

Fitting a pseudo 2D spectrum to extract T2 in ssNake

6th January 2024

1 Introduction

This tutorial will go through processing of 2D dataset, fitting a 1D spectrum using Czjzek model, extracting the amplitude of subsequent 1D in the pseudo 2D dataset, then fit the amplitudes vs time with the 'Relaxation Curve' model. The objective is to see how to extract parameters from a series of fits in order to fit them.

You don't need to have done the CzjzekFitting tutorial before.

The 'Incr copy' option mentioned in the Czjzek fitting part of this tutorial is only supported from ssNake version 1.5.

2 Dataset and sample information

For this tutorial, we will use a ^{27}Al spectrum recorded with a hahn echo pulse sequence. The data was acquired on a 18.8 T Bruker spectrometer under 20 kHz Magic Angle Spinning. The pulse sequence is $\text{P90} - \tau - \text{P180} - \tau - \text{acquisition}$. The FID is recorded from the top of the echo.

It was saved as a pseudo 2D dataset varying the echo delay. The initial echo delay was $\tau = 5$ rotor periods (250 μs) and the delay was incremented by $\tau = 5$ rotor periods (250 μs) for subsequent rows. T2 relaxation occurs during $2 \times \tau$.

The sample is mesoporous alumina Al_2O_3 provided by Cláudia Morais. On the 1D spectra you can see 3 sites with typical Czjzek distribution pattern. 4 coordinated aluminum site Al_{IV} at about 65 ppm, five coordinated aluminum site Al_{V} at about 36 ppm and 6 coordinated aluminum site Al_{VI} at about 9 ppm.

In such case fitting the 3 sites is mandatory as using integral or peak picking would produce biased value due to overlapping sites.

3 Processing

Open the dataset choosing the 'ser' file in data/2 folder. Switch to ppm units if not default. Stay on the 1D plot mode.

First use zero filling (Matrix \rightarrow Sizing) and choose 2048 point size.

Second, correct for digital filter (Tools \rightarrow Correct Digital Filter). The digital filter part will be

shifted to the end of the FID.

Do Fourier Transform (ctrl-f) and rephase the spectrum (Tools → Phasing → Autophase 0th). Correct baseline (Tools → Baseline Correction), excluding region 200 ppm → -200 ppm. Fit with a polynomial or sine/cosine function of degree 2 or 3. Check the 'Fit traces separately' button. Validate with 'Ok'.

4 Fitting the first spectrum with Czjzek model

This is similar to Czjzek Fitting tutorial. If you are familiar with it you can probably skip this section.

Select the 'Fitting → Czjzek' fitting model. We will use 3 sites with approximate chemical shift of 75 ppm, 43 ppm and 12 ppm and about 7 ppm of chemical shift distribution. In general, the chemical shift lies on the left hand side of second order quadrupolar lineshape. This also applies to Czjzek distribution and is only moderated by chemical shift distribution. Remember that gaussian broadening models chemical shift distribution and lorentzian broadening models relaxation! In such sample relaxation is usually negligible, we can leave lorentzian broadening to the default 10 Hz value. Fix (check the box) Lorentzian broadening and free (uncheck the box) gaussian broadening.

Now we need to pre-calculate a spectrum library to fit the Czjzek distribution. Click on 'Library' button. Select the correct spin number (5/2 for ^{27}Al). Choose MAS: 'infinite MAS' and keep 'Satellites' button unchecked as no satellite spinning sideband is visible. Click on 'Generate' button to create the library in memory.

We can now run a simulation by clicking 'Sim' button. However, with default σ value of 1 MHz, the typical right hand side tail is not visible. We need to increase the Cq distribution (σ). You can try $\sigma = 2, 3, 4$ or 5 for site 1 but the lineshape will not change to the expected shape. This is because the library is not adequate as can be seen by clicking the 'show' button. Maximum Cq calculated for the distribution is 4 MHz by default. We need to increase it to a value about $4 \times \sigma$ and the average Cq in the distribution is about $C_q = 2\sigma$. You will need a maximum Cq of about 20 MHz. We can further refine the simulation accounting for real spinning speed as one observe tiny spinning sidebands. For that we open the Library window and change to MAS: 'Finite MAS'. Set spinning speed to 20 kHz. #sidebands 16 is more than enough as sidebands are very small (this is a parameter for which convergence should be checked!). 'Generate' the library again. Then refine the fit clicking 'Fit' again. The fit result can be see in Fig. 1. At that point, I suggest to export the fit 'Parameters to file' via the 'Import/Export' button.

You will also find good fitting parameters that you can import in 'data/2/pdata/1/Al2O3_JF3_fit.txt' file to reproduce this figure.

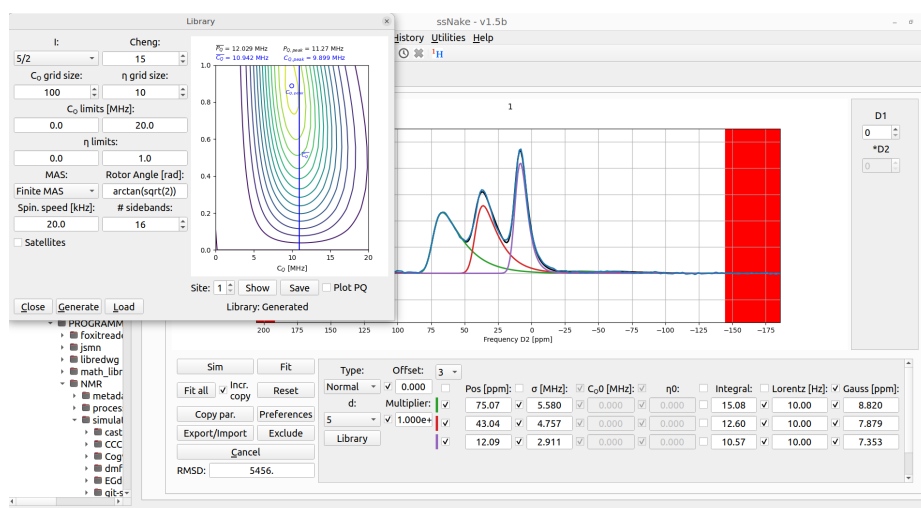


Figure 1

5 Fitting all spectra for integral

Now that the first 1D spectrum is properly fitted we will use this fit to get the integral of all three sites in all spectra. If you scroll through D1 dimension (spin button on right hand side of the spectrum), you will notice that subsequent rows of the pseudo 2D have initial fitting parameters. Come back to row 0 and check all parameter buttons except for the integral parameter. This can be done for all sites for each parameter selecting the parameter name check button. (Export again the 1D fit parameters to file...)

We now need to copy the first row parameters to other rows: Click on 'Copy par' button.

You can now click on 'Fit all' button to run the fitting procedure for each row. You may need to repeat several times the 'Fit all' action if convergence is not reached. Go through the different rows to verify the different fits.

One problem that can arise is that for large numbered rows, the starting point of the fit is far from convergence. Generally, the spectra are evolving smoothly from one row to the next one. Therefore a better approach is to copy the parameters from previous row. In a T2 measurement, the amplitude of the spectra is monotonically decreasing. So starting from row 0 we will check the 'Incr. copy' check button. When not checked 'Fit all' fits all rows without performing parameter copy. When 'Incr copy' is checked a fit/copy procedure is done: fit row 0 then copy the fitted parameters to next row, fit row 1, copy fitted parameters to row 2 and so on...

If one needs to refine further the fit for each row, subsequent call to 'Fit all' should be done with 'Incr. copy' option unchecked.

Once the fit for all rows is satisfactory one can export the amplitude parameter to new workspace. From 'Import/Export' window select 'Parameters to workspace'. Then check 'Export all slices' and 'Integrals' boxes before clicking 'Ok'. You can give an explicit name to the new workspace like 'T2s'.

We now have 3D pseudo dataset. D3 dimension contains echo time, D2 dimension holds the

different sites (3 rows [0..2] for 3 sites), D1 dimension holds the different parameters that were exported to workspace. In our case only integrals were exported so there is only one row for this dimension.

We need to check that the echo time scale is correct. In our dataset the initial echo delay between 90° pulse and 180° pulse was 5 rotor period (i.e. 250 μ s under 20 kHz MAS). The total echo delay was therefore at 10 rotor periods (500 μ s) and the increment the same. We need to redefine the x axis scale. An increment of 500 μ s second corresponds to a spectral window of 2 kHz. So you can set 2 kHz in the Sweepwidth entry. The starting value remains 0 but this won't affect the T2, but only the initial amplitude. If you need to get the correct amplitude also, then you need to use the 'Plot → User X-axis' menu to define the time x-axis. Select the linear input and set the start and stop time values in seconds:

start value 500e-6, stop value 500e-4 (we have 100 points) and click 'Ok'.

6 Fitting T2 decay curves

6.1 Exporting extracted parameters

Now, data is ready to be used for T2 fitting. One could want to export the data in text mode to process them further in third party software. This can only be done on 1D or 2D data. But our data is currently 3D. So we need to extract a 2D slice. This can be done using the menu 'Workspace → Slice to workspace'. The plotted data must be in stack plot or 2D contour mode, not in 1D slice otherwise only a 1D spectrum would be sliced to a new workspace. Now we can export the new workspace with 'File → Export → ASCII (1D/2D) or CSV(1D/2D)' menu. The CSV (Comma Separated Values) data will appear in columns :

Time, Site1_real, Site1_imag, Site2_real, site2_imag, site3_real, site3_imag.

6.2 T2 fitting

Let's fit the T2 decay. Select menu 'Fitting → Relaxation curves'. We need to fit data with an exponential decay function. We will fix the 'Constant' to 0 and the 'Coefficient' to 1. Check the box beside them not to fit these parameters. One can fit the first site T2. Finally, click 'Copy par.' then 'Fit all' several times to reach reasonable convergence. As seen in figure 2, you should find T2 value of 7.8 ms, 6.4 ms and 4 ms for sites 1 (Al_{IV}), 2 (Al_V) and 3 (Al_{VI}) respectively.

As ^{27}Al is quadrupolar spin, there might be more than one decay component for T2. Also, the peaks seem to shift slightly with echo delay indicating that there might be more components or that low C_q in the distribution relax faster. Further exercise: try to fit relaxation with 2 components releasing the Coefficient parameters and fixing the Amplitude.

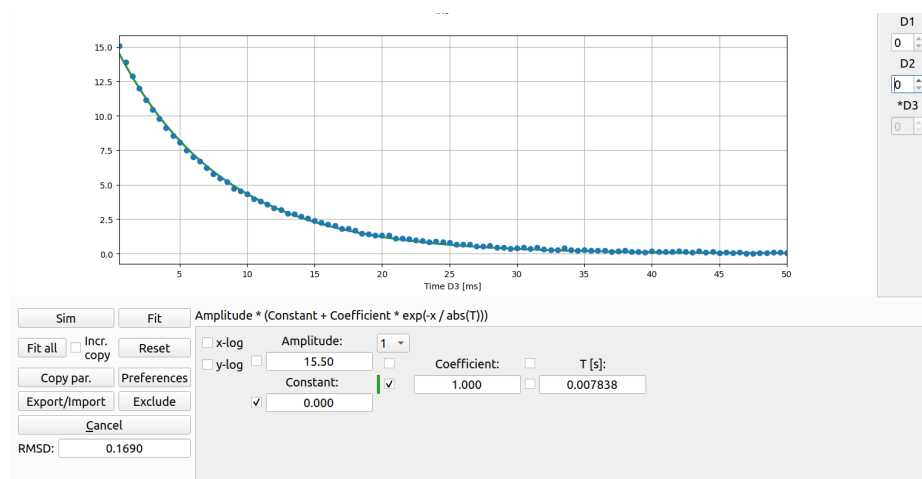


Figure 2