CHE502 Chemical and Statistical Thermodynamics
Topic 1
The Molecular View, Radiation and Energies

URL: `http://theo.ism.u-bordeaux.fr/PBopp/vistec.2020.2021`

Introduction

The contents of this 'topic' belongs to the fields of general chemistry, physical chemistry, or molecular physics

We will first simply recall facts and trust that you have already learned them (even engineers) in some class or other in your undergraduate curriculum.

Look at the facts stated below and STUDY your favorite textbook, or the Internet.

In this class, and in CHI501 in the next semester, we will mostly (almost exclusively)
dwell on the **molecular** (or **microscopic**) level,
in contrast to the **macroscopic** level (experiments and observations in the lab).
This 'molecular' viewpoint may be more familiar to you from organic chemistry, where arguments usually involve a single, or very few, molecules.

The macroscopic view is, eg., the one you know from (phenomenological) thermodynamics.
If you write, eg. $pV = nRT$, the quantities p, V, T cannot be associated with a single molecule, they belong to large (macroscopic) quantities of molecules,
ie. if one writes $pV = nRT = n \cdot N_{\mathrm{A}} \cdot k_{\mathrm{B}}T = N \cdot k_{\mathrm{B}}T$ for large numbers N.
(*If you do not know the exact meaning of the symbols,* **read up!**)

Why it is important for engineers to master the molecular viewpoint

Students of chemistry have usually been introduced to this approach in physical chemistry, organic chemistry, or physics (and sometimes, at an extremely simplified level, also in inorganic chemistry)

Students of engineering usually are taught only the macroscopic approach (phenomenological thermodynamics (eg various empirical equations of state such as van der Waals, virial expansion, Wagner equations ...), fluid dynamics (Navier Stokes), etc.). These equations usually contain 'free' parameters, which are fitted (see Topic 4)
to reproduce certain properties of certain systems.
Since these equations are just fits, they do not contain any (or very little) physics, they can thus safely be used in the range for which they were fitted
(eg $T_1 < T < T_2$ or $p_1 < p < p_2$, but not outside such ranges)
(extrapolation, see examples of (over)fitting in topic 4)

It has been more and more recognized in modern chemical engineering (and other branches of engineering) that real progress needs an understanding of the molecular mechanisms underlying an observation

It is the purpose of CHI502 and CHI501 inside the VISTEC curriculum to provide the basis for such an understanding

How do we 'know' about molecules (since we usually cannot see them with our eyes)

If you think about it, you will see that most everything we know about molecules comes from studying their interaction with electromagnetic radiation

This interaction can occur in two fundamentally different ways:

– The molecule changes the energy of the electromagnetic radiation
  this is usually referred to as **spectroscopy**
   examples include: Infrared (IR) spectroscopy, various NMR methods ....)
   keywords: absorption, emission, resonance. .....
   (We will look at this in some detail)

– The molecule does **not** change the energy of the electromagnetic radiation,
  only its direction of propagation
  this is usually referred to as **scattering**
   example: X-ray catering
   (We will not study this very much)

Spectroscopy

As we will see in topic 2, the easiest way to discuss these interactions between electromagnetic radiation and a molecule is **quantum mechanics**.
(*it can equivalently be done in classical terms, thus the term 'resonance': molecules are understood as 'little radio antennas' that absorb or emit radiation*).
We shall use the quantum mechanical view here.

We first state here apodictically
(ie. without any argument or demonstration, **read up and see next topic**):

– electromagnetic radiation (emr) can be considered as a flux of **quanta**
high intensity ↔ many quanta (per time (and surface) unit),
low intensity ↔ few quanta ....

– if the emr has a frequency $\nu = \frac{\omega}{2\pi} = \frac{c}{\lambda}$ (look up the symbols)
then a quantum of this radiation has the energy $E = h\nu = \hbar\omega$.

– A molecule has several possibilities to exchange energy with emr.

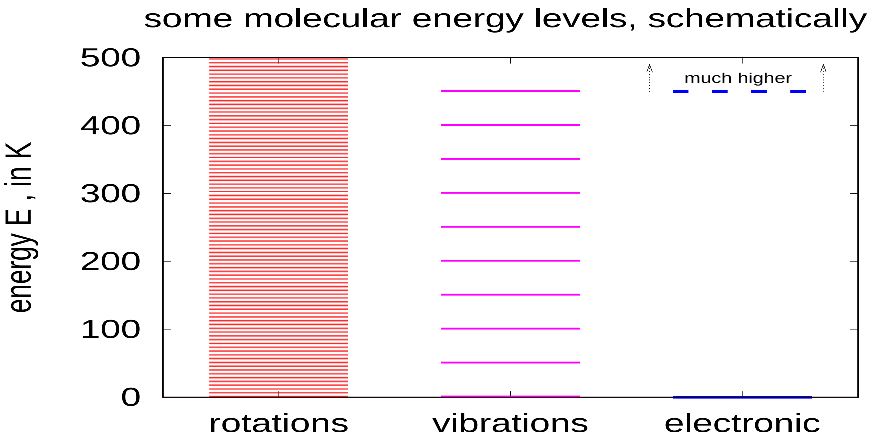
– Each of these possibilities is characterized by the type of quanta that the molecule can exchange with the emr

The electromagnetic spectrum

⇒ textbooks

⇒ http://theo.ism.u-bordeaux.fr/PBopp/vistec2019.2/lecture2019.1.pdf
page 26-27

Study which energy reservoirs of a molecule (see next page) can exchange energy with which range of frequencies (or wavelengths) of the emr



rotations: spacing of levels ≈ 1 or 2 K, vibrations: spacing of levels ≈ 50 K
electronic levels spacing ≈ 1000 K or more

details see later (quantum mechanics)

Is light (electromagnetic radiation) a 'wave' (Huygens) or a flux of 'particles' (Newton)?
Answer: both

For **spectroscopy**, it is best to consider radiation as a flux of 'particles' called quanta (quantities of energy). This 'corpuscular' description is related to the 'wave' theory by the equations

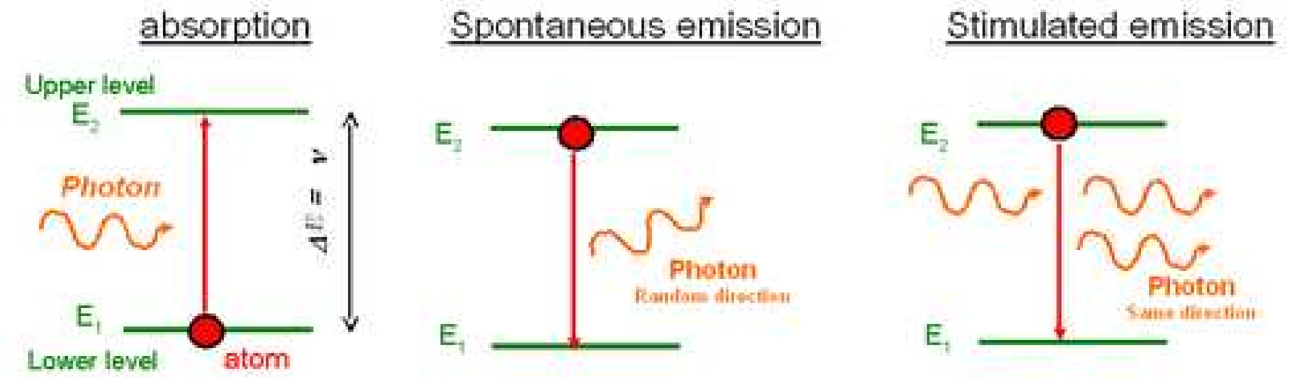
$$E^{\text{photon}} = h \cdot \nu = \hbar \cdot \omega \quad , \quad \lambda \cdot \nu = c \quad , \quad \omega = 2\pi \cdot \nu$$

where E^{photon} is the energy of such a quantum.
→ a high intensity radiation (eg a laser beam) is simply a very strong flux of quanta, each quantum having the same energy

A **necessary** condition for a molecule to absorb energy from the radiation is that there are in the molecule two states (energy levels) E_1 and E_2 such that

$$h \cdot \nu = E^{\text{photon}} = E_2 - E_1$$

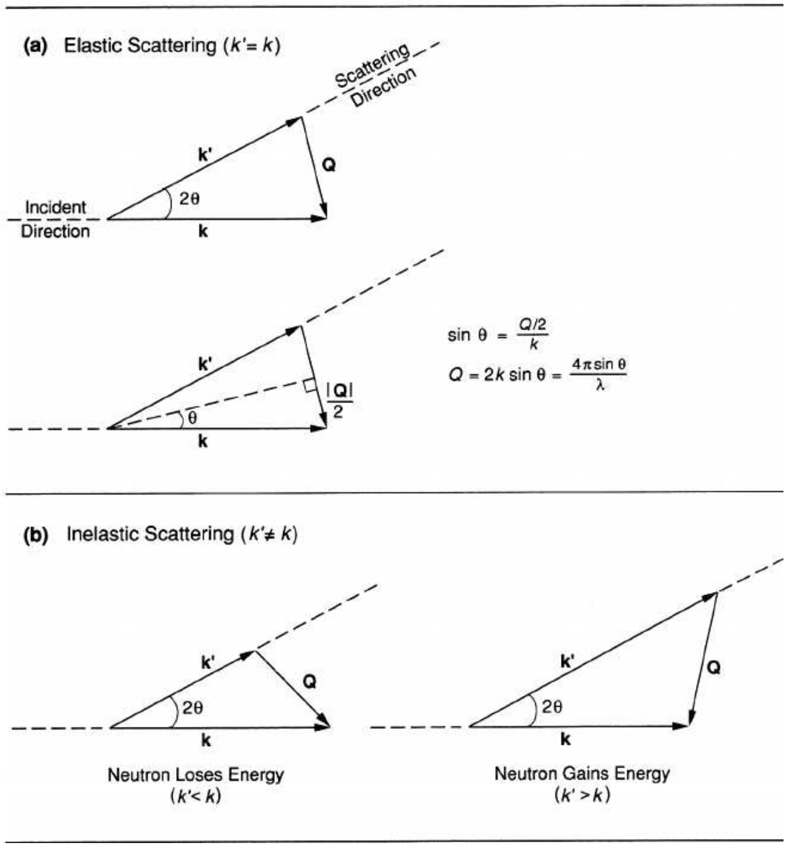
"Necessary" condition means that there will never be absorption if this condition is not met, but other conditions (selection rules) may apply too.
This is true at low fluxes of photons (absorption of one photon at a time),
ie not in very strong laser beams → non-linear optics



For **scattering** we use more easily the wave description. We define a 'wave vector' $\vec{k}$, which gives the direction of propagation of the wave and has the magnitude (module) $|\vec{k}| = \frac{2\pi}{\lambda}$

In 'elastic' scattering, only the direction of $\vec{k}$ is changed
in 'inelastic' scattering the module $|\vec{k}|$ (ie the wave length, ie the energy*) is also changed

* ie the system absorbs quanta of energy $h \cdot \nu_1$ and emits quanta of another energy $h \cdot \nu_2$.
→ at least 3 energy levels must be involved, see Raman effect



$$q = \Delta k$$

Bragg's law

same for radiation
(called 'Stokes' and 'Anti-Stokes' in Raman)

To study the exchange of energy between a molecule and emr,
we can consider, to a good approximation, that a molecule has
several **separate** possibility to do this,
ie. to remove (**absorb**) quanta from the emr, to store this energy,
and to release (**emit**) (usually the same, sometimes different) quanta

In order of **increasing energy** of the quanta, we have the possibilities
(which sometimes overlap) for:
- emr to interact with nuclear spins (NMR)
- emr to interact with electronic spins (ESR)
- emr to interact with motions (translations, rotations) of the molecule(s)
  (dielectric spectroscopy, microwaves, (far-)infrared (IR), Raman spectroscopies)
- emr to interact with molecular vibrations (IR, Raman. ...)
- emr to interact with the 'outer' electrons in molecules (optical spectroscopies, UV)
- emr to interact with the 'inner' electrons in molecules (UV, X-rays, Auger, ,..)
- emr to interact with the nuclei (γ rays, not interesting in chemistry, we'll soon see why)

When energy goes from the emr into one energy reservoir (say electrons), we say that this system (the electrons) have been **excited**

We consider these mechanisms to be independent of each other
This means that energy in one system (say vibrations) will not (or only very slowly) leak into another system (say spins).
This is very often true, but not always.

Quantum mechanics teaches that each system can exist ONLY in a (finite) number of **STATES** (see topic 2), eg only with discrete energies $\mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3, ...$

Thus ONLY quanta with energies $E = \hbar\omega = \Delta\mathcal{E} = \mathcal{E}_j - \mathcal{E}_i$ usually with $j = i + 1$, can be absorbed or emitted by this system, ie exchanged with the emr

This is a most fundamental principle,
it is known as 'Ritz' principle, or many other names.
READ! READ! READ!

A more detailed discussion of emr, the (historic) names for the various
domains of frequency ν
(or $\omega = 2\pi\nu$, or energy E or wavelength λ, all connected since $\lambda \cdot \nu = c$ and $E = h \cdot \nu$)
can be found in any
⇒ book on physical chemistry, CHE502 lecture notes from previous years

We now need to study, in the next topic, the basic ideas of quantum mechanics
Nobody ever said that this is simple
It took the smartest people 25 years (from 1900 to almost 1930) to get acquainted
and accept it
(*and when I (Phiippe) was a student, some of my old professors still had doubts,*
as had, btw, A. Einstein)
Today chemistry (among many other fields) cannot do without

The field where quantum mechanics first became important in chemistry is molecular chemistry

So we have to think a little bit about: "What is a molecule?"

– A molecule consists of several nuclei and electrons, which interact with each other
  (A nucleus (plural nuclei) consists of protons and neutrons, but that is not important in chemistry. It is in physics, though)
– The interactions between nuclei and electrons are electrostatic (Coulomb's law)
– These interactions make it that the total energy of the system (nuclei+electrons) is lower when these particles stay together rather than as separate atoms
– These interactions are what chemists call 'bonds'
– These bonds are not rigid (fixed length), but can, within certain limits, change their lengths
  This is why they are often described as little springs
– These bonds can 'break', ie. two bonded atoms to not stay together forever
  (but usually for a very long times)
  This is something one can know from entropy
– The exact description of these 'bonds' is the field of quantum chemistry

– Such interactions also exist between molecules (intERmolecular interactions)
(measurable if the molecules are not too far apart)
– The fact that these intermolecular interactions are different is mostly responsible for the different properties of gases, liquids, and solids
(freezing point, melting point, viscosity, miscibility, Debye temperature, ...)

You already studied some of this with Aj. Montree for (single) molecules,
ie only intramolecular energies (and their variations, eg for the IR spectra)
We will look at this later in more detail, in particular:
- at the electrons, their energies and their wave functions ψ
- at he nuclei (which move (vibrate) and thus give rise to IR and Raman spectra)
we will mostly study their energies ($\rightarrow$ spectra) and
not so much their wavefunctions, often called ϕ (or Φ, or Ψ or ...),
(*we'll also understand the reasons for this choice!*)

Linking the molecular properties (essentially interactions) with thermodynamic (and other macroscopic) observables is the main purpose of statistical thermodynamics, also called statistical mechanics, many-particle physics, ...

Many macroscopic observables are linked with each other by the equations of (phenomenological) thermodynamics, eg. equations like:

$$H = U + pV \ , \ S = \text{........} \ , \ c_v = \frac{\partial ..}{\partial ..}, \ \ldots \ \text{ etc etc etc}$$

Review this if you have forgotten

Remember: many phenomena that we observe in condensed phases (liquids, solids), but also in dense gases, result from large numbers of molecules
A single molecule does not have an entropy, a pressure, a viscosity, ...

We will thus now first look at some of the fundamental aspects of quantum mechanics, which was found to be the correct description of small objects like atoms and molecules.

When we have done this, we will come back to molecules, study their interactions and how we can use the knowledge about them to compute things (observables) that depend on large numbers of molecules, and on the conditions (such as temperature) under which these assemblies are kept

Remember how sensitive to temperature certain things are:
if your body temperature is below 35^oC (308K) or above 43^o (316K),
a variation of about 2.5%, you are in big trouble