CHE 502 Chemical and Statistical Thermodynamics

1st semester, academic year 2018/19 (Sept.3 – 14, 2018)

CHE 501 Modeling of Molecules, Materials and Processes

2nd semester, academic year 2018/19 (Feb. 4 – 15, 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://loriot.ism.u-bordeaux.fr/vistec2018/vistec2018.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, *X*/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

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 $\Rightarrow$ (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* $\rightarrow$ *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)
....

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

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

heat capacity

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

chemical potential

$$\mu = \frac{\partial U}{\partial N} \left(\frac{\partial H}{\partial N}, \frac{\partial G}{\partial N} \ldots \right) \text{ depending on conditions}$$

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

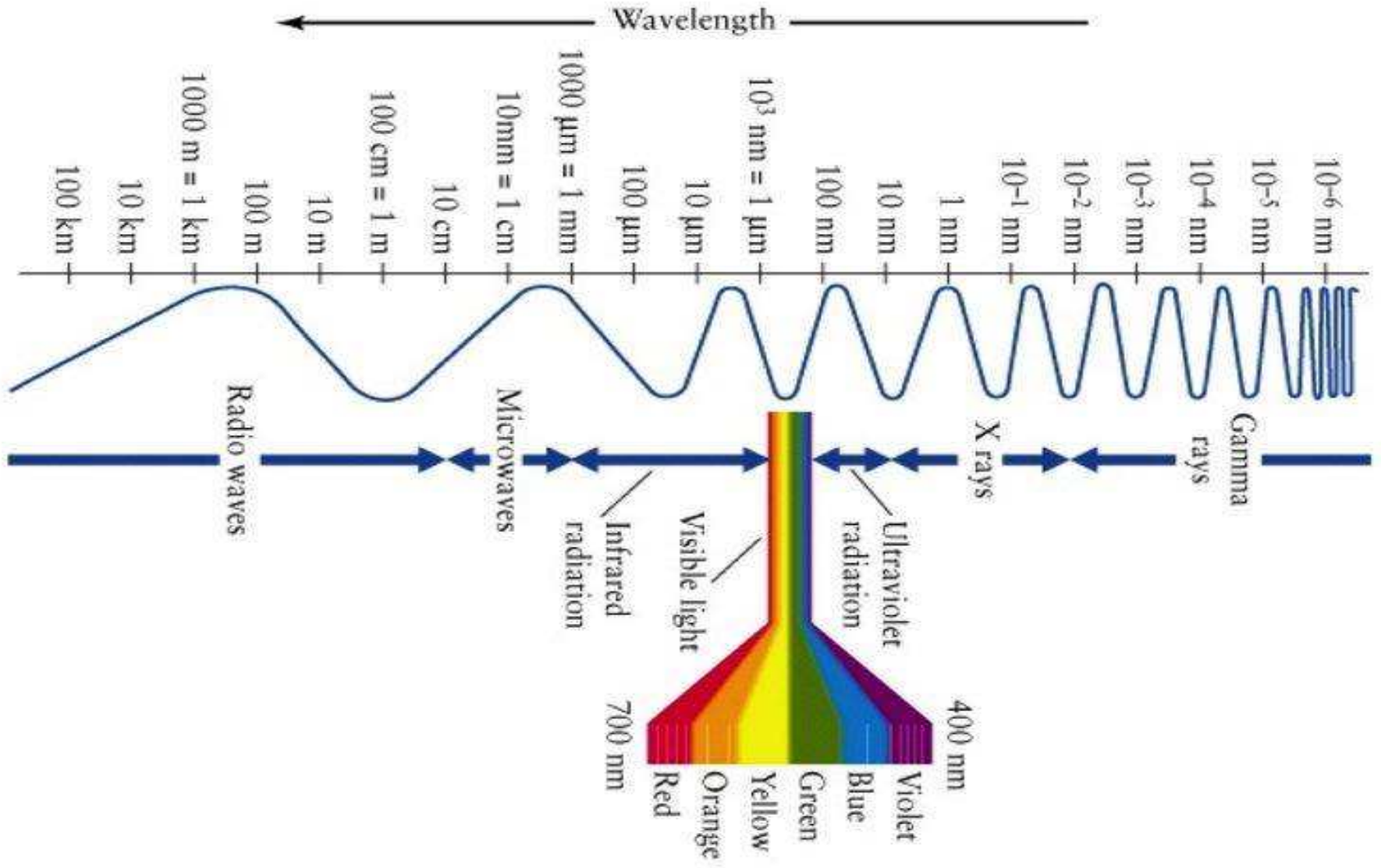
http://vergil.chemistry.gatech.edu/notes/quantrev/node20.html

→ 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:

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

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

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

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

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 ($\rightarrow$ 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 !
$\rightarrow$ 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":

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

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

$\lambda >$ particle dimension : $'$quantum$'$ behavior : (uncertainty principle, 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

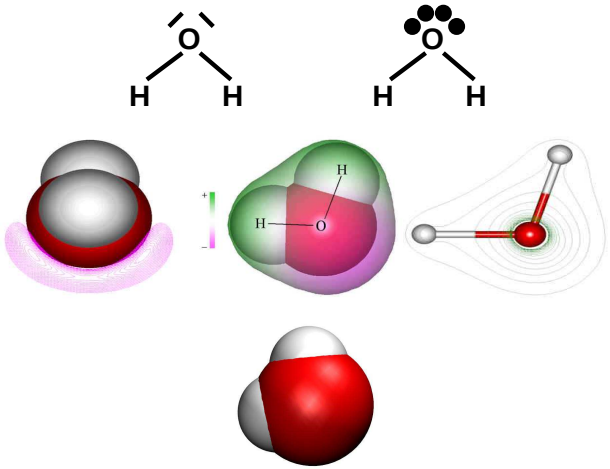
Keywords (which you should remember) for the solution of the Schrödinger equation for the electrons at fixed positions of he nuclei:

- 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

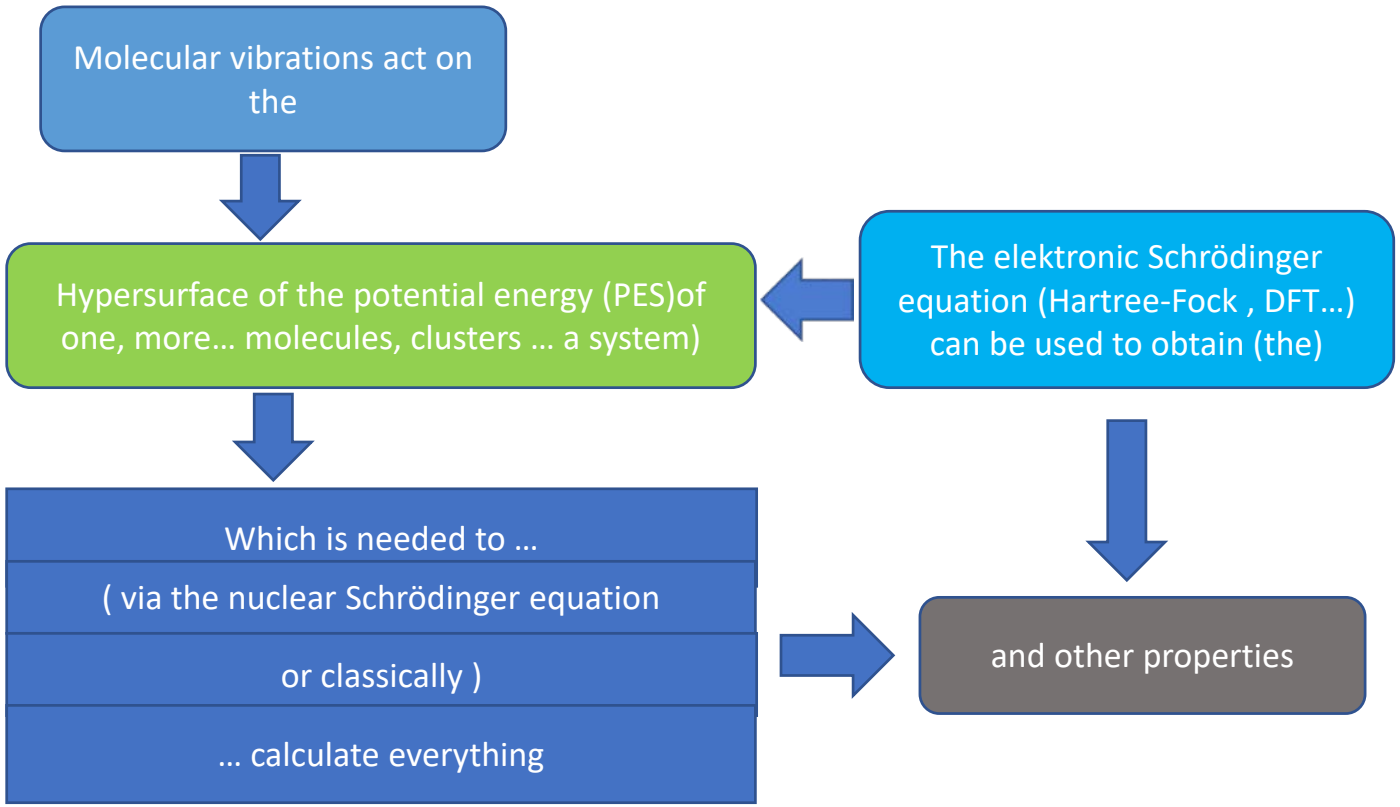
nothing more

Topic:
Modeling the molecular interactions

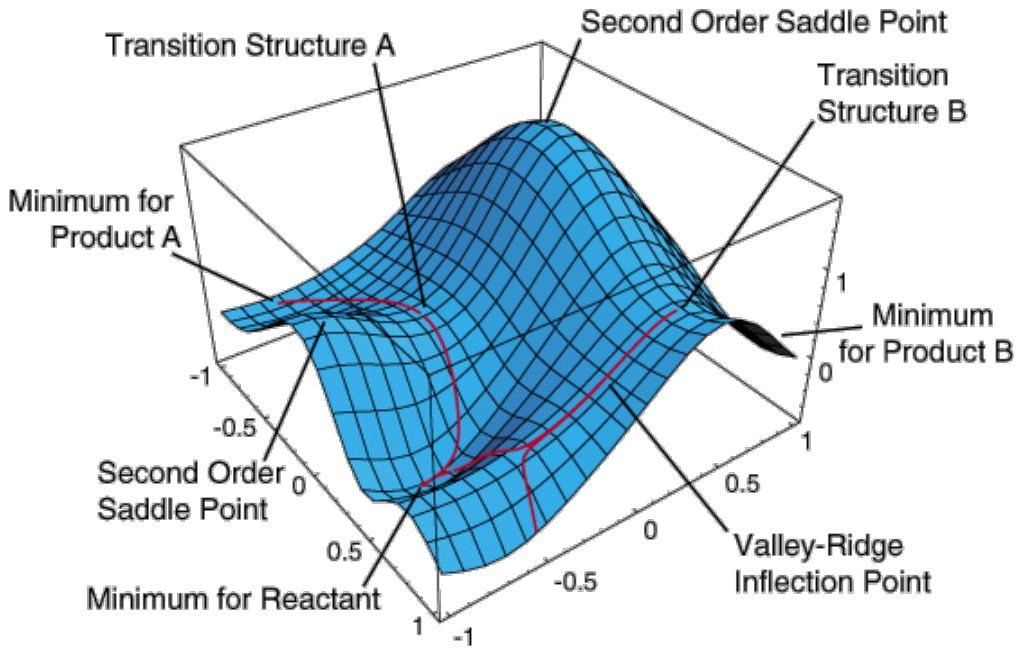
The PES of a molecule (cluster …)

- Without PES no chemistry and no molecules:
  - every ‘Molecule’ would be different (its energy would not only depend on its geometry but also on its history.
- The Born-Oppenheimer – approximation states that a PES exists.
- But: one PES for each electronic state.
- The PES allows a eine topographical interpretation of reactions and conversions of molecules.
- Next slide

To remember: Relations



The PES of a molecule (cluster …)



Modeling the molecular interactions - general

- **The potential energy in an N-particle system V = f(r) must be expressed in some tractable way since it needs to be *known* and it needs to be *calculable*.**
- **It can either be calculated quantum mechanically or be derived from a mathematical expression ('energy formula') that includes some physics.**

Modeling the molecular interactions - general

Which energy formulas are useful ?

- **For $r_{ij}=0$, E_{ij} should be ∞**
  - **… not fulfilled by $\exp(-a\, r_{ij})$**
- **For $r_{ij}=\infty$, E_{ij} should be 0**
  - **… not fulfilled by a polynomial in r_{ij}**
- **Normally, E_{ij} should have none or one minimum**
  - **No minmum $\rightarrow$ repulsion**
  - **One minimum $\rightarrow$ attraction**
- **Sometimes but rarely, E_{ij} has one maximum (and therefore how many minima ?)**

Modeling the molecular interactions - general

(discuss Electron-electron interaction
Long- and short range, Energy vs. force …

The potential energy in the pair approximation:

In the pair approximation one assumes that the total energy is a sum of pairwise interactions. For example, if Eij is set to be a sum of ak/rk terms:

- **The total energy is then:**
  (*ji* … pairs of molecules
  lm* … interaction centers in pair *ij
  ***k* … term in sum over 1/r powers)**

$$\mathbf{V}_{tot} = \sum_{ij} \sum_{lm} \sum_{k} \frac{a_k}{r_{lm}^k}$$

The potential Energy V

Functional forms:

Sutmann chapter 2

- The pair approximation needs distances as input:

  Angular $\rightarrow$ Radial

$$\mathbf{V}=\sum_{ij}\mathbf{f}_{kl}(C_{ij}) \qquad \mathbf{V}=\sum_{\mathbf{ij}}\sum_{kl}\mathbf{f}(\mathbf{r}_{kl})$$

$$\mathbf{f}(\mathbf{r}_{ij})=\sum_{k=1}^{n}\frac{a_k}{r_{ij}^k}$$

Modeling the molecular interactions

Deficiencies of the pair approximation:

The pair approximation is a truncation of the energy expression:

E=f(i)+f(ij)+f(ijk)+f(ijkl)…

the pair term is always the most important …

… but unfortunately the series converges slowly

- Polarisability normally what causes the largest deviation from the pair approximation
- Charge transfer
- Directional effects (bonds)

Polarisability concepts, examples for going beyond the pair approximation, …

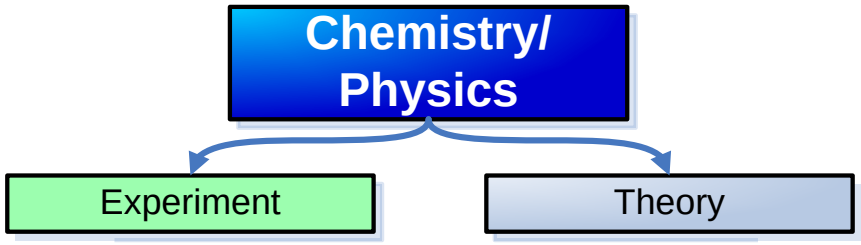
Discussion: polarisation

Potential Energy Functions II: step-by-step

Potential functions

(**1**) What it is about …

Chemistry/ Physics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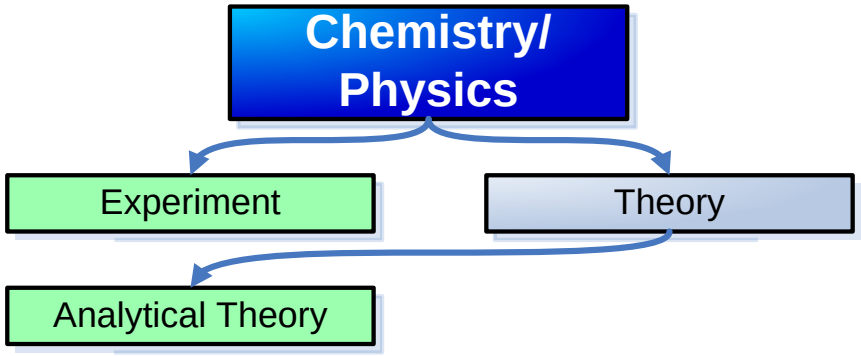
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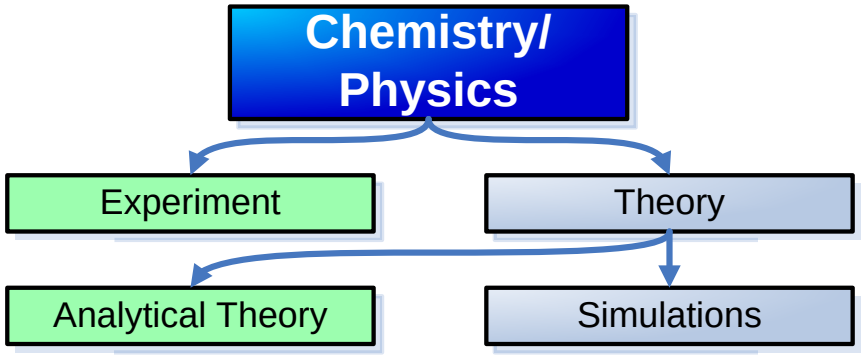
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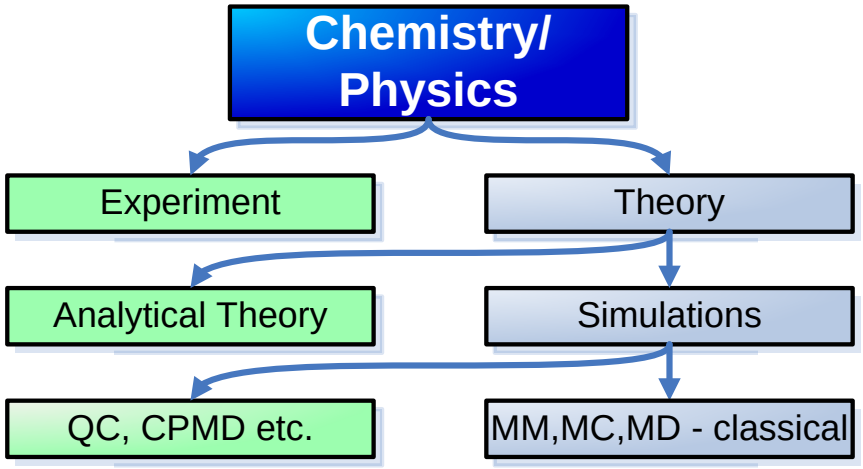
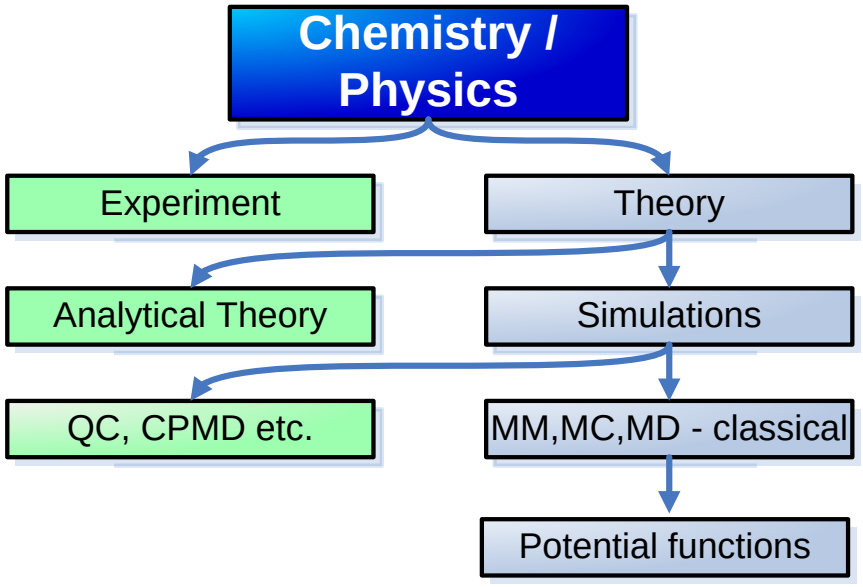

Chemistry/
Physics
Experiment
Theory
Analytical Theory
Simulations
QC, CPMD etc.
MM,MC,MD - classical


Chemistry / Physics
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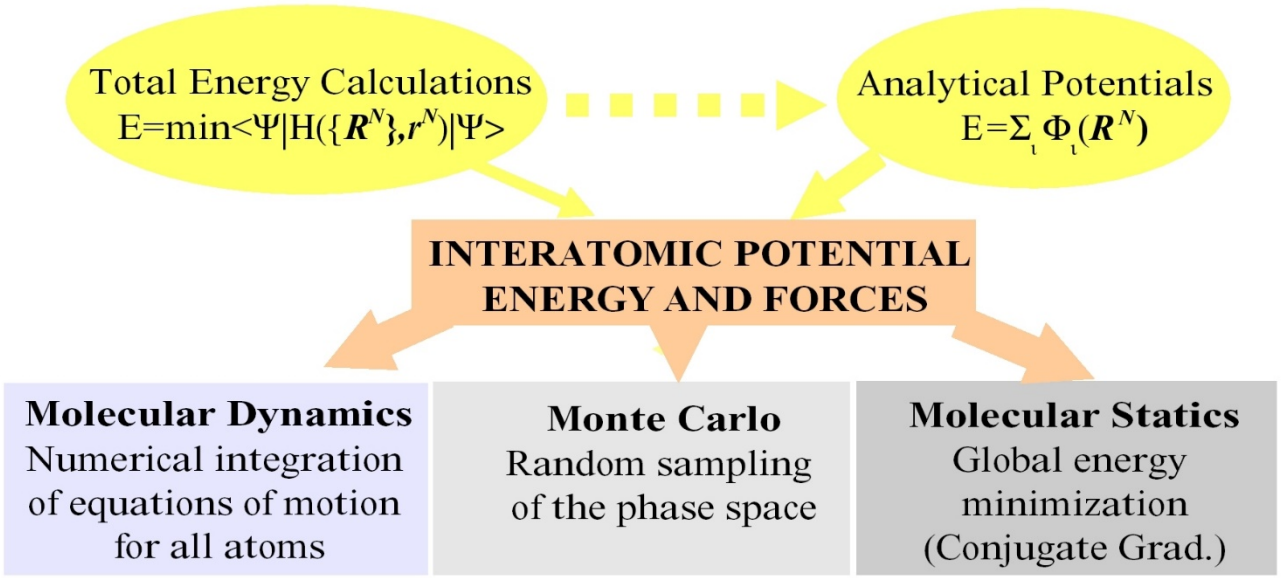
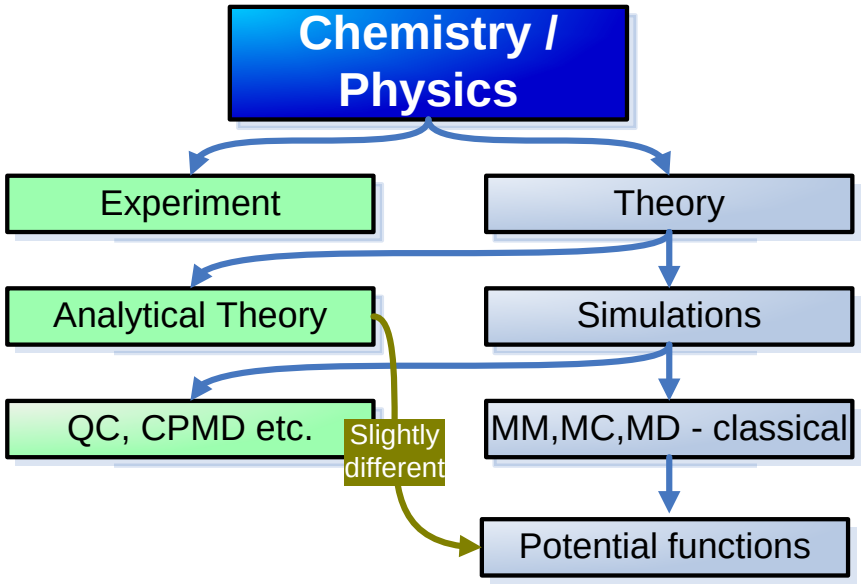
MM,MC,MD - classical
Potential functions

Atomistic Computer Simulation Methods




Chemistry / Physics
Experiment
Theory
Analytical Theory
Simulations
QC, CPMD etc.
Slightly different
MM,MC,MD - classical
Potential functions

Potential functions

An analytical potential function is an expression for the total energy of a system as function of the atomic coordinates.

Potential functions

Why does one need them ?
(in the context of molecular simulations)

Properties via Simulations ?

- A system consists of n particles. (Atoms, molecules, ions ...).
  Their behavior results from their electronic structure which governs the interaction between them (their attraction and repulsion).
- A potential energy function E which is a scalar function of the coordinates of the particles is containing all this in is containing all information about these interactions.
- How can one calculate macroscopic properties from E ?

(Macroscopic properties could be, for example:

- the pressure p=f(V),
- average geometries at a given temperature or
- (vibrational, electronic) spectra ?

- This is normally not possible in a simple way.
- One needs MD simulations because of the lack of analytical formulas.
  There are no formulas like ‘p=nRT / V’ for properties of real systems.

- Therefore, there are two problems
- The first one is the **potential energy function** $E_{pot}=f(X)$.
- *Experience (of the last 30 years) has shown that quantum chemistry is a powerful tool to tackle the problem of the potential energy function.*
- The second problem is the **calculation of properties** if $E_{pot}=f(X)$ is known. Computer simulations (especially MD) can do this numerically.

- (**2**)
  The general scheme of fitting quantum chemically derived data to analytical expressions:
  How to get a potential function

Potential functions

i.E. Lennard-Jones

$$E = E_{LJ} + E_{qq}$$

$$E_{LJ}(r) = \left\{ 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \right\}$$

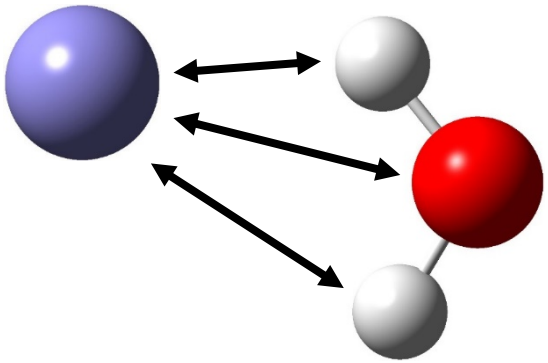
$$E_{qq}(r) = \frac{q_i q_j}{r_{ij}}$$

r is the distance between 2 atoms

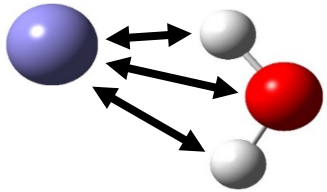
Potential functions

$$E(r_{ij}) = \left\{ 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] \right\} + \frac{q_i q_j}{r_{ij}}$$

For a water molecule interacting with i.E. an atomic ion I^+ there would be 3 such terms:



We can write the formula slightly different so that it becomes a polynomial in 1/r:



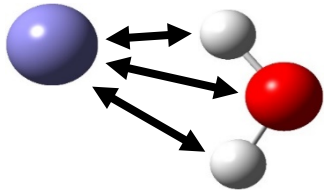
$$E(r_{ij}) = \frac{A}{r_{ij}^{12}} + \frac{B}{r_{ij}^{6}} + \frac{q_i q_j}{r_{ij}}$$

We need different parameters A,B for the interaction between I^+-O and I^+-H but the two I+-H interactions have the same parameters A,B. The total interaction energy is:

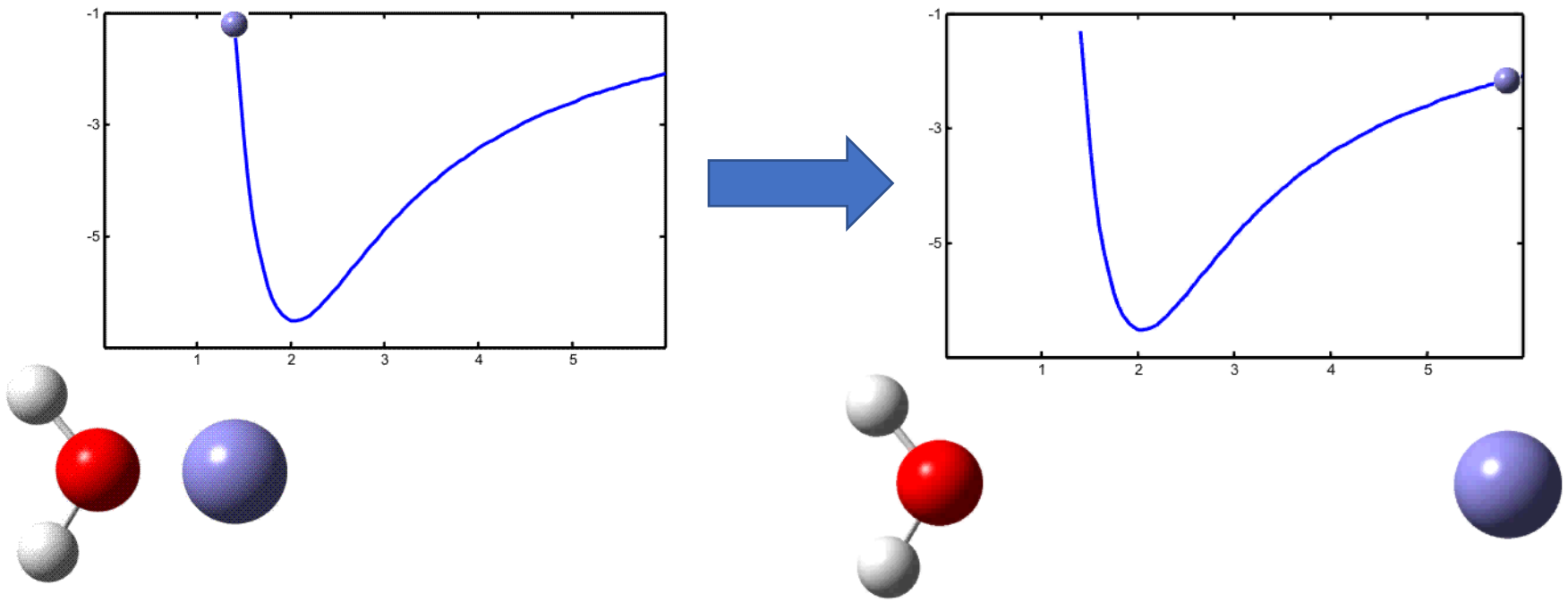
$$E_{I^+-W} = \frac{A_{I^+-O}}{r_{I^+-O}^{12}} + \frac{B_{I^+-O}}{r_{I^+-O}^{6}} + \frac{q_{I^+} q_O}{r_{I^+-O}} +$$
$$+ \frac{A_{I^+-H}}{r_{I^+-H^1}^{12}} + \frac{B_{I^+-H}}{r_{I^+-H^1}^{6}} + \frac{q_{I^+} q_H}{r_{I^+-H^1}} +$$
$$+ \frac{A_{I^+-H}}{r_{I^+-H^2}^{12}} + \frac{B_{I^+-H}}{r_{I^+-H^2}^{6}} + \frac{q_{I^+} q_H}{r_{I^+-H^2}}$$

We have now the 7 parameters

$$A_{I^+-O}, B_{I^+-O}, A_{I^+-H}, B_{I^+-H}, q_{I^+}, q_O, q_H$$



- In general, a set of atoms in a certain environment (like H in H_2O which, for example, is different from H of CH_4) is called a ‘class’. In this example, atoms and classes are the same.
- The q – parameters are *class-specific* parameters for which good values often can be calculated via so-called ‘population analysis’, (atomic partial charge analysis), a standard quantum chemical method.
- The A and B – parameters are *class-pair specific* parameters that can be calculated via fitting to quantum chemical energies.


-1
-3
-5
1
2
3
4
5
-1
-3
-5
1
2
3
4
5

To consider:

- Many orientations and distances
- Scanning a 3-dimensional (in the example) or 6-dimensional (in the general case) space.
- Computationally demanding
- The energy is linear in the A, B – parameters in a polynomial expression. Expressions like ‘exp(-C r)’ are also commonly used, where this is not the case.

(3) The (non)additivity of interactions

- A formula like $$E_{I^+-H_2O} = \sum_{O,H,H} \frac{A}{r^{12}} + \frac{B}{r^6} + \frac{q_i q_j}{r}$$

  describes the interaction between the ion and water. If we have many water molecules, can we simply say:

$$E_{total} = \sum_{(H_2O_i)} \sum_{O_i,H_i,H_i} \frac{A}{r^{12}} + \frac{B}{r^6} + \frac{q_i q_j}{r} + E_{H_2O} \; ?$$

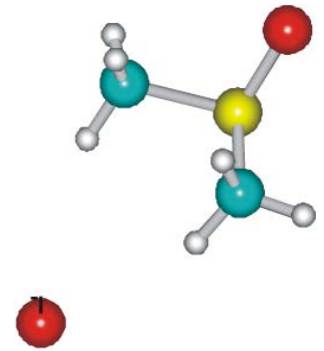
- If we do so, we use the so-called pair approximation.

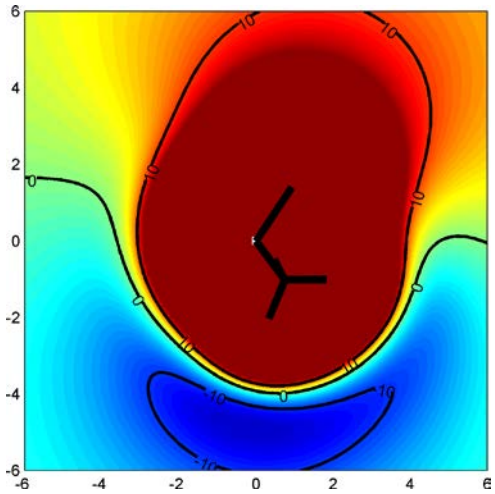
(4)
An example (where the pair approximation is used):

Interaction between Be^{2+} / I^- and DMSO:

After the construction of the potential energy function, it must be checked.

- Example for I^-:



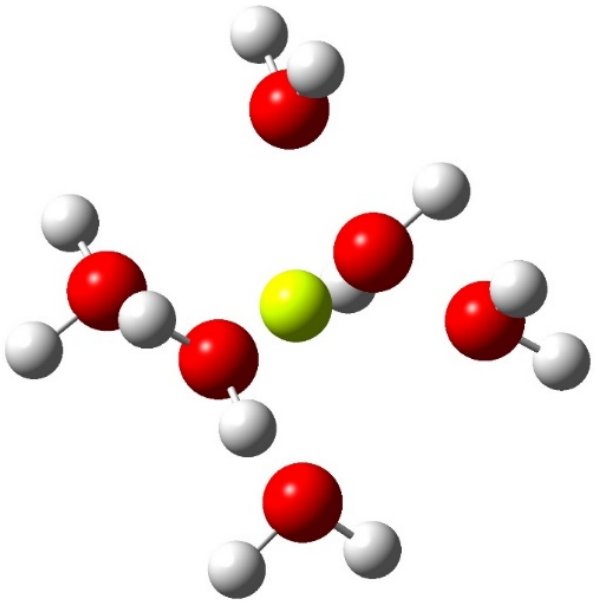


-14 kcal/mol →

∞

(5)
Another example (beyond the pair approximation)

The pair approximation is often not good enough, especially for ion-ligand interactions:



$AlCl_3$ in water with the following potential energy function:

Interatomic potentials for the intermolecular interactions (in Å and kJ mol^{-1}).[a]

$$V_{OO}(r) = 604.620/r + 111.91 \times 10^3/r^{8.8591} - 1.045(\exp(-4(r-3.4)^2) + \exp(-1.5(r-4.5)^2))$$

$$V_{OH}(r) = -302.31/r - 26.0725/r^{9.19912} - 41.8229/(1+\exp(40(r-1.05))) - 16.7292/(1+\exp(5.49305(r-2.2)))$$

$$V_{HH}(r) = 151.155/r + 418.395/(1+\exp(29.9(r-1.968)))$$

$$V_{AlO}(r) = -2750.51/r - 2495.69/r^2 + 266001\exp(-3.89948r)$$

$$V_{AlH}(r) = 1375.26/r + 160.655/r^2 + 287.458\exp(-0.35461r)$$

$$V_{ClO}(r) = 916.563/r - 111.380/r^2 + 379670\exp(-3.20906r)$$

$$V_{ClH}(r) = -458.281/r + 1.88974 \times 10^{26}\exp(-33.977r)$$

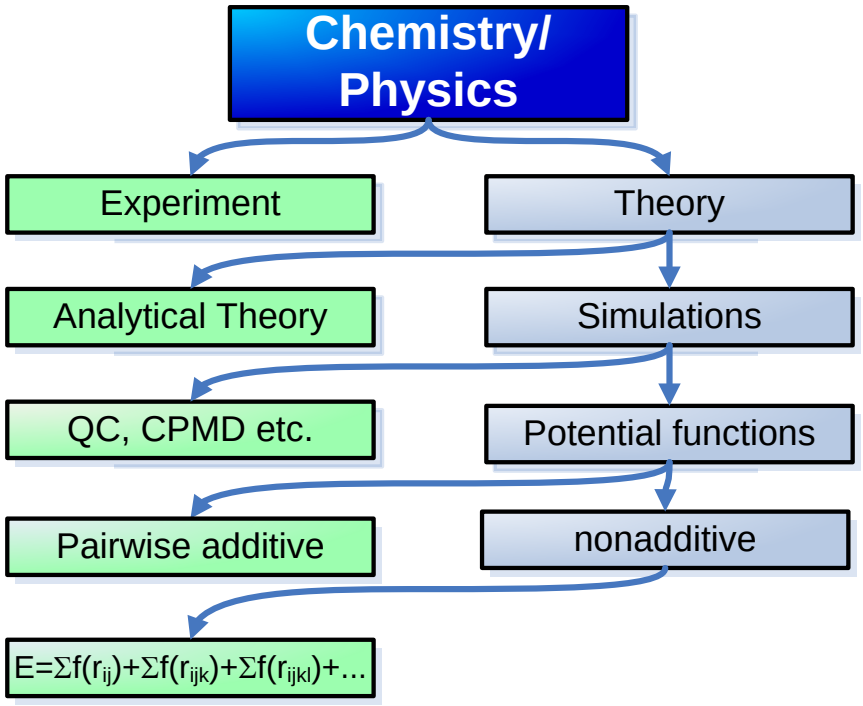
$$V_{AlAl}(r) = 12505.0/r - 2360.20/r^2 + 5228.69\exp(-1.038r)$$

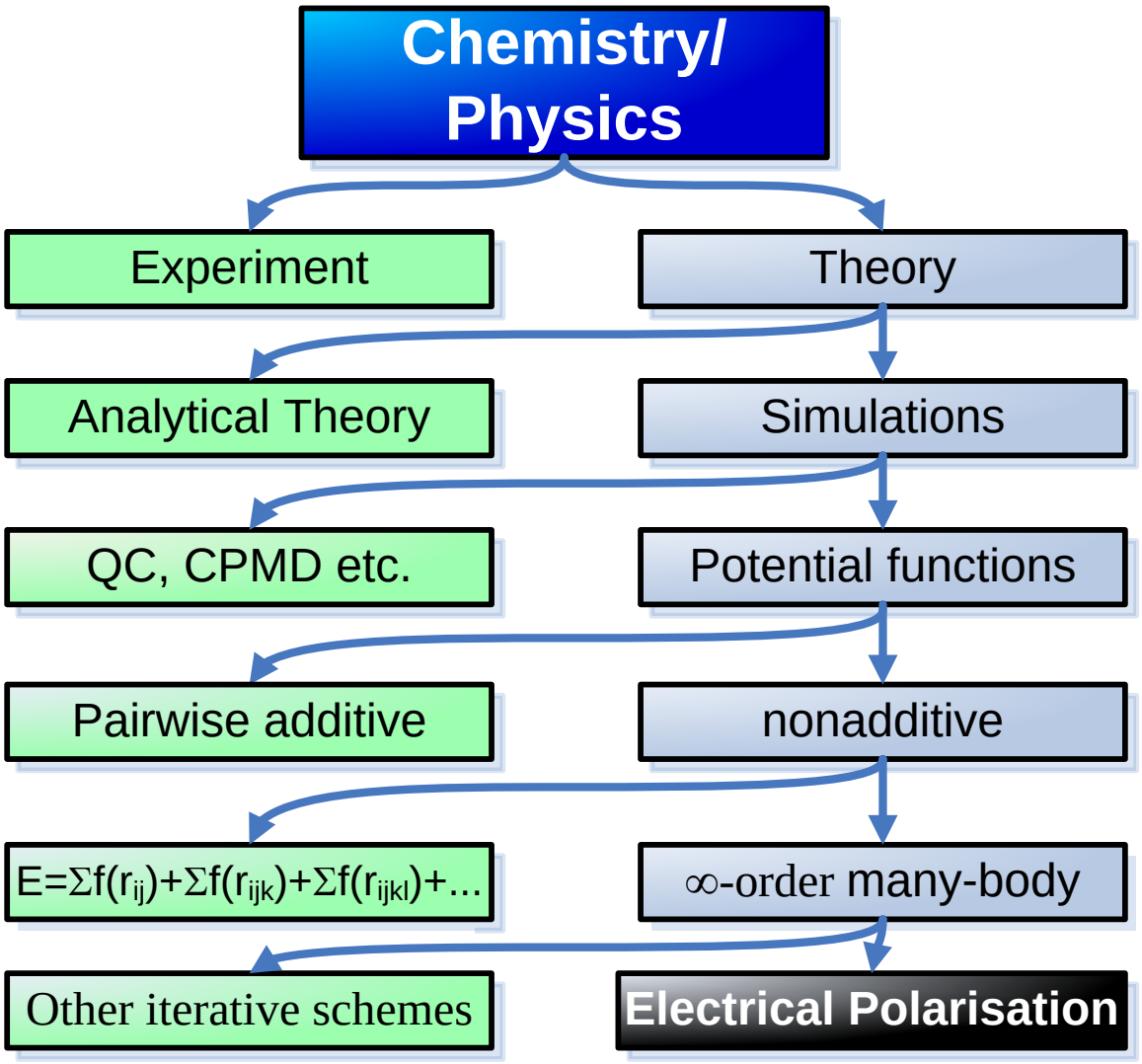
$$V_{AlCl}(r) = -4168.14/r - 1115.36/r^2 + 373934\exp(-3.68r)$$

$$V_{ClCl}(r) = 1389.29/r + 28674.4/r^6 + 917099\exp(-3.39r)$$

$$V_{OAlO}(r_1, r_2, \alpha) = 74.8588(0.0641288 + (\pi - \alpha)^2)^2\exp(-0.246481(r_1^2 + r_2^2))$$

[a] in the last line, α is the O–Al–O angle.


Chemistry/
Physics
Experiment
Theory
Analytical Theory
Simulations
QC, CPMD etc.
Potential functions
Pairwise additive
nonadditive
E=Σf(r_ij)+Σf(r_ijk)+Σf(r_ijkl)+...


Chemistry/
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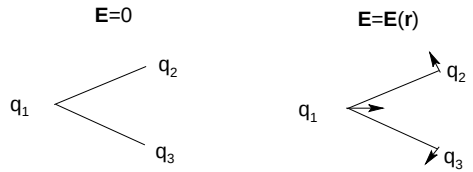
Potential functions
Pairwise additive
nonadditive
E=Σf(r_ij)+Σf(r_ijk)+Σf(r_ijkl)+...
∞-order many-body
Other iterative schemes
Electrical Polarisation

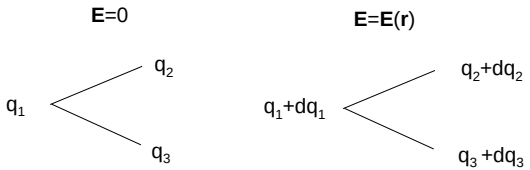
Ways to deal with nonadditive interactions: The point-dipole model (PDM):

Atomic polarizabilities α_i are assigned to some molecular site and the electric field induces the formation of a point dipole μ_i



The fluctuating charge model (FQ):

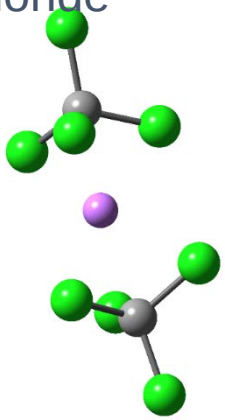
Charges are allowed to fluctuate according to the electronic properties of the molecule as atomic electronegativity and atomic hardness.

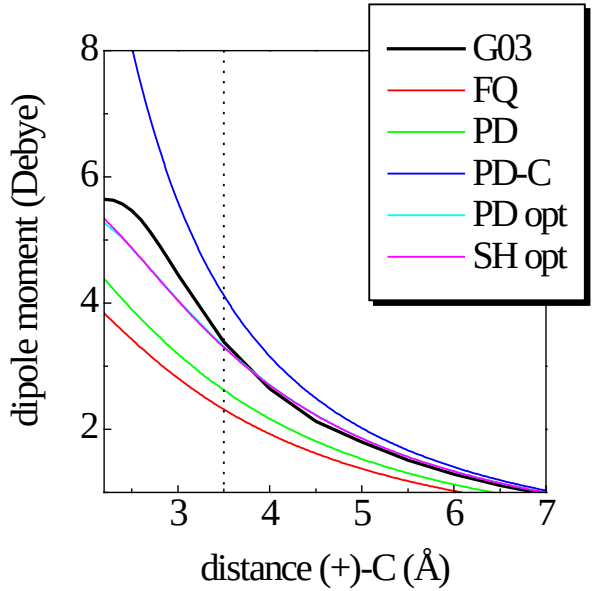


$dq_1 + dq_2 + dq_3 = 0$

Comparison of the behaviour of these ‘polarisation models’:

Example:
Li^+ ion near
Carbon
Tetrachloride

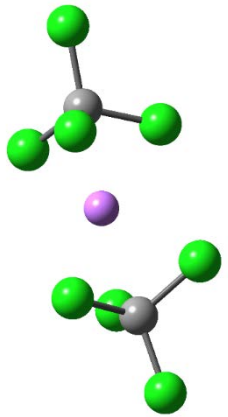




Conclusion:

Induced dipole moments (=polarization) can be large.
The effect on the electrostatic energy can be large

(keep in mind, however, that Li^+ ion near carbon tetrachloride is an extreme example.)



Modeling the molecular interactions: The reality for everyday systems

Normally one divides between:

- Inter- and
- intramolecular interactions

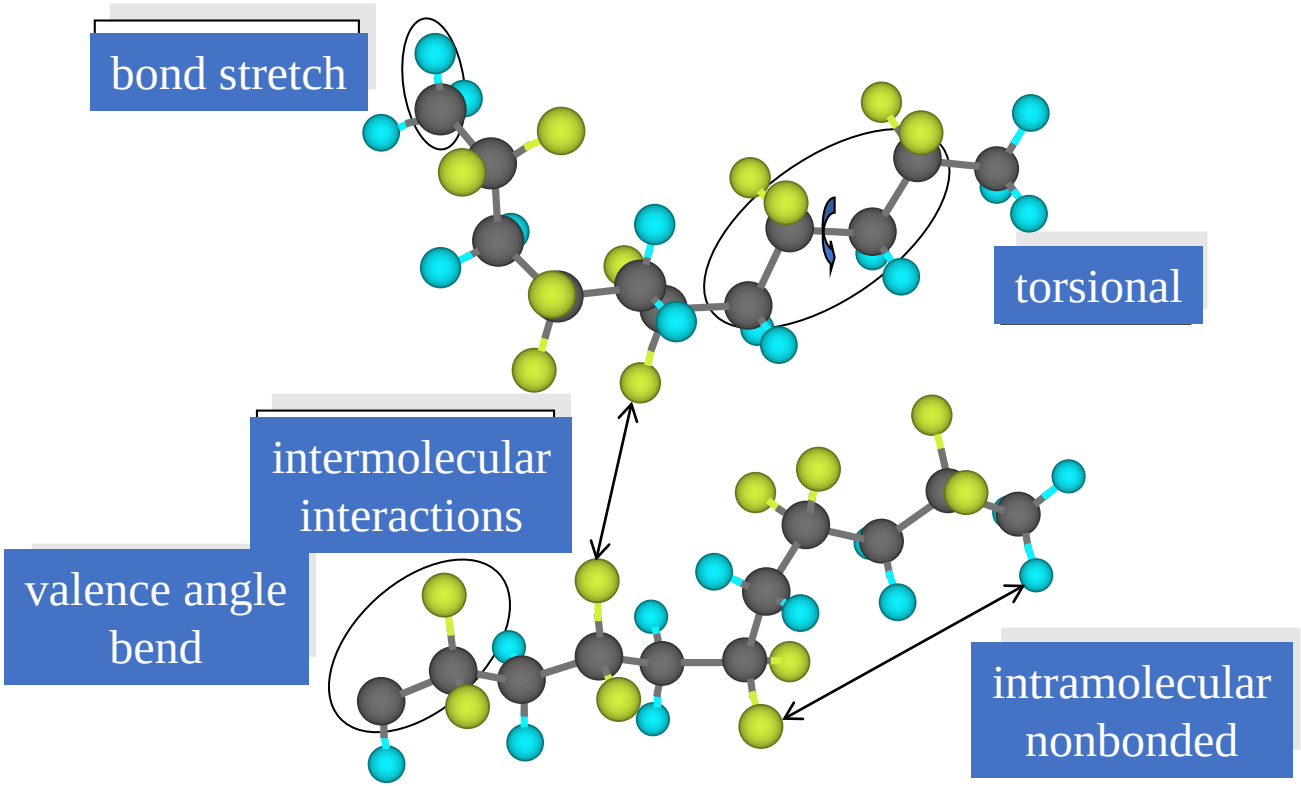
Modeling the molecular interactions

Inter- and intramolecular interactions

Why distinguish between them ?

- In the ideal case, no difference
- In reality:
  - Equal treatment leads is difficult/expensive
  - Examples
    - UFF
    - Central force model of water
    - Reactive potentials
- Why is it advantageous to differenciate ?
  - Bond breaking is difficult to describe
  - Angular (3body) and 4-body terms are natural and needed in a network of bonded atoms (A-B-C-D)
  - but difficult and less necessary between non-bonded atoms (H2O-M++-OH2)

1) Typical intermolecular energy functions (=force field)



Every atom will be affected by the potential energy functions of every atom in the system. Either from

- Bonded Neighbors
- Non-Bonded Atoms
  (=other atoms in the same molecule or atoms from different molecules)

$$V(R) = E_{bonded} + E_{non-bonded}$$

2) Non-Bonded Atoms

In the simplest case, there are three types of potential energy which we need to consider for the interaction between non-bonded atoms:

- Repulsion of electron shells
- van der Waals Potential

$$E_{non-bonded} = E_{repulsion} + E_{van-der-Waals} + E_{electrostatic}$$

The Lennard-Jones form is a compromise between accuracy and fast computability.

Repulsive (~r^{-12}) and van der Waals (~r^{-6}) potential terms:

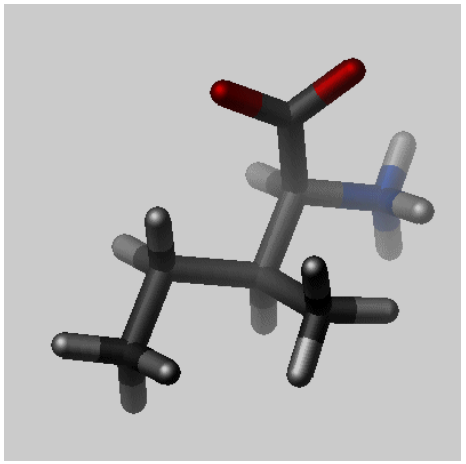
$$E_{Lennard-Jones} = \sum_{\substack{nonbonded \\ pairs}} \left(\frac{A_{ik}}{r_{ik}^{12}} - \frac{C_{ik}}{r_{ik}^{6}} \right)$$

Scaling, parameters, alternative versions, accuracy, deficits, improvements, physical foundations

Electrostatic Potential

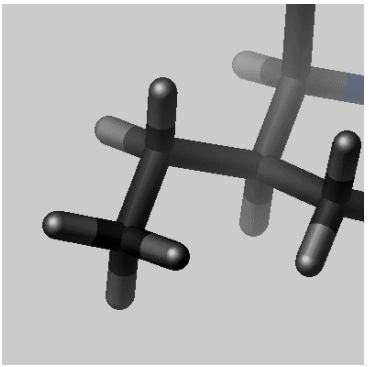
$$E_{electrostatic} = \sum_{\substack{nonbonded \\ pairs}} \frac{q_i q_k}{Dr_{ik}}$$

Bonded Atoms

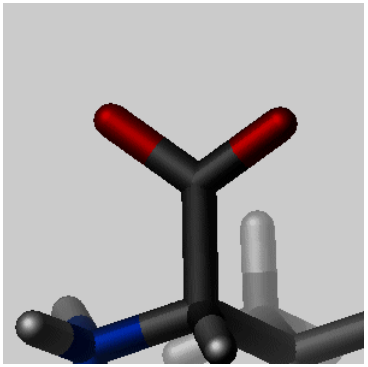


$$E_{bonded} = E_{bond-stretch} + E_{angle-bend} + E_{rotate-along-bond}$$

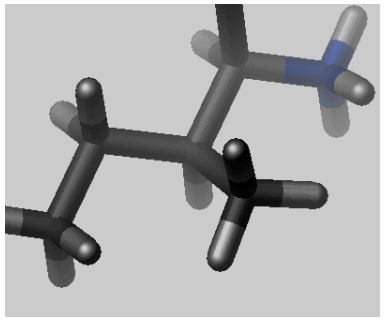
$$E_{bond-stretch} = \sum_{1,2\,pairs} K_b (b - b_0)^2$$



$$E_{bond-bend} = \sum_{angles} K_\theta (\theta - \theta_0)^2$$



$$E_{rotate-bond} = \sum_{1,4\,pairs} K_\phi (1 - \cos(n\phi))$$



Side issue:
the electrostatic energy in a crystal: Ewald

$$U = \underbrace{\frac{1}{4\pi\epsilon_0}\sum_{\mathbf{n}}^{\dagger}\sum_{i=1}^{N}\sum_{j=i+1}^{N} q_i q_j \frac{\mathrm{erfc}(\alpha|\mathbf{r}_{ij}+\mathbf{n}|)}{|\mathbf{r}_{ij}+\mathbf{n}|}}_{\text{Real-space term}}$$

$$+ \underbrace{\frac{1}{\epsilon_0 V}\sum_{\mathbf{k}>0}\frac{1}{k^2}e^{-\frac{k^2}{4\alpha^2}}\left\{\left|\sum_{i=1}^{N} q_i\cos(\mathbf{k}\cdot\mathbf{r}_i)\right|^2 + \left|\sum_{i=1}^{N} q_i\sin(\mathbf{k}\cdot\mathbf{r}_i)\right|^2\right\}}_{\text{Reciprocal-space term}}$$

$$- \underbrace{\frac{\alpha}{4\pi^{\frac{1}{2}}\epsilon_0}\sum_{i=1}^{N} q_i^2}_{\text{Point self-energy}} - \underbrace{\frac{1}{4\pi\epsilon_0}\sum_{n=1}^{M}\sum_{\kappa=1}^{N_m}\sum_{\lambda=\kappa+1}^{N_m} q_{n\kappa}q_{n\lambda}\frac{\mathrm{erf}(\alpha|\mathbf{r}_{\kappa\lambda}|)}{|\mathbf{r}_{\kappa\lambda}|}}_{\text{Intra-molecular self energy}}$$

$$- \underbrace{\frac{1}{8\epsilon_0 V\alpha^2}\left|\sum_{i=1}^{N} q_i\right|^2}_{\text{Charged system term}} + \underbrace{\left[\frac{1}{6\epsilon_0 V}\left|\sum_{i=1}^{N} q_i\mathbf{r}_i\right|^2\right]}_{\text{Surface dipole term}}$$

κ, λ indices of sites within a single molecule

N total number of charged sites
M total number of molecules
N_m number of sites on molecule m

$\mathbf{p}_i$ co-ord of site i relative to molecular centre-of-mass,

$\mathbf{r}_i - \mathbf{R}_i$

q_i charge on absolute site i

$q_{m\kappa}$ charge on site κ of molecule m

$\mathbf{r}_i$ Cartesian co-ordinate of site i

$\mathbf{r}_{ij}$

$\mathbf{r}_j - \mathbf{r}_i$

α real/reciprocal space partition parameter
π_{lm} instantaneous stress tensor

δ_{lm} Kronecker delta symbol

l, m xyz tensor indices

V volume of MD cell

Ewald force

$$= \underbrace{\frac{q_i}{4\pi\epsilon_0} \sum_{\mathbf{n}}^{\dagger} \sum_{\substack{j=1 \\ j\neq i}}^{N} q_j \left\{ \frac{\operatorname{erfc}(\alpha|\mathbf{r}_{ij}+\mathbf{n}|)}{|\mathbf{r}_{ij}+\mathbf{n}|} + \frac{2\alpha}{\sqrt{\pi}} e^{-\alpha^2|\mathbf{r}_{ij}+\mathbf{n}|^2} \right\} \frac{\mathbf{r}_{ij}+\mathbf{n}}{|\mathbf{r}_{ij}+\mathbf{n}|^2}}_{\text{Real-space term}}$$

$$+ \underbrace{\frac{2}{\epsilon_0 V} \sum_{\mathbf{k}>0} q_i \frac{\mathbf{k}}{k^2} e^{-\frac{k^2}{4\alpha^2}} \left\{ \sin(\mathbf{k}\cdot\mathbf{r}_i) \sum_{j=1}^{N} q_j \cos(\mathbf{k}\cdot\mathbf{r}_j) - \cos(\mathbf{k}\cdot\mathbf{r}_i) \sum_{j=1}^{N} q_j \sin(\mathbf{k}\cdot\mathbf{r}_j) \right\}}_{\text{Reciprocal-space term}}$$

$$+ \underbrace{\left[\frac{q_i}{6\epsilon_0 V} \left(\sum_{j=1}^{N} q_j \mathbf{r}_j \right) \right]}_{\text{Surface dipole term}}$$

en.wikipedia.org/wiki/Ewald_summation

Sketching the Ewald potential

(discuss TV shape, infinity considerations, convergence,

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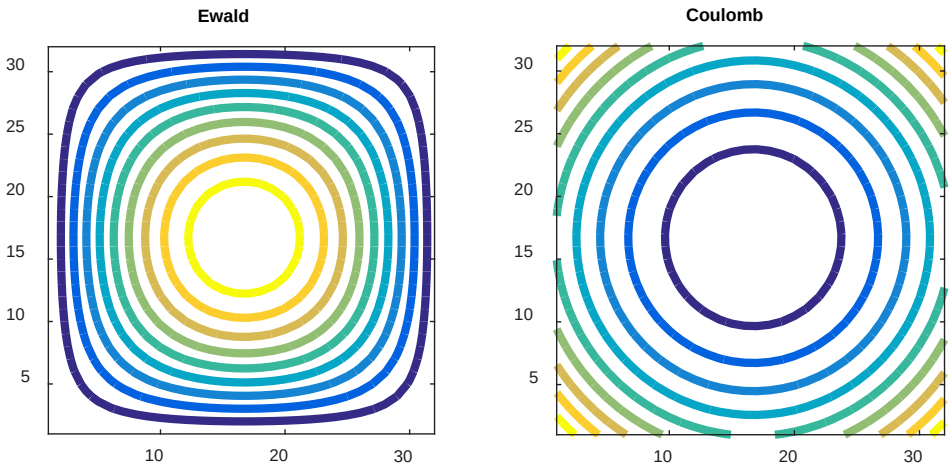
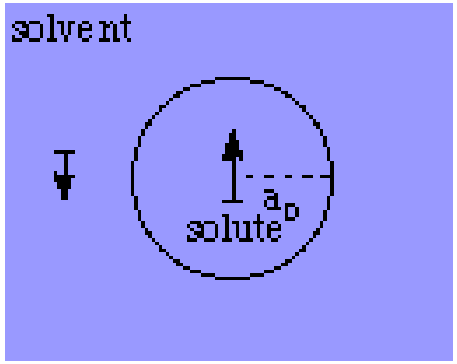
(discuss TV shape, infinity considerations, convergence,

```
[x y]=meshgrid(0:0.1:pi);
z1=sin(x).^2.*cos(y).^2;
subplot 121
[a,b]=contour(z1);
set(b,'linewidth',3); axis
square
title('Ewald');
z2=(x-pi/2).^2+(y-pi/2).^2;
subplot 122
[c,d]=contour(z2);
set(d,'linewidth',3); axis
square
title('Coulomb');
```



Reaction field:

simpler, not periodic, equally good as Ewald
Also useful in quantum chemistry



$$\vec{R} = \frac{2(\varepsilon - 1) \cdot \vec{\mu}}{(2\varepsilon + 1) \cdot a_0^3}$$

$\vec{R}$ = reaction field

a_0 = cavity radius

$\vec{\mu}$ = molecular dipole moment

Bond breaking

In many instances, potentials where bonds can break are needed.

For example (the so-called Tersoff-Abel potential):

$$E = \sum_{i>j} f_{ij}(r_{ij}) \left[\phi_R^{ij}(r_{ij}) - \frac{b_{ij} + b_{ji}}{2} \phi_A^{ij}(r_{ij}) \right] .$$

$$b_{ij} = (1 + \sum_{k(\neq i,j)} f_{ik}(r_{ik}) g_{ik}(\theta_{ijk}) \exp[2\mu_{ik}(r_{ij} - r_{ik})])^{-1/2}$$

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 \approx$37°C
and dead if it is $T \approx$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?

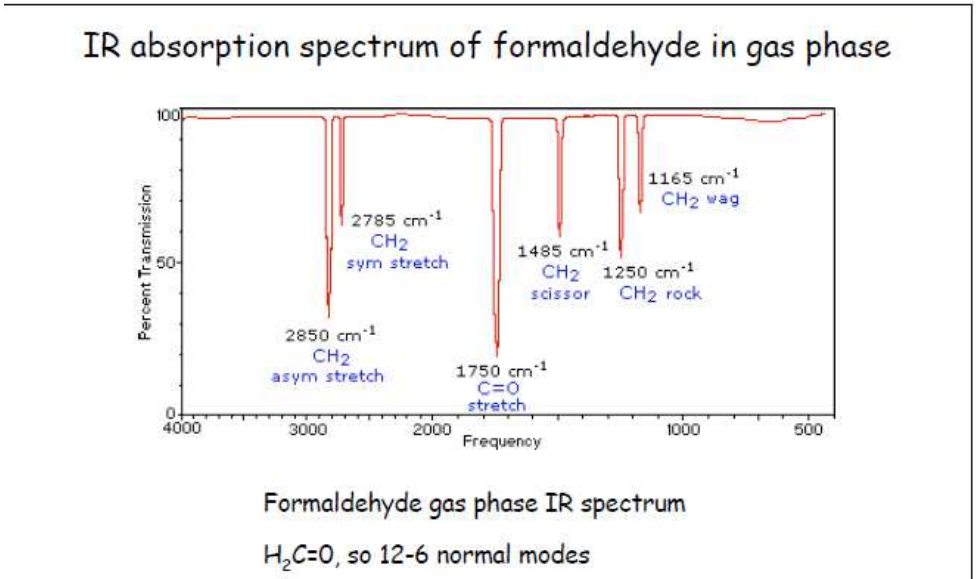
Under which conditions?

---

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?



1 molecule

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

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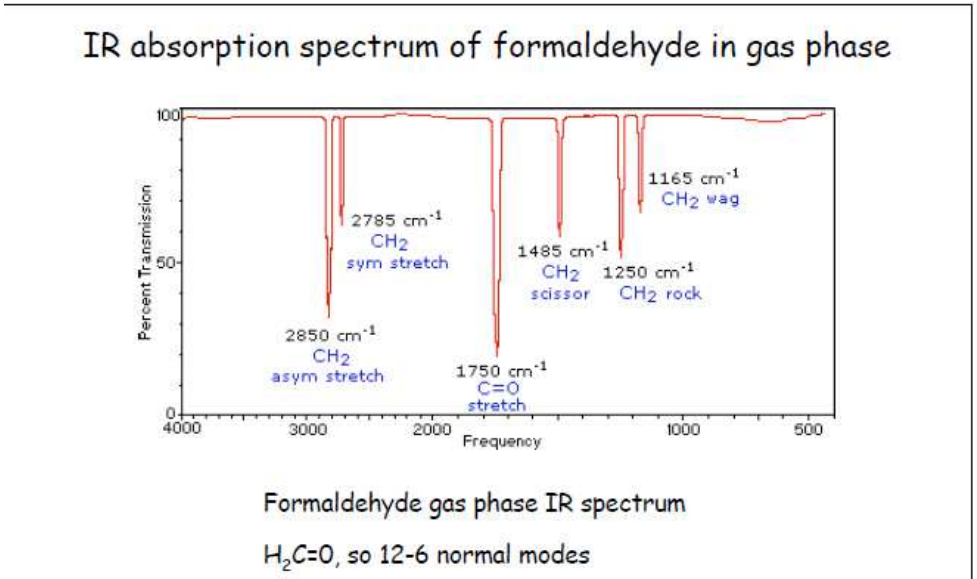

some $\mathbf{10^{17}}$ molecules (10^{-6} N_A)

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 ($\rightarrow$ 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**.

⇒ **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 ,
$\hat{H}\psi = E\psi$		viscosity, ...
$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t}$		$p, V, T, Q, \Delta U, S, ...$
Schrödinger equation		observables
$\rightarrow$ need to simplify		thermodynamics,
(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.

* 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)

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)
($\rightarrow$ 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 $\rightarrow$ 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: $\rightarrow$ 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, ... ($\rightarrow$ 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 $M_i \cdot \frac{\partial^2 \vec{r}_i}{\partial t^2} = \vec{F}_i(.....) \quad i = 1, ..., N$.
$\rightarrow$ 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	$\Rightarrow$	almost impossible except in very simple cases
classical mechanics highly simplified problems e.g. particle in the box, rigid rotor harmonic oscillator	$\Rightarrow$	analytical theory $\rightarrow$**partition function** Part 4
classical mechanics, Born-Oppenheimer interaction models	$\Rightarrow$	**Computer simulations** MD or MC Parts 5,6
(some) electrons QM nuclei classical	$\Rightarrow$	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_1N_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)

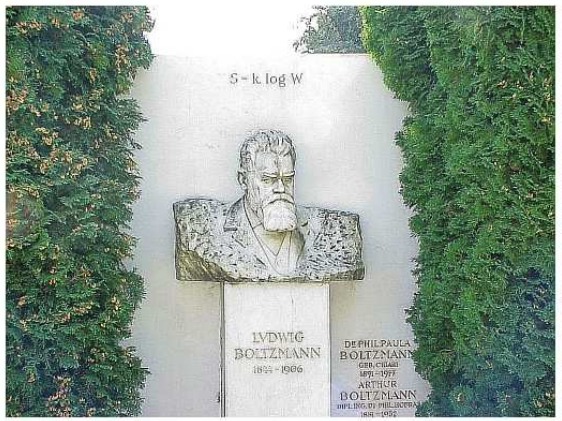
under conditions of ..... constant,
the partition function is called **.....**

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

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



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

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

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

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

For an equilibrium

$$\nu_a A \; + \; \nu_b B \; \leftrightharpoons \; \nu_c C \; + \; \nu_d D$$

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

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)

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

From Ω (NVE)

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

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 $\rightarrow$ 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

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

(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

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

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

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

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:

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

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

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

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)

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

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

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

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 qs 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*)

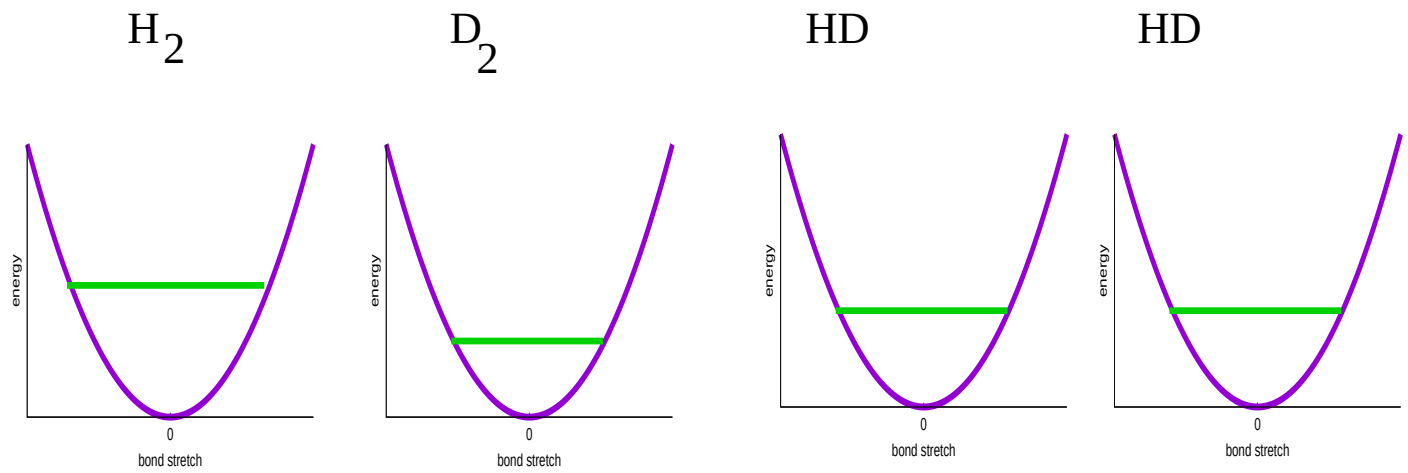
$$\mathrm{H_2 + D_2 \rightleftarrows 2HD} \quad , \quad \mathrm{K} \neq \frac{2^2}{1 \cdot 1} = 4$$

– 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



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

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

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

$$\text{Energy balance :} \qquad 1.207 \qquad < \qquad 1.225$$

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:

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

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, $\rightarrow$ 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:

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

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

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:

$\rightarrow$ Your spectroscopy class (IR, Raman)

$\rightarrow$ Statistical mechanics (the Ωs for the vibrational partition function)

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