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FFC APPLICATION NOTE: FITTEIA

Introduction to Fitteia data-fitting software and case study: fitting NMRD data for $MnCl_2$

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Introduction to Fitteia

Fitting relaxometry data, including NMRD profiles from Fast Field Cycling (FFC) NMR relaxometry is a problem which researchers have approached using different tools, both non-specific commercial software and self-developed software. To date there is no commercial software program for specific use with FFC relaxometry data [1]. ***Fitteia*** is a possible solution which can be adopted and adapted specifically for FFC relaxometry data. ***Fitteia*** is an open online model fitting platform (developed by Prof. Pedro Sebastião from the University of Lisbon) throughout many years of experience in fitting relaxometry data. It does not require the installation of local software or the purchase of a software license and, in addition, it can be accessed from any operating system [2].

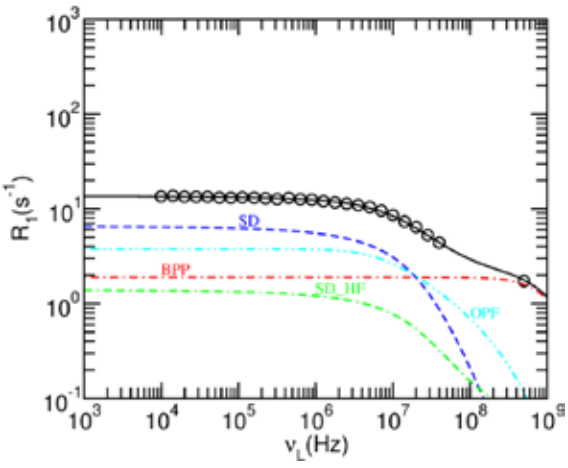

FIG. 1:
Example of fitting performed using Fitteia on an NMRD profile of an Ionic liquid. The black line fitting the experimental data is the graphical representation of the used model. The different relaxation contributions to the final result are represented by the curves depicted with different colours. (From [6]).

The Fitteia library

Fitteia is provided with a library of relaxation models for molecular rotations, translational self-diffusion, RMTD, cross-relaxation, order director fluctuations in nematic and smectic LC phases, Rouse model, paramagnetic relaxation, etc. This library can be easily extended and new models can be added by the users.

What Fitteia allows the users to do

The ***Fitteia*** platform allows the user to:

- Obtain the graphical representation of experimental results and/or mathematical functions;
- Obtain the numerical fit to experimental data of arbitrary user-defined linear and/or non-linear functions dependent on "n" fitting parameters and "x" experimental variables;
- Work on the data using an integrated programmable calculator;
- Use an integrated *Matlab*-like calculator;
- Write professional-quality reports using *LaTeX*;
- Print out documents in PDF, PNG, JPG, EPS formats using the fit results;
- Register through a email/password security process to assure the user's privacy;
- Share the working folders with other selected users
- Use three different expertise levels (e.g. Basic, Advanced, Expert);
- Save/recover the results;
- Make use of two levels of user privileges.

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Apart from fitting the NMRD profiles, it's important to highlight that the ***Fitteia*** software is provided with:

- Calculator module;
- Plotter module;
- Increased privileges modality.

The calculator module

After a fit, the function parameters obtained are exported to the Calculator module. The Calculator web form layout shows a text box area where the user can write equations and expressions and perform different types of calculations including tables and/or vector operations. By default, the Calculator starts with a list of examples that can be studied as a tutorial text.

The plotter module

The user can produce any kind of graphs by using ***Fitteia***'s Plotter module.

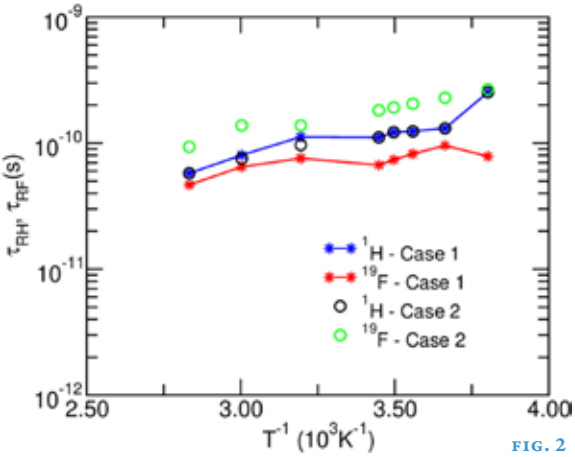

FIG. 2

FIG. 2:
Example of plots of the correlation times for both cations (^{1}H) and anions (^{19}F) as a function of temperature in two different cases.

FIG. 3:
Fitteia allows the user to insert the relaxation models from the library and also to write them on his own.

FIG. 4:
Fitteia's functions library webpage.

The increased privileges modality

For advanced model fitting the provided functions might not be enough and new complex functions might be required. If they are not included in the system a user can ask for additional privileges in order to be able to develop more elaborated functions and libraries. The only difference noticed by the users is the layout of the fitter module as it includes additional text boxes for the user's additional C code.

Stelar case study: how to fit the NMRD profile of a paramagnetic compound of manganese cloride ($MnCl_2$)

Herein, we will go through a case study provided by Stelar which the user can find on the ***Fitteia*** platform. The NMRD profile of a paramagnetic sample, 2mM manganese chloride ($MnCl_2$) is provided. The final purpose of the fitting is to extract the values of the dynamical parameters which characterize the sample. In this case, the fitting model is made up of 2 contributions, one from the "**Inner Sphere**" and one from the "**Outer Sphere**" mechanisms. Referring to **FIG. 3**, in the box called "Function (written in C)", two different functions are used to recall the two contributions:

$$\mathbf{R_1 = R1ISsbm(f, q, C, ...) + R1OSabhf(f, C, s, ...)}$$

where "R1ISsbm" recalls the "Inner Sphere" equation and "R1OSabhf" recalls the "Outer Sphere" equation. Furthermore, if the user clicks on "Specific function's library" (indicated by the black arrow in **FIG. 3**, the webpage shown in **FIG. 4** will open.
Referring to **FIG. 4**, by clicking on "**NMRDpedia**" the user will have a detailed description of both the "**Inner Sphere**" (**IS**) and "**Outer Sphere**" (**OS**) theories. The contribution to relaxivity from the **IS** model originates from the water molecules coordinated with the paramagnetic complex. The contribution to relaxivity from the **OS** model instead, comes from the water molecules slowly diffusing in proximity of the paramagnetic complex.

Link to the **IS** paramagnetic relaxation model:
fitiwiki.vps.tecnico.ulisboa.pt/mediawiki/index.php/Inner_sphere
Link to the **OS** paramagnetic relaxation model:
fitiwiki.vps.tecnico.ulisboa.pt/mediawiki/index.php/Outer_sphere

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The NMRD profile of the Stelar standard sample of $MnCl_2$ (2mM) is displayed in **FIG. 5**. The profile was acquired with 30 field points logarithmically distributed in the range from 0.01MHz to 40MHz at the temperature of 25 °C.

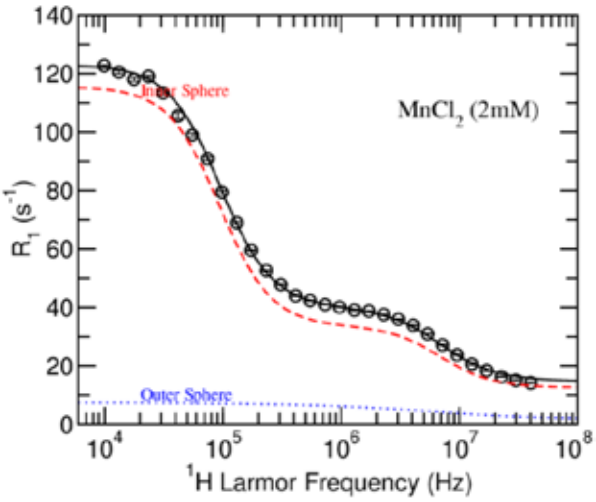

FIG. 5:
NMRD profile of the Stelar standard sample of $MnCl_2$ (2mM). The fitting line is traced in black, the IS contribution in red and the OS contribution in blue.

In **FIG. 6**, the list of the parameters which are required to fit the NMRD profile are reported. On the left of the parameters, the user is given the choice of ticking either the options "Fix" or "Free". By choosing the option "Fix", the fitting will be performed keeping fixed the value of the corresponding parameter. On the contrary, by selecting "Free", the fitting algorithm will modify the value of the parameter in order to optimize the final result.
However, care is required here because if several parameters are left free at the same time, they could assume wrong values even if the final fitting appears to be good. This is due to a sort of "compensation effect" between the many parameters.
As a rule in general, it is advised to fix the values of those parameters that are known, or at least, it is advised to enter the range of variability of these parameters. The range of variability of a parameter can be set by writing the minimum value (in the box called "Min") and the maximum value (in the box called "Max") which is desired for that parameter to assume.

Free/Fix	Name	Value	Min	Max
◉ / ○	tv	8.7825e-12		
◉ / ○	tr	3.9233e-11		
◉ / ○	tm	1.8600e-06		
○ / ◉	r	2.8300e-10		
○ / ◉	a	3.8000e-10		
○ / ◉	D	2.2000e-09		
○ / ◉	Delta2	6.0000e+17		
○ / ◉	FermiCC	2.3900e+07		
○ / ◉	C	2.0000e+00		
○ / ◉	q	6.0000e+00		
○ / ◉	s	2.5000e+00		
○ / ◉	SolvMmass	1.8000e-02		
○ / ◉	density	1.0000e+00		

Fit Plot

FIG. 6:
List of the parameters used to fit the experimental data and their values obtained from the fitting.

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(2) Sebastião, P. J. (**2013**). *The art of model fitting to experimental results*. European Journal of Physics, 35(1), 015017;
(3) Sebastião P. J., Gradisek A., Pinto L. F. V., Apih T., Godinho M. H. & Vilfan M., (**2011**), *Fast field-cycling NMR relaxometry study of chiral and nonchiral nematic liquid crystals*, The Journal of Physical Chemistry B, 115(49), 14348-14358.