frac{E}{k_\mathrm{B}} = 30$ K.

However, the energy of vaporization (again $\frac{E}{k_\mathrm{B}}$) is about 750 K

How can this be?

In an (NVE)-MD simulation, you decide on the number of particles N and the box volume V, your system thus has a (number-)density of $\rho = \frac{N}{V}$.
In experiments, it is easier to control the density than to control the volume
(*how can you control density or volume in experiments?*)

The relation between pressure and density, $p(\rho)$, (e.g. $p = nR\rho T$ in an ideal gas) in a simulation may not be the same as in the experiment
(p *can be computed from the forces*)

What can you do about this?

more exam questions

Books

P.W. Atkins, Physical Chemistry, *XY*th Edition, Oxford University Press
for general physical chemistry

D.A. McQuarrie, Statistical Mechanics, Harper & Row
for molecular partition function, equilibria, and everything on liquids

E. B. Wilson, J. C. Decius and P. C., Cross Molecular Vibrations
The Theory of Infrared and Raman Vibrational Spectra, Dover Books
THE classic on normal modes and vibrational spectra

C. Kittel, Introcuction to Solid State Physics, Wiley
The title says it all

R.K. Pathria (and P.D. Beale in later editions)
Statistical Mechanics, Elsevier
`http://home.basu.ac.ir/~psu/Books/[Pathria_R.K.,_Beale_P.D.]_Statistical_mechanics.pdf`
for the introduction to the 'partition function'

8: more books

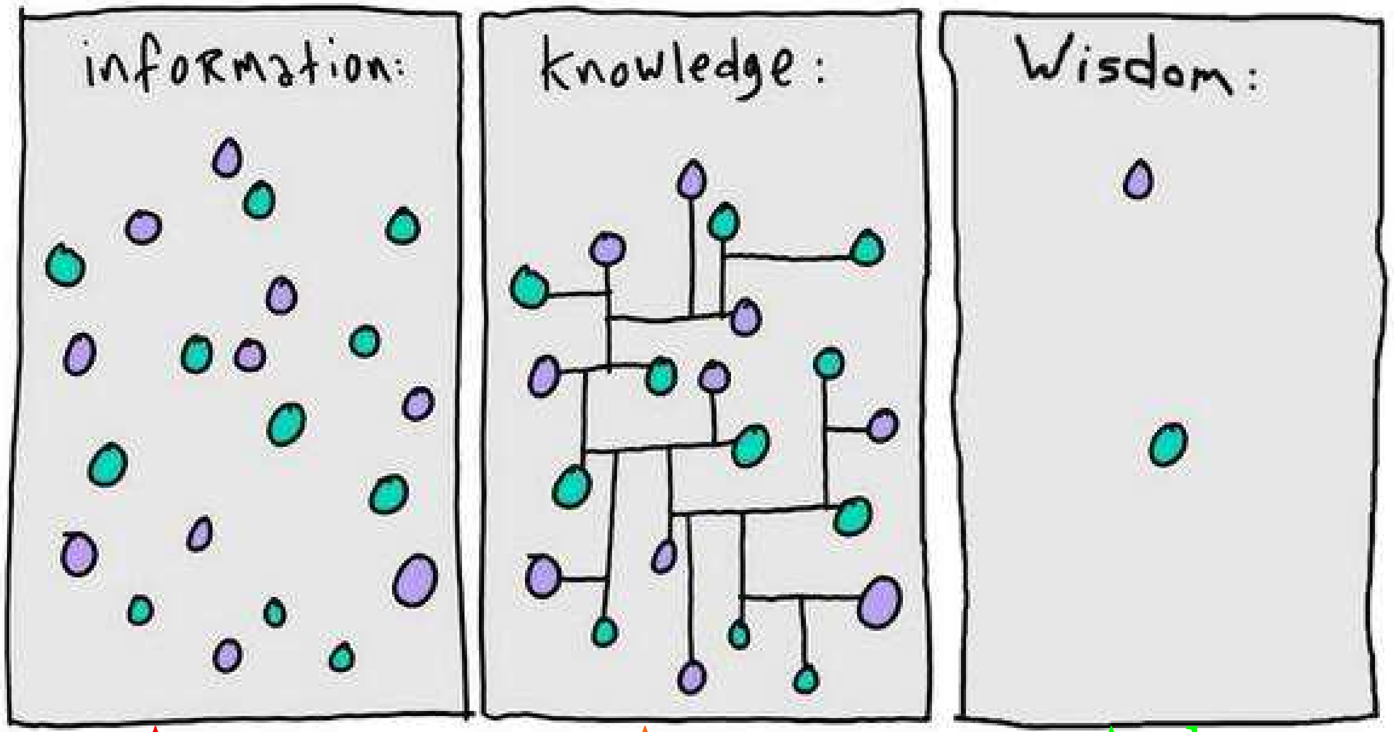
M.P. Allen, D.J. Tildesley,
Computer Simulation of Liquids, Oxford Science
detailed explanations of the fundamentals, with FORTRAN codes
`http://www.ccl.net/cca/software/SOURCES/FORTRAN/allen-tildesley-book/f.00.shtml`

I.R. Levine, Quantum chemistry, Prentise Hall
one of my favorite QC books
`http://www.slideshare.net/diegogarciadossantos/0835quantum-chemistry-5th-edition-by-ira-n-levine`

More free books at:
`http://www.freebookcentre.net/Chemistry/Quantum-Chemistry-Books.html`

I have some of these books as pdf files

Conclusion



⇑ start ⇑ now ⇑ later

This is the end, my friend

(The Doors, 1967)