NUS: non-uniform sampling

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NMR-spectroscopy uses the nuclear spin that can be thought of as a mixture between gyroscope and magnet.
The frequency of the rotation of the spin in a magnetic field is what we are interested in.
The frequency is measured by using the little magnet to induce a current in a coil.
An RF-pulse is used to “start” the magnet. Because of signal-to-noise we repeat the excitation-detection
While the frequency of one line is easy to analyze from the time-signal...

...it is difficult from more than one
That’s why we do a Fourier-Transformation!
For which we have to digitize the signal. Then we can use the DFT or FFT to process data fast.
The DFT only sorts points
The maximum frequency that we want to detect determines the sampling rate: Nyquist condition.
What about resolution, i.e. separating two lines? To do that we have to sample many points!
This comes for free in a 1D!

If $t_{acq}$ gets longer one can shorten $t_r$. 
A multidimensional spectrum is created by repetitive recording of a one-dimensional spectrum with systematic changes in the pulse-sequence....
….resulting in a two-dimensional FID
The first FT yields the "interferogram"
The second FT yields the two-dimensional spectrum
Spectra are usually viewed as contour plots
In a 3D the repetition has to be done in two indirect dimensions independently.
That is why multidimensional spectra take so much longer

1D, 1024 points, 8 scans  
12 sec

2048 points do not (!!) take longer

2D, 1024 x 1024, 8 scans  
4,3 hours

1024 x 2048 points take 8,6 hours

3D, 1024 x 128 x 128, 8 scans  
54,6 hours

4D, 1024 x 32 x 32 x 32, 8 scans  
109,2 hours

4D, 1024 x 128 x 128 x 128, 8 scans  
291 days

The reason is the DFT!
The DFT is fast but also has some limitations:

Points have to be sampled in equidistant intervals

The distance between points determines the maximum frequency that can be sampled

Missing points at the beginning, in the end or in the center cause distortions

Good resolution in nDs requires long experiment time !!
NUS: non-uniform sampling

indirect dimension

all points
NUS: non-uniform sampling

indirect dimension

initial points missing
NUS: non-uniform sampling

indirect dimension

last points missing
NUS: non-uniform sampling

indirect dimension

points missing inbetween
NUS: non-uniform sampling

Maximun-Entropy Reconstruction

Multi-Dimensional Decomposition
exponentially-decaying signal

sine-modulated signal (e.g. cosy-experiment)

\[\text{indirect dimension}\]
non-decaying signal (e.g. ct-experiment)
In 3D there are two indirect dimensions

64 x 128 complex points
exponentially-decaying signals in 3D

512 out of 8192 (64 x 128) complex points

non-decaying signal in 3D

512 out of 8192 (64 x 128) complex points

**sampling limit**

the sample provides sufficient S/N and the data have to be recorded far too long to achieve enough resolution

*NUS can drastically shorten the experiment time*

**sensitivity limit**

the sample requires an extended experiment time to achieve a sufficient S/N anyway and the required resolution can easily be obtained

*NUS can provide more flexibility*
We are clearly in the sampling limit!

$^{13}$C: the ct-delay is 27 msec, the increment is 132 $\mu$sec
we can collect 200 complex points (400 FIDs)

$^{15}$N: the ct-delay is 22 msec, the increment is 220 $\mu$sec
we can collect 100 complex points (200 FIDs)

The full 3D would therefore consist of 80 000 FIDs

Assuming 4 scans and 0.8 sec relaxation delay this amounts to 80 hours, while 1 hour is enough for S/N!
Projections of a dataset with $100 \times 200 = 20000$ full points, i.e. 80 hours spectrometer time
if we cut this to 8 hours “classically” (32* x 64* = 2048 full points) we have less resolution
by cutting to 8 hours the sampling is drastically reduced:

\[32^* \times 64^* = 2048 \text{ full points}\]
ct-HNCA of SH3 @900 MHz

2048 out of 20000 (10.2%)
NUS: non-uniform sampling

ct-HNCA of SH3 @900 MHz

8 hours instead of 80

traditional

Peter Schmieder 20.09.2013
ct-HNCA of SH3 @900 MHz

8 hours instead of 80 traditional
ct-HNCA of SH3 @900 MHz

256 out of 20000 (1.3%)
ct-HNCA of SH3 @900 MHz

256 out of 20 000: 1 hour instead of 80
### Acquisition of NUS data in topspin 3.1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PULPROG</td>
<td>MFhncowg_nus_psf</td>
<td>Current pulse program</td>
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<tr>
<td>AQ_mod</td>
<td>DQD</td>
<td>Acquisition mode</td>
</tr>
<tr>
<td>FnMODE</td>
<td>States</td>
<td>Acquisition mode for 2D, 3D etc.</td>
</tr>
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<td>FnTYPE</td>
<td>traditional(planes)</td>
<td>nD acquisition mode for 3D etc.</td>
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<tr>
<td>TD</td>
<td>1024</td>
<td>Size of fid</td>
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<tr>
<td>DS</td>
<td>4</td>
<td>Number of dummy scans</td>
</tr>
<tr>
<td>NS</td>
<td>16</td>
<td>Number of scans</td>
</tr>
<tr>
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### Non-uniform sampling

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Acquisition of NUS data in topspin 3.1

NUSLIST is the sampling schedule, which can also be created independently (it is a vc-list)

Parameter to create the sampling schedule:
NusAMOUNT gives the percentage of points (NusPOINTS) selected
Acquisition of NUS data in topspin 3.1

The points in the NUSLIST are also ordered randomly so that reasonable processing is possible without waiting for the experiment to finish.

The list is stored in the dataset under the name “nuslist”

How many points have been recorded is stored in the parameter NusTD for each dimension while the TD only gives the maximum number of points
Acquisition of NUS data in topspin 3.1

Parameter to adjust the sampling schedule:
- **NusJSP** if a cosine-modulation due to coupling is present
- **NusT2** if there is a decay due to relaxation
Acquisition of NUS data in topspin 3.1

using NusJSP and NusT2

\[ t_{\text{max}} = 20 \, \text{msec} \]

\[ J = 50 \, \text{Hz} \]

\[ \frac{1}{2}J = 10 \, \text{msec} \]

\[ t_{\text{max}} = 15 \, \text{msec} \]

\[ T_2 = 5 \, \text{msec} \]
Processing of NUS data in topspin 3.1

NUS is recognized by the command `ftnd` and `mdd` is started automatically

```
ftnd
```

**NAME**

`ftnd` - nD processing including Fourier transform (≥ 3D)

**DESCRIPTION**

The command `ftnd` processes nD data performing fid baseline correction, linear prediction, window multiplication, Fourier transform and phase correction. The command automatically recognizes the data dimensionality and handles data of dimension ≥3D. In TOPSPIN 2.1, `ftnd` has been tested by Bruker on 3D, 4D, 5D and 6D data. Note that 3D data can also be processed with the conventional commands `tf3`, `tf2`, `tf1` and `ft3d`.

As an example, `ftnd` is described here for a 4D dataset. It takes the following three arguments:

- `<direction>`
  the direction(s) to be processed. Allowed values are:
  
  0: all directions, in the order defined by AQSEQ.
  4321, 4312, 4231, 4213, 4132, 4123: all directions in specified order
  4, 3, 2, or 1: F4, F3, F2 or F1, respectively.
Thank you