PSE797MR
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# INTRODUCTION TO SOLID STATE NMR (1)

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# WHAT CAN SSNMR DO?

- Many aspects of materials can be probed
  - Chemical structure
  - Phase structure of heterogeneous materials and composites
    - Crystalline/amorphous; rigid/soft; domain structures and sizes
  - Molecular dynamics
    - e.g. glassy vs rubbery
    - Zeolite vs the trapped gas/liquid molecule in the cage
  - Can be quantitative
- Challenges
  - Needs to tailor method according to the problem
  - Complex theories
- Objective
  - Awareness of the potentials of ssNMR
  - You can properly set up and interpret several essential ssNMR experiments
  - You can gain some insights into the morphology and dynamics of some classical solid-state materials
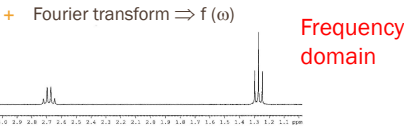
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## ORGANIZATION OF THE COURSE

- ✖ Basic Theory
  - ✛ Technical challenges of solid-state NMR
  - ✛ Several most important techniques for overcoming these challenges
- ✖ Examples and interpretation
  - ✛ You are welcome to submit your own research samples
- ✖ Very simple math, but a lot of concepts
  - ✛ You will need to not leave them as scattered pieces of brick but connect them into a building (*how*?)
- ✖ Grades:
  - ✛ Quizzes (50%)
  - ✛ Report: interpret some ssNMR spectra (50%)
- ✖ No final exam
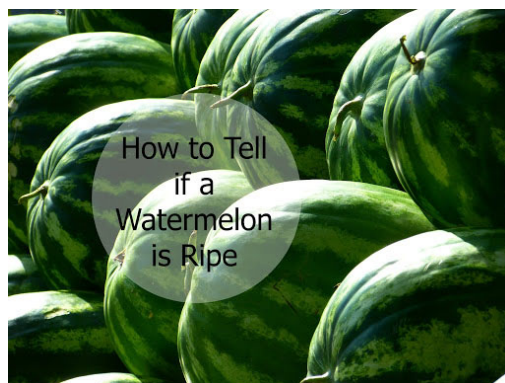- ✖ References: (1) class slides; (2) the NMR "booklet": "A Brief Introduction to NMR"
  - ✛ https://websites.umass.edu/weiguoh/?p=771

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## NMR – NUCLEAR MAGNETIC RESONANCE

| **Piano** | **NMR** |
|---|---|
| Strings | Nuclei in sample |
| Tension on strings | Magnetic field |
| Strike the key! | Pulse(s) |
| $\Rightarrow$ Music | $\Rightarrow$ Signal F (t) |

$^{13}C$ ⎯⎯ 90° ⟶ Time domain

✛ Fourier transform $\Rightarrow$ f ($\omega$)    Frequency domain

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How to Tell
if a
Watermelon
is Ripe

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# BASIC CONCEPTS OF AN NMR EXPERIMENT

- ✖ We are only concerned with the magnetic properties of the nuclei (magnetic moments, or magnetization)
- ✖ At equilibrium, these little magnets are aligned parallel to external magnetic field (*z* direction)
    - + Just like what your compass will do
    - + They won't give out signal at this state
- ✖ A 90º "excitation" pulse rotates the magnets to the horizontal plane so that they give out signal

A pulse diagram: 
90º
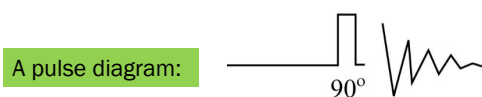
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# LARMOR EQUATION

$$\omega = \gamma \, B$$

✖ $\omega$ is signal frequency of the nucleus
✖ $\gamma$ (gyromagnetic ratio) is a property of the nucleus
 ✚ All nuclei of the same isotope have the same $\gamma$, regardless of its chemical environment
  ✖ $\gamma$ ($^{13}C$) ~ ¼ of $\gamma$ ($^{1}H$)
 ✚ On a 400MHz spectrometer, frequency of $^{13}C$ ~ 100 MHz
  ✖ A "600 NMR" means that its $^{1}H$ frequency is 600 MHz
  ✖ *What is the $^{13}C$ frequency on a 600MHz instrument?*
✖ B is magnetic field strength
 ✚ Contains many terms from all sorts of interactions between magnetic moments
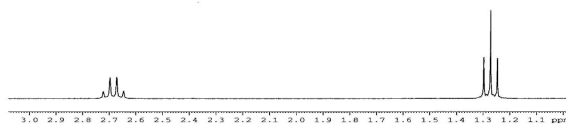


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# AN IMPORTANT RELATIONSHIP IN FOURIER TRANSFORMATION

The "uncertainty principle":

✖ $\Delta\nu = \dfrac{1}{\pi\Delta t}$
✖ A long-lasting signal (time domain) corresponds to a narrow peak on the spectrum (frequency domain)
✖ A fast-decaying signal (time domain) corresponds to a broad peak on the spectrum (frequency domain)

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# THEORETICAL DESCRIPTIONS OF NMR

- ✖ Quantum mechanics
  - ✚ Rigorous
  - ✚ Complex
- ✖ Energy level model
  - ✚ approximation
  - ✚ In a magnetic field, nuclei is divided into two populations: up and down
  - ✚ Suitable for understanding relaxation phenomena; unsuitable for describing pulsed NMR experiments
- ✖ Vector model
  - ✚ approximation
  - ✚ The net magnetization moment can be represented by a vector
  - ✚ Motions of moments or vector: <u>precession</u> (the rotation of the moment axis under the influence of an external force field)
    - ✖ Examples of moments: a moving bicycle; a spinning top; the Earth
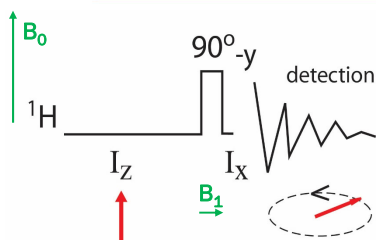  - ✚ Suitable for understanding the effect of pulses

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- ✖ What is the difference between a spinning top and a dead one?
- ✖ The axis of the precession is along the external force field
- ✖ NMR experiments are basically toying with "spinning tops"



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# VECTOR MODEL OF NMR



- ✖ In the beginning, magnetic moments $I$ is aligned parallel to $B_0$
  - ＋ *Distinguish the arrows representing <u>fields</u> and the arrows representing <u>moments</u>*
- ✖ A RF (radio frequency) pulse cancels the effect of $B_0$ and generates a horizontal magnetic field $B_1$, which makes the magnetic moments <u>precess on a vertical plane</u>
  - ＋ The effect of $B_0$ is only canceled during pulsing; it's fully present when not pulsing
- ✖ Flip angle $\propto$ pulse length (e.g. a 180º pulse is twice as long as a 90º pulse)
- ✖ During detection, magnetic moments <u>precess on the horizontal plane</u> and gives out signal

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# MAJOR INTERACTIONS IN NMR

- ✖ Shielding effect from electrons: ***chemical shift***
- ✖ Interaction between nuclei: ***dipolar coupling***
- ✖ Why should we care about interactions?
  - ＋ Each interaction produces a magnetic field, thus a new peak position
    - ✖ If the above interactions did not exist, the NMR spectrum would be a single, extremely sharp peak
  - ＋ A lot of interactions generate a lot of peaks in various positions, resulting in a very broad peak
- ✖ We use various types of pulsing techniques to eliminate certain interactions so that we can selectively study the interactions that we are interested
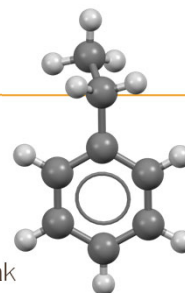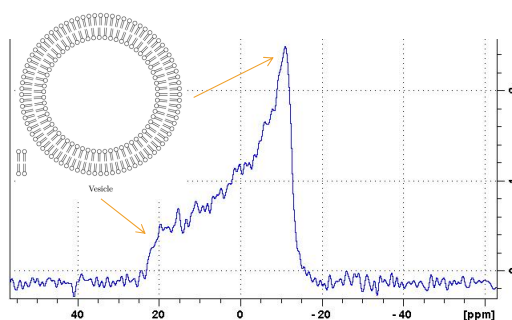
$$\omega = \gamma\, B$$

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# THE COMPLEX SITUATION OF NMR IN THE SOLID STATE

✖ Chemical shift value of a nucleus depends on its relative orientation with regard to the magnetic field – "chemical shift anisotropy" (CSA)

+ Result: each atom gives not a single peak but a "horned" pattern



$^{31}P$ spectrum of a liquid crystalline state phospholipid. Such a shape is often called the "powder pattern".

If you dissolve a phospholipid sample in $CDCl_3$, what would its $^{31}P$ spectrum look like?

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# INTERACTION BETWEEN NUCLEI: DIPOLAR COUPLING

✖ J-coupling in solution NMR: 1-150 Hz
+ Gives multiplet splittings
+ Orientation independent

✖ Dipolar coupling in SSNMR: ca. 50 kHz
+ Orientation dependent
+ $^1H$-$^1H$: broadens $^1H$ spectra
+ $^1H$-$^{13}C$: broadens $^{13}C$ spectra
+ Both intra- and intermolecular dipolar coupling are present
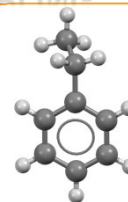
Proton NMR spectra of three poly (urethane urea) (PUU) elastomer samples.



PUU2k

PUU1k

PUU650
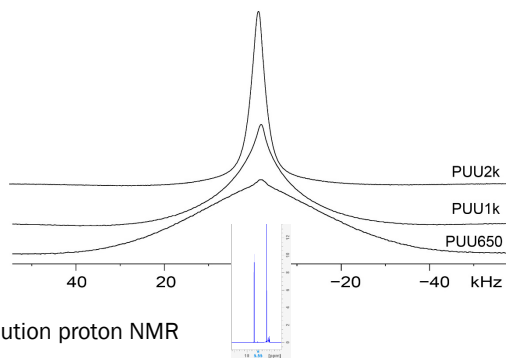
*W. Hu et al., Polymer 2013*

A typical solution proton NMR spectrum

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# MOTIONS OF MOLECULES

- ✖ Molecules tumble fast in liquid
    - + Rate ($\Omega$): $>10^{12}$ s$^{-1}$ for small molecules
        - ✖ Motion is in random direction and random speed. $\Omega$ is an "average"
    - + Correlation time ($\tau_c$): inverse of $\Omega$
    - + Motion is faster at higher temperature
- ✖ Effect of molecular motion to spectra: significant when $\Omega >= \Delta\delta$ (peak width; ~ strength of magnetic interactions)
    - + "frequency fight"
    - + $^1$H NMR peak width of a rigid organic material ~ 50 – 70 kHz (> 100 ppm)
    - + $^1$H NMR peak width of a rubbery polymer ~ 1 kHz
    - + $^1$H NMR peak widths of solution-state spectra usually < 1 Hz
- ✖ A broad range of motional states in the solid state: crystalline; glassy; rubbery; liquid crystalline; crosslinked; etc.

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# T$_1$ AND T$_2$ RELAXATIONS



Equilibrium          Non-Equilibrium          Equilibrium
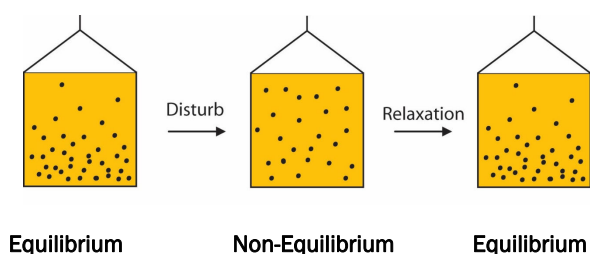
- ✖ Magnetic moments are in the excited state when pulsed
    - + And they need to come back to the resting place
- ✖ Relaxation: process from high-energy (excited) state to low-energy (equilibrium) state
- ✖ Understanding of relaxation is critical for SSNMR
- ✖ T$_1$ and T$_2$ relaxations are not molecular relaxations
    - + However, these relaxations are driven by molecular relaxations
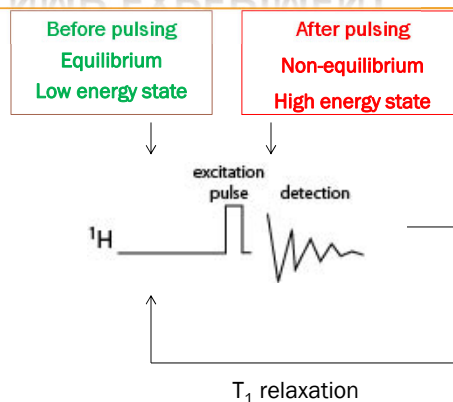
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# RELAXATIONS IN VECTOR MODEL

$$90^o_{-y}$$

$^{13}C$ _____

$I_z$      $I_x$

Eql. state      Non-eql. (excited) state
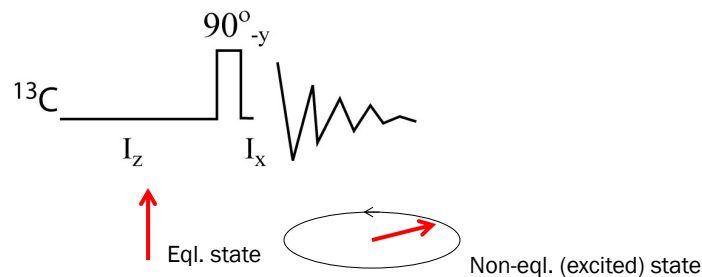
- ✖ $T_1$: $I_z$ coming back from 0 to 1
- ✖ $T_2$: $I_{xy}$ coming back from 1 to 0
- ✖ $T_1$ and $T_2$ are independent processes
- ✖ Rotation of magnetic moment by pulsing is fast and coherent; rotation of magnetic moment by relaxations is slow and incoherent

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# A BASIC NMR EXPERIMENT

| Before pulsing | After pulsing |
|---|---|
| Equilibrium | Non-equilibrium |
| Low energy state | High energy state |

excitation pulse    detection

$^1H$ _____

$T_1$ relaxation

- ▪ Pulse sequence
- ▪ $T_1$ is the time to recover to equilibrium after each pulsing
  - – Getting the "pool" ready for the next scan
- ▪ maximum signal is obtained when $T_1$ relaxation is complete before the next scan comes

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# $T_1$ RELAXATION: IMPORTANT FACTORS

- $T_1$ relaxation must be facilitated by some energy source
  - Magnetization is very difficult to relax by itself - "fluctuation" is necessary
    - Unlike the pulp in orange juice or the electrons in UV/Vis
    - *More like apples on the tree: you have to shake or kick the tree to fell the apple!*
    - $T_1$ of a rigid organic solid sample could be > 1000 s
- Two factors drive $T_1$ relaxation:
  - Strength of dipolar coupling between the nuclei
  - Rate of fluctuation of the interaction (*a steady push on the apple tree won't work*)

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# CONCEPT REVIEW

- What are the three basic components of a NMR experiment? How is it similar to the "watermelon tapping" experiment?
- What effect does a pulse generate to a magnetization?
- What are the strengths and shortcomings of the three theoretical models of NMR?
- Why do magnetic interactions generate broadening of NMR peaks? Use Larmor Equation to explain
- If you double the length of a 90° pulse, how should you call this new pulse? Why?
- A powder pattern is a strange-looking horned pattern. Why?
- For a molecular dynamical process, what is the relationship between its rate and correlation time? How do they respond to increase of temperature, respectively?

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## CONCEPT REVIEW

- How wide is a typical $^1$H spectrum of a rigid polymer? What factor determines this peak width? At increasing temperature, how would the spectrum change? What is the mechanism?
- Why does $T_1$ relaxation affect signal intensity?
- How does $T_1$ of a rigid polymer sample change when you heat it up?
- What molecular processes generate the fluctuation of force that drives $T_1$ relaxation?

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