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# The art of model fitting to experimental results

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## Abstract

Model fitting to experimental results is presented within the context of graduate physics laboratories and generalized to other graduate and post-graduate levels, and diverse research fields. In most cases the analysis of experimental results, in terms of mathematical models available to describe the obtained results, extends beyond the numerical minimization of statistical estimators, like the chi-square, in the model's parameter space. Dedicated fitting procedures, not easily or directly available in common data analysis software's packages, are required to obtain the best fitting set of parameters that present a consistent physical meaning. A simple but powerful web-based solution is presented, and its relative advantage in comparison with known commercial and open source solutions is discussed.

Keywords: model fitting, data analysis

 Online supplementary data available from [stacks.iop.org/EJP/35/015017/mmedia](http://stacks.iop.org/EJP/35/015017/mmedia)

(Some figures may appear in colour only in the online journal)

## 1. Introduction

The model fitting of experimental results is a teaching subject considered in physical sciences and engineering graduate courses. The most basic and common example concerns the case of the fit of a straight line to a data set where the dependent observable depends linearly on an independent variable. This case is often presented together with the statistical concept of one-dimensional linear regression and further extended to multiple dimensions [1]. The numerical procedure most often used to estimate the slope and intercept in a linear fit is the least-squares minimization [1]. This simple model fit can be made using a large variety of software packages, some of them well known to both teachers and students. In a recent work Peterlin [2] presented a comparison between spreadsheet versus

statistics suite solutions for data analysis and graphing in physics laboratories. Simple linear regressions and polynomial regressions can be performed using both spreadsheet and dedicated software packages. However, in the case of more complex nonlinear and/or multidimensional model fits, the spreadsheet approach often becomes impractical and other more dedicated statistical suites (either commercial or open source) have to be considered [2].

In introductory physics laboratories, it is often required to analyse experimental results with physical models that have nonlinear dependences on the physical parameters. An electrical oscillatory circuit might be one such case [3]. A serial circuit with an ac power supply, a resistor,  $R$ , a capacitor,  $C$ , and a coil,  $L$ , might operate in different regimes, depending on the type of voltage being applied to the circuit and the values of  $R$ ,  $C$  and  $L$ . Another example is the classical mechanical system formed by a mass suspended on a spring. Within the elastic limit the length of the spring depends linearly on the value of the mass in a static experiment or presents a motion with a damped amplitude (oscillatory or not) after an initial spring's elongation/compression. When subjected to an external oscillatory force, the spring-mass system might present a resonance when the frequency of the external force matches the resonance frequency of the system that depends on the elastic constant of the spring, the value of the suspended mass and the friction's coefficient, respectively.

In advanced physics laboratories students and researchers need to analyse experimental results obtained with different experimental techniques such as: x-ray diffraction, nuclear magnetic resonance (NMR) and polarizing optical microscopy, to name a few. These experimental results are in most cases analysed in terms of nonlinear physical models. In professional research work, experimental results obtained for a studied system often include different observables and depend on one or more experimental variables. In those cases, the best results are obtained when the data analysis is performed with a global best-fitting target. This goal adds a degree of complexity to the model-fitting procedures that cannot be easily addressed using spreadsheet software and in some cases requires considerable expertise in the use of some of the dedicated statistical suites available, like those referred to by Peterlin [2]. The approach to obtain the best global model fit to a set of experimental results, where different observables and independent variables have to be considered, requires a set of skills that extends the basic technical competence in numerical analysis and least-squares minimization.

Another important issue concerning data analysis in physics laboratories is the possibility of collaborating with other students in the same problem (team work). The possibility of sharing data space, models, plots and solutions, in addition to the possibility of continuing the work away from the laboratories, can also be an important point when choosing the computer solution to use for the data analysis. In advanced research work, the collaboration might include researchers across the world. The existence of web services as repositories of files that can be shared among different users help to overcome part of this problem. However, the use of commercial software might in some cases be a serious limitation to off-campus work and in some cases prevents the sharing of software solutions due to license limitations that might restrict the use of conventional software packages.

In this work, a web-based solution is presented (available at <http://fitteia.org>) for professional model fitting, graphing, data analysis and report writing that can also be used for teaching at both graduate and post-graduate levels<sup>1</sup>. This solution spares users the overhead technical work associated with the least-squares minimization, data plotting and report writing, necessary when using conventional software packages, thus allowing users to focus on the

<sup>1</sup> Users can register, or reset their login password, using a valid email address. The system assigns a password that users can change afterwards. The user can be assigned one of two privilege levels: normal and privileged. The user has three running modes available: basic, advanced and expert (<http://fitteia.org>).

‘art’ of model fitting and parameter’s estimation. The system allows for a considerable increase of the user’s flexibility to perform his work and independence regarding his choice of both hardware and operating system. Personal computers (laptop or desktop), main-frame computers, tablets and smartphones are devices that can be used to fully access the system without losing performance.

## 2. Three theoretical models

### 2.1. Damped harmonic oscillator

One physics experiment that can be used to illustrate some aspects of advanced model fitting to experimental results concerns the description of motions in a spring–mass system consisting of a mass,  $m$ , suspended on a spring with elastic constant  $K$ . In static equilibrium, the length of the spring,  $\Delta\ell$ , depends on the equilibrium between the weight and on the spring’s elastic force. Therefore,

$$\Delta\ell = \frac{g}{K}m, \quad (1)$$

where  $g$  is gravitational acceleration. The mass remains at its vertical position of equilibrium,  $z_0$ .

In general terms, the equation of motion that describes the position of the mass with respect to its equilibrium position  $Z = z - z_0$  is the well-known second degree differential equation

$$\frac{d^2Z(t)}{dt^2} + \frac{b}{m} \frac{dZ(t)}{dt} + \frac{K}{m} Z(t) = \frac{F_{\text{external}}(t)}{m}, \quad (2)$$

where  $b$  is the friction coefficient and  $F_{\text{external}}(t)$  is a user-defined external force acting on the system. Equation (2) has several solutions. In the case of  $F_{\text{external}}(t) = 0$ , the equation of motion  $Z(t)$  depends only on the system’s parameters  $m$ ,  $b$  and  $K$ .  $\omega_0 = \sqrt{K/m}$  is the natural frequency of the system and  $\lambda = b/(2m)$  is the damping coefficient. The particular solution of equation (2) when  $\lambda < \omega_0$  is

$$Z(t) = Z_M e^{-\lambda t} \cos(\omega t + \phi), \quad (3)$$

where  $\omega = \sqrt{\omega_0^2 - \lambda^2}$ .  $\phi$  and  $Z_M$  depend on the initial conditions of the motion. Starting from its initial position  $Z(0)$  the mass  $m$  oscillates around the equilibrium position  $z_0$  with period  $T = 2\pi/\omega$  and decreasing amplitude.

If  $\lambda \geq \omega_0$ , the mass  $m$  has a damped aperiodic motion towards its final position  $z_0$  starting from  $Z(0)$ .

In the particular case  $F_{\text{external}}(t) = F_0 \cos(\omega_a t)$  and  $\lambda < \omega_0$ , it is easy to demonstrate that

$$Z(t) = Z_M e^{-\lambda t} \cos(\omega t + \phi) + A(\omega_a) \cos(\omega_a t + \alpha), \quad (4)$$

where

$$A(\omega_a) = \frac{F_0}{m \sqrt{(\omega_0^2 - \omega_a^2)^2 + 4\lambda^2 \omega_a^2}} \quad (5)$$

and

$$\tan \alpha = \frac{2\lambda \omega_a}{\omega_0^2 - \omega_a^2}. \quad (6)$$

Obviously, other external forces will produce different permanent regimes after the initial natural motion of the mass vanishes.

## 2.2. X-ray diffraction

In advanced physics laboratories, students often have contact with x-ray diffraction experiments where it is possible to obtain structural information about condensed matter systems. In the case of soft matter systems that do not present long-range structural order, large-angle diffraction profiles can reveal details of the local molecular organization in the range from  $10^{-10}$  to  $5 \times 10^{-9}$  m [4].

X-ray counters used in the experiments often produce profiles with a large number of points. The x-ray profiles where the scattered intensity is plotted as a function of scattered vector amplitude can, in some cases, be described by a sum of the Gaussian profiles

$$I(q) = I_0 + \sum_{k=0}^N a_k e^{-(q-q_k)^2/b_k^2}, \quad (7)$$

where  $I_0$  is the background contribution,  $q_k$ ,  $a_k$  and  $b_k$  are the wave vectors, amplitudes and line widths of each characteristic structural distance numbered with index  $k$ , respectively.

## 2.3. NMR relaxation

Condensed matter physics students, at the PhD level, occasionally have to obtain molecular dynamics information using NMR relaxometry (NMRD) [5, 6]. The proton spin-lattice relaxation rate,  $T_1^{-1}$ , as a function of frequency and temperature might present features that can be interpreted in terms of relaxation models that are associated with different types of molecular motions [5–8]. Molecular rotations and reorientations (R), translational self-diffusion (SD) and slow collective motions are common examples considered when analysing NMRD results obtained for isotropic liquids and liquid crystals [6]. In the case of an isotropic phase of a liquid crystal of ellipsoid molecules  $T_1^{-1}$  can be approximated by

$$T_1^{-1} = (T_1^{-1})_R + (T_1^{-1})_{SD} + (T_1^{-1})_{OPF} \quad (8)$$

with

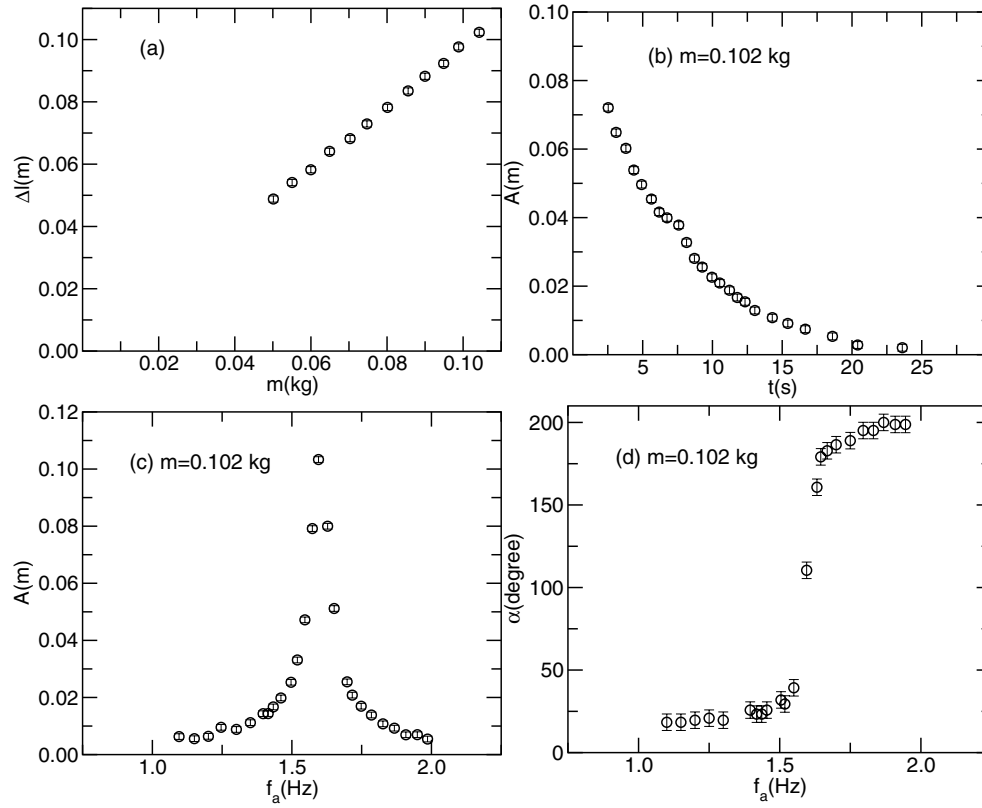
$$(T_1^{-1})_R = A_R \left[ \frac{\tau_S}{1 + \omega^2 \tau_S^2} + \frac{4\tau_S}{1 + 4\omega^2 \tau_S^2} + \frac{\tau_L}{1 + \omega^2 \tau_L^2} + \frac{4\tau_L}{1 + 4\omega^2 \tau_L^2} \right], \quad (9)$$

$$(T_1^{-1})_{SD} = \frac{9}{8} \gamma^4 \hbar^2 \left( \frac{\mu_0}{4\pi} \right)^2 \frac{n\tau_D}{d^3} [T(\alpha, \omega\tau_D) + 4T(\alpha, 2\omega\tau_D)] \quad (10)$$

and

$$(T_1^{-1})_{OPF} = \frac{A_{OPF}}{\omega^{1/2}} \int_{\omega_{Cl}/\omega}^{\omega_{Ch}/\omega} \frac{\sqrt{x}}{1 + (x + \omega_0/\omega)^2} dx. \quad (11)$$

In this relaxation model (equation (8)),  $\tau_L$  and  $\tau_S$  are correlation times associated with molecular rotations/reorientations along the long molecular axis and around a perpendicular axis, and  $\tau_D$  is a correlation time associated with the translational diffusion displacements.  $n$  is the density of spins and  $d$  is the distance of the closest lateral approach between molecules [9].  $\omega_{Cl}$  and  $\omega_0$  are low cut-off frequencies, and  $\omega_{Ch}$  is a high cut-off frequency associated with fluctuations of order (OPF) observed close to the isotropic–nematic transition.  $A_R$  and  $A_{OPF}$  are pre-factors that depend on addition physical parameters of the liquid crystal compound (see the electronic supplementary information (ESI), available from [stacks.iop.org/EJP/35/015017/mmedia](http://stacks.iop.org/EJP/35/015017/mmedia)).  $\tau_S$ ,  $\tau_L$  and  $\tau_D$  are temperature dependent and are usually described by Arrhenius laws  $\tau_S = \tau_{S_{ref}} \exp(E_S(T^{-1} - T_{ref}^{-1})/8.31)$ ,  $\tau_L = \tau_{L_{ref}} \exp(E_L(T^{-1} - T_{ref}^{-1})/8.31)$  and  $\tau_D = \tau_{D_{ref}} \exp(E_D(T^{-1} - T_{ref}^{-1})/8.31)$ , respectively.  $T_{ref}$  is a reference temperature and  $E_S$ ,  $E_L$  and  $E_D$  are activation energies.



**Figure 1.** Experimental results obtained for a spring–mass system [10], as explained in the text. (a) The spring’s length as a function of the suspended mass; (b) amplitude of oscillation measured at time  $nT$ ,  $n = 0, 1, 2, 3, \dots$ , where  $T$  is the oscillation period; (c) amplitude of oscillation measured as a function of the frequency of the harmonic applied force; (d) phase difference between the mass motion’s amplitude and the applied force as a function of the oscillation frequency of the force.

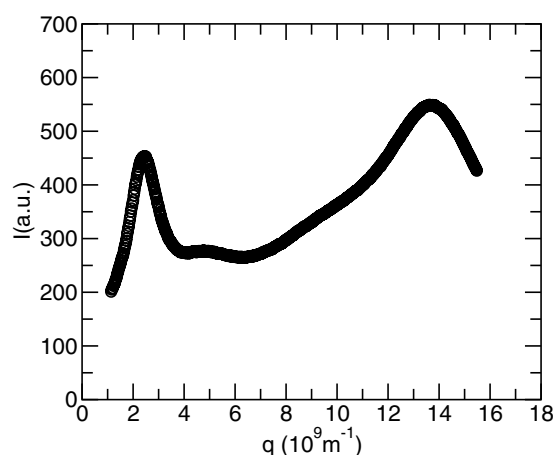
### 3. Experimental results

#### 3.1. Damped harmonic oscillator

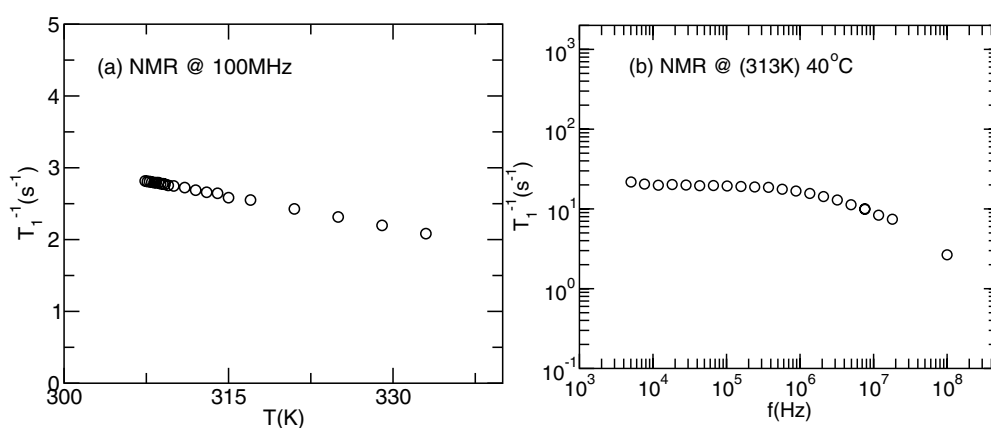
Using a damped harmonic oscillator experimental setup [10], which includes a spring with unknown elastic constant  $K$ , a mass  $m = 0.102$  kg, and a unknown friction coefficient  $b$ , it is possible to obtain four sets of experimental results corresponding to the motions of the harmonic oscillator, described by the model equations (1), (3), (5) and (6). These experimental results are presented in figures 1(a), (b), (c) and (d), respectively. The position of the mass was determined with an uncertainty of  $\pm 10^{-3}$  m. The frequency of the oscillation of the external force acting on the system was controlled with a resolution of  $\pm 0.01$  Hz. The phase difference between oscillations of the mass and the external force was measured with an uncertainty of  $5^\circ$ . The results of figure 1(b) were obtained regularly with a sampling time equal to the period of oscillation.

#### 3.2. X-ray diffraction

In figure 2 is presented the x-ray diffraction profile obtained for a liquid crystal compound using Cu  $K_\alpha$  radiation with a wave length  $\lambda = 1.54$  Å.



**Figure 2.** X-ray diffraction profile obtained for a liquid crystal compound.



**Figure 3.** Experimental  $^1\text{H}$  spin-lattice relaxation rates: (a) results obtained at a fixed frequency for a Larmor resonance frequency of 100 MHz; (b) results obtained as a function of the Larmor frequency for a fixed temperature  $T = 40^\circ\text{C}$ .

### 3.3. NMR relaxation

In figure 3 are presented the hydrogen proton spin-lattice relaxation rate experimental results as a function of temperature for a fixed Larmor frequency of 100 MHz, and as a function of frequency for a fixed temperature. The results for frequencies below 20 MHz were obtained using fast field cycling NMR relaxometry [11–13]. For the measurements at 100 MHz, standard NMR relaxometry techniques were used [7].

## 4. Model fits

The analysis of experimental results presented in figures 1–3 with respect to the physics models previously introduced requires the fitting of the models' equations to the experimental

results in order to obtain the physical parameters relevant for each system. One common way to obtain the best fit is by the minimization of the least squares

$$\chi^2(p_1, \dots, p_m) = \sum_{k=1}^N \frac{(y_k^e - y_k^f(p_1, \dots, p_m, x_k^e))^2}{\sigma_k^{e2}}, \quad (12)$$

where  $y_k^f(p_1, \dots, p_m, x_k^e)$  is the value of the model equation calculated for the value  $x_k^e$ , and the model parameters  $p_k$  with  $k = 1, \dots, M$ ,  $(x_k^e, y_k^e \pm \sigma_k^e)$  are the experimental points  $1, \dots, N$ , with  $\sigma_k^e$  being the experimental uncertainty of  $y^e$ . In most experiments, the uncertainty of the independent variable is controlled in order to reduce its influence on the measured observable. The case where the uncertainties of both  $x$  and  $y$  are important will be addressed below.

A rule of thumb, in normal practice, is that a ‘moderately’ good fit is obtained when the value of  $\chi^2(p_1, \dots, p_m) \simeq N - M$  ( $N - M$  being the number of degrees of freedom) is obtained after the minimization [14].

The  $\chi^2$  minimization considering the model equations (1), (3)–(8) presents different types of challenges. Technically, the fit of equation (1) to the data of figure 1(a) is the most simple one and can be considered a trivial case. The fits of the other model equations require more sophisticated numerical methods to perform the least-squares minimization and some user skills in the use of the available software packages.

On *fitteia*’s website (see footnote 1), users can perform both simple and advanced model fits to experimental data with different degrees of complexity using a common interface that drastically reduces the user’s overhead work required to perform identical data analysis using other software packages. The *fitter* module available presents three distinct sections: (1) data, (2) plot parameters, and (3) function and parameters. In the data section the experimental points are introduced as a table with three columns where the values of ‘ $x^e$ ’, ‘ $y^e$ ’ and ‘ $\sigma^e$ ’ (one point  $(x_k^e, y_k^e \pm \sigma_k^e)$  per line) are separated by tab characters or white spaces. Copy and paste actions from spread sheet tables or text files can help filling up the data table. In the plot parameters section, the plots can be set according to the data being analysed. The model equation  $y = f(p_1, \dots, p_m, x_k^e)$  is introduced in the one-line text box in the function and parameters section, using the syntax of language C. Both dependent and independent variable names ( $y$  and  $x$ ) and the parameter names ( $p_1, \dots, p_M$ ) have to be declared (additional information is available in the ESI, available from [stacks.iop.org/EJP/35/015017/mmedia](http://stacks.iop.org/EJP/35/015017/mmedia)).

The *fitteia*’s *fitter* module core is a powerful minimization routine from the CERN library called MINUIT [15]. MINUIT contains three different minimization methods SCAn, SIMplex and MIGrad. A sequential use of these methods and a call to MINUIT MINOS method to compute the uncertainties of the fitting parameters is a powerful strategy to find the best absolute minimum of equation (12). As with all minimization routines the user should provide an ‘educated guess’ of the initial values of the fitting parameters to minimize the computation time and to avoid stopping the minimization on a local minimum in the parameters’ space. Nevertheless, *fitteia* has proven to be quite robust with respect to this issue and all parameters are initialized with a finite value to prevent some unnecessary mistakes.

#### 4.1. Damped harmonic oscillator

The first step in the analysis of the experimental results obtained for the damped harmonic oscillator is to obtain the best numerical model fit to each data set of the experimental results separately.



**Table 1.** Model parameters obtained from the best model fits to the experimental results explained in the text.  $m = 0.102$  kg.

Data Figure	$\Delta\ell(m)$ 1(a)	$A(t)$ 1(b)	$A(f_a)$ 1(c)	$\alpha(f_a)$ 1(d)	All 4
$K$ (N m <sup>-1</sup> )	$9.9 \pm 0.2$	—	$10.359 \pm 0.006$	$10.27 \pm 0.03$	$10.4 \pm 0.1$
$d_0$ (10 <sup>-3</sup> m)	$-0.6 \pm 1.3$	—	—	—	$2.7 \pm 0.3$
$\lambda$ (s <sup>-1</sup> )	—	$0.139 \pm 0.004$	$0.163 \pm 0.003$	$0.12 \pm 0.02$	$0.142 \pm 0.001$
$Z_0$ (m)	—	$0.103 \pm 0.002$	—	—	$0.105 \pm 0.001$
$Z_\infty$ (m)	—	$0.003 \pm 0.001$	—	—	$0.002 \pm 0.001$
$F_0$ (N)	—	—	$0.037 \pm 0.001$	—	$0.033 \pm 0.001$
$a_0$	—	—	—	$0.32 \pm 0.03$	$0.34 \pm 0.02$

In the case of the spring's elongation as a function of the suspended mass (figure 1(a)) the model used was  $\Delta\ell = (g/K)m + d_0$ .  $d_0$  was introduced in equation (1) to take into account possible offsets in the experiment, when measuring  $\Delta\ell$ .

In the case of the data set corresponding to the free damped oscillations, equation (3) can be simplified when the experimental measurements are made regularly at times  $t = t_0 + nT$ , where  $T$  is the period of oscillation,  $n = 0, \dots, N$ ,  $Z(t_0 + nT) = (Z_0 - Z_\infty)e^{-\lambda nT} + Z_\infty$ .  $Z_\infty$  should be null, but it can be introduced to take into account possible offset deviations from the initial equilibrium value.

In the case of forced oscillations, the amplitude of oscillation  $A(\omega_a)$  given by equation (5) can be written in terms of  $f_a = \omega_a/(2\pi)$ ,  $A(f_a) = (F_0/m)[(K/m - 4\pi^2 f_a^2)^2 + 16\pi^2 \lambda^2 f_a^2]^{-1/2}$ . As for the phase difference between the external force oscillations and the mass oscillations  $\alpha$  given by equation (6) some attention is required since  $\arctan(x)$  changes by a value of  $\pi$  when the argument changes sign. Therefore, using the ( $? : \cdot$ ) conditional operator equation (6) can be written as  $\alpha = (f_a < \sqrt{K/(4\pi^2 m)}) ? \arctan(4\pi \lambda f_a / (K/m - 4\pi^2 f_a^2)) + \alpha_0 : \arctan(4\pi \lambda f_a / (K/m - 4\pi^2 f_a^2)) + \alpha_0 + \pi$ ,  $\alpha_0$  is an offset angle.

The fitting parameters obtained from each best fit to the experimental results are presented in table 1. The fitting PDF reports produced with *fitteia*'s *report* module can be found in the ESI (available from [stacks.iop.org/EJP/35/015017/mmedia](http://stacks.iop.org/EJP/35/015017/mmedia)).

When analysing the fitting parameters in table 1, it becomes obvious that the independent fits of  $\Delta\ell(m)$ ,  $A(t)$ ,  $A(f_a)$  and  $\alpha(f_a)$  give different results for the physical parameters of the system  $K$  and  $\lambda$ . The differences depend on the influence of the experimental conditions and experimental uncertainties of the experimental results. A discussion is required in order to conclude about the values of  $K$  and  $\lambda$  for the system.

The analysis of the experimental results in figure 1 can be improved if a detailed analysis of the experimental uncertainties is made and if the analysis of the experimental results is made by performing a fit that takes into account all data and a global least-squares minimum target.

In the case of the forced oscillations, it should be mentioned that the experimental uncertainty of both the amplitude of oscillation  $A(f_a)$  and the phase difference  $\alpha$  should be estimated taking into account the stability of the external force. Indeed, if the external frequency varies within the range  $f_a \pm \sigma_{f_a}$ , then

$$\sigma_k^{e2} \simeq \sigma_k^{y2} + \left( \frac{dy}{df_a} \right)_k^2 \sigma_{f_a}^2. \quad (13)$$

From equation (13), it is clear that  $\sigma_k^e \simeq \sigma_k^y$  unless  $\sigma_k^y \sim \sigma_{f_a} |dy/df_a|_k$ , which means that the uncertainty of  $f_a$  is relevant, particularly when  $|dy/df_a|_k$  is large.

The derivative  $dy/df_a$  must be calculated numerically [16]; otherwise, the use of the fitting model to compute the propagated uncertainty would introduce a bias in the minimization procedure. The *fitter* module of *fitteia* includes a calculator text box in the data section where users can introduce a sequence of operations involving the columns of the data table. Removing, adding and reordering of columns become quite easy, in addition to calculations involving columns. Therefore, starting from the columns in the data table (e.g. corresponding to ' $f_a$ ', ' $A$ ' and ' $\sigma^A$ '), the calculations associated with equation (13) can be done by executing the following *fitteia* instructions:

```
c1 c2 c3 0.01
c1 c2 c3 dc2/dc1 c4
c1 c2 sqrt(c3*c3+c4*c4*c5*c5)
```

Each line of the above sequence transforms the data table into another. The first line transforms the three-column table into a four-column table keeping columns 1–3 and adding a fourth column with a constant value '0.01' corresponding to  $\sigma_{f_a}$ . The second line in the sequence transforms the four-column table by moving column four to the fifth position and introducing in the fourth position the numerical derivative of column two with respect to column one. Finally, a three-column table is obtained with columns one and two equal to the original ones and putting in third position a column with the values of  $\sigma_k^e$  calculated according to equation (13). The effect of the correction on the experimental error bars can be observed in figures 4(c) and (d).

The least-squares minimization, with a global minimum target that takes into account all data and the different model equations, is fairly simple using *fitteia*. This type of problem is equivalent to a multidimensional fit. *fitteia*'s 'Expert' user mode presents an interface where a second independent variable can be introduced and used as a flag in nested conditional tests that help to apply the proper physical model to the corresponding experimental data. Naming the second independent variable 'flag', we can use the statement 'flag = 1' for  $\Delta\ell(m)$ , 'flag = 2' for  $A(t)$ , 'flag = 3' for  $A(f_a)$  and 'flag = 4' for  $\alpha(f_a)$ . In the data text box, the experimental results are introduced in blocks separated by reserved comment lines '# DATA flag = 1', etc.

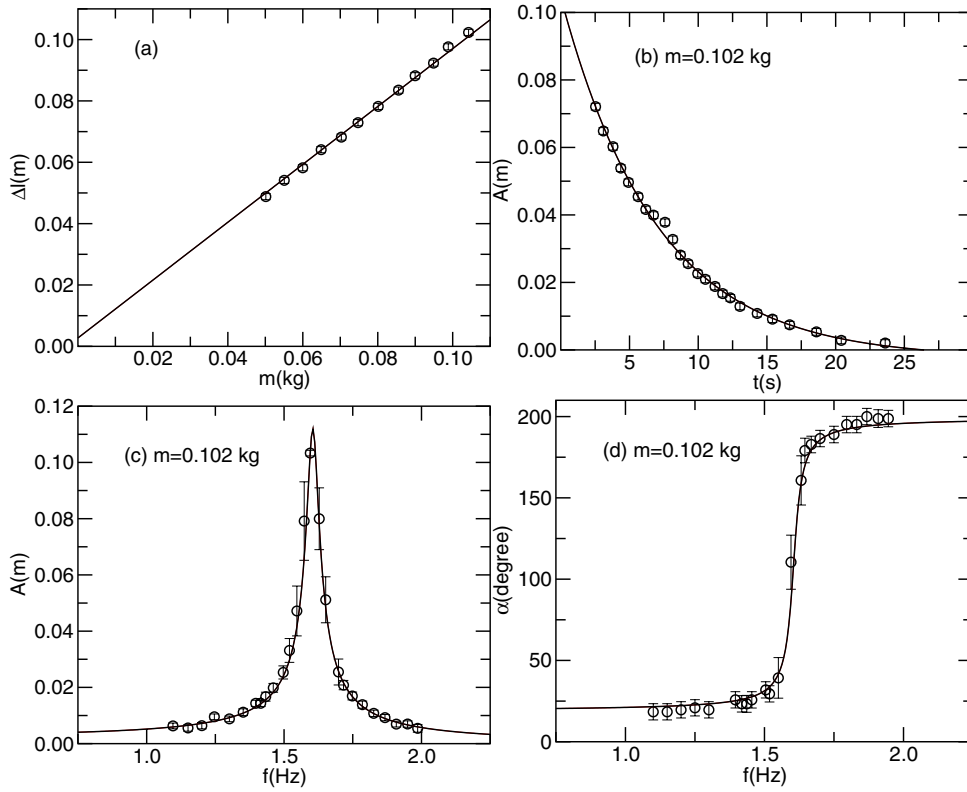
Defining  $x$  and  $y$  as the generic independent and dependent variables, respectively, the generic model equation can be written using the  $(?:)$  conditional operator in a nested sequence.

```
y=(flag==1) ? g/K*x+d0 :
(flag==2) ? (Zt0-Zinf)*exp(-l*x)+Zinf :
(flag==3) ? F0/m/sqrt(pow(K/m-4*pi*pi*x*x, 2.0)+16*pi*pi*l*l*x*x) :
(x>sqrt(K/m)/(2*pi)) ? (atan(2*l*2*pi*x/(K/m-4*pi*pi*x*x))+pi+a0)*180/pi :
(atan(2*l*2*pi*x/(K/m-4*pi*pi*x*x))+a0)*180/pi
```

In the case of 'flag = 4' an additional test is required to choose the proper expression on the calculus of  $\alpha(f_a)$  according to the condition  $\omega > \omega_0$ .  $\exp(x) \equiv e^x$ ,  $\text{pow}(x, p) \equiv x^p$ ,  $\text{sqrt}(x) \equiv \sqrt{x}$  and  $\text{atan}(x) \equiv \arctan(x)$ .

In this way, the minimization of equation (12) takes into account all experimental results and selectively considers each model equation according to the corresponding data set.

$$\chi^2(K, \lambda, d_0, Z_{t_0}, Z_{t_\infty}, F_0, a_0) = \sum_{k=1}^{N_1} \frac{(\Delta\ell_k^e - \Delta\ell_k^t(K, d_0, m_k))^2}{\sigma_k^{e2}} + \sum_{k=1}^{N_2} \frac{(A_k^e - A_k^t(\lambda, Z_{t_0}, Z_{t_\infty}, t_k))^2}{\sigma_k^{e2}} \\ + \sum_{k=1}^{N_3} \frac{(A_k^e - A_k^t(K, \lambda, F_0, f_{a_k}))^2}{\sigma_k^{e2}} + \sum_{k=1}^{N_4} \frac{(\alpha_k^e - \alpha_k^t(K, \lambda, F_0, f_{a_k}, a_0))^2}{\sigma_k^{e2}}. \quad (14)$$



**Figure 4.** Experimental results obtained for a spring–mass system [10], taking into account the uncertainties of both  $x$  and  $y$  in the case of plots (c) and (d). (a) The spring’s length as a function of the suspended mass; (b) amplitude of oscillation measured at time  $nT$ ,  $n = 0, 1, 2, 3, \dots$ , where  $T$  is the oscillation period; (c) amplitude of oscillation measured as a function of frequency of the harmonic applied force; (d) phase difference between the mass motion’s amplitude and the applied force as a function of oscillation frequency of the force.

As it happened that  $K$  and  $\lambda$  are present in different model equations, the global minimization searches for the values for these parameters that minimize  $\chi^2$  and consequently minimize all terms in equation (14) in a consistent way.

*fitteia* presents a simple interface that helps users to prepare the figures with the plots of the fitting curves according to the details of each data set.

In figure 4 are shown the best fits obtained using the above described global minimization procedure (additional information can be found in the ESI, available from [stacks.iop.org/EJP/35/015017/mmedia](http://stacks.iop.org/EJP/35/015017/mmedia)). As can be observed in figures 4(c) and (d), the consequence of propagating the uncertainty in the frequency  $f_a$  to variables  $A(f_a)$  and  $\phi(f_a)$  is to obtain larger error bars for the experimental points where  $dy/dx$  is larger.

The values of the fitting parameters for this fit are presented in column ‘all’ in table 1. A discussion about the advantages of both minimization approaches can be made but the important point here is to present the two strategies.

#### 4.2. X-ray diffraction

The data analysis of the experimental results of the x-ray diffraction experimental presented in figure 2 presents a different type of challenge with respect to the previous example. First, the

**Table 2.** Fitting parameters (as presented in the ESI fit report generated by *fitteia*, available from [stacks.iop.org/EJP/35/015017/mmedia](http://stacks.iop.org/EJP/35/015017/mmedia)) obtained from the fit of model equation (7) to the experimental results of figure 2.  $\chi^2_t = 8.782\,04$ .

$a = 153.21 \pm 5.4086$	$a2 = 200 \pm 29.723$
$a0 = 252.52 \pm 15.052$	$b2 = 4 \pm 0.12931$
$b0 = 1 \pm 0.014\,206$	$q2 = 10.419 \pm 0.12\,791$
$q0 = 2.4294 \pm 0.040\,112$	$a3 = 300 \pm 9.6683$
$a1 = 93.836 \pm 7.8405$	$b3 = 2.3904 \pm 0.142\,58$
$b1 = 1.7183 \pm 0.294\,67$	$q3 = 14.164 \pm 0.0804\,98$
$q1 = 4.7695 \pm 0.148\,36$	

data set has 685 points, more than eight times the number of points of the previous example; second, we know in advance that the model fit is composed of a sum of several Gaussian curves and besides being necessary to obtain the curve that represents the sum there are clear advantages in being able to see each contribution separately.

The number of experimental points is not a limitation as far as the computation time remains acceptable, but even for a moderate number of points the fit of a nonlinear function with ten or more independent fitting parameters can be very CPU demanding. Therefore, a good strategy to analyse a large experimental data set is to choose a subset of the experimental points larger than the set of fitting parameters in order to obtain a first fit and then use the obtained fitting parameters as starting guess values for the final fit with all data. *fitteia*'s fitter module helps to achieve this by providing two conditional pre-processing commands, '# fitif (condition), (sampling step)' and '# plotif (condition), (sampling step)', that can be introduced in the DATA text box as reserved comment lines. The first command is considered when fitting, the second command is considered only when plotting the data and the fitting curves using the model parameter values (e.g. simulating the dependent variable as a function of the independent variable using the model equation). '# fitif 1, 10' can be used to select a subset of the experimental data where one point every ten points is considered for the fit. The condition here is always '1' so the test is applied to all data points.

*fitteia*'s fitter module also helps users to generate curves that can be plotted together with the curve that corresponds to the model equation. If the  $q$  and  $y$  are the independent and dependent variables the scattered x-ray intensity can be modelled by equation (7) with four Gaussian contributions and an offset constant.

$$y = a + a0*\exp(-\text{pow}((q-q0)/b0,2.0)) + a1*\exp(-\text{pow}((q-q1)/b1,2.0)) + a2*\exp(-\text{pow}((q-q2)/b2,2.0)) + a3*\exp(-\text{pow}((q-q3)/b3,2.0))$$

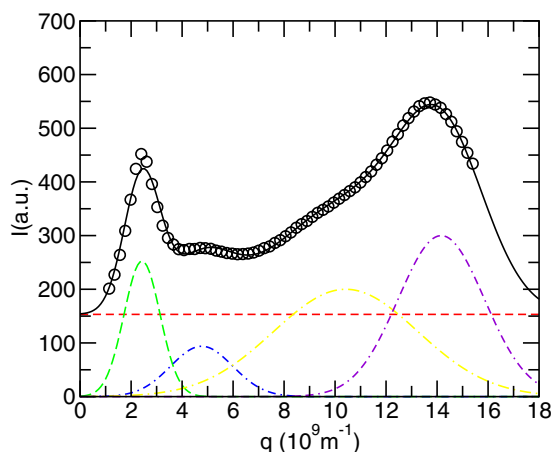
If the plus symbol '+' is replaced by '\+', in the above expression, then, after compilation, the *fitteia*'s fitter interface is modified and allows for the selection of the line type, color and label of the curves associated with the terms added with each '\+'. In the following case

$$y = a \setminus + a0*\exp(-\text{pow}((q-q0)/b0,2.0)) \setminus + a1*\exp(-\text{pow}((q-q1)/b1,2.0)) \setminus + a2*\exp(-\text{pow}((q-q2)/b2,2.0)) \setminus + a3*\exp(-\text{pow}((q-q3)/b3,2.0))$$

each term will be represented by its corresponding plot line according to the values of  $a_k$ ,  $b_k$  and  $q_k$ .

In figure 5 is presented the best fit obtained using both the pre-processing command '# fitif 1, 10' and the contributions corresponding to all the terms in the model equation.

There is a clear advantage in observing separately the contributions to total scattered intensity since, in addition to the best-fitting curves, simulation plots can put into evidence the effects of the model parameters separately. In table 2 are presented the values of the model



**Figure 5.** X-ray diffraction results fitted with model equation (7). The fit was done considering a subset of the experimental data (as an example of *fitteia*'s features), as explained in the text.

parameters corresponding to the best fit. They are presented as they are obtained from the *fitteia* report without taking into account the coherent correspondence between the significant digits in both values and uncertainties.

#### 4.3. NMR relaxation

The analysis of the NMR data of figure 3 using model equation (8) with contributions (10) and (11) presents in addition to the technical problems referred to previously an additional technical challenge. In fact, the contribution of equation (11) must be obtained numerically and the integral has to be calculated every time the function is called. In addition, some of the functions used are too cumbersome to be introduced using a simple line of text. One solution for these problems is to ask the *fitteia* system's manager to include the necessary functions in the user functions library. Another solution is to use *fitteia* with an increased level of privilege. In the latter, users are allowed to program their own functions library and freely program the necessary code for their needs.

In the case of equation (8), all functions are already available in the system. The equation to be fitted to the spin-lattice relaxation data,  $T_1^{-1}$ , taking into account both its dependence on the temperature,  $T$ , and on the Larmor frequency,  $f$ , can be written taking advantage of the previous examples. In *fitteia*'s expert mode, it is possible to define a model that considers different independent variables (in the case of the spring-mass system three independent variables were considered). For the NMR data we can consider  $z \equiv T_1^{-1}(T, f)$  and define  $x$  and  $y$  as independent variables. The meaning of  $x$  and  $y$  is either frequency or temperature depending on the context. In any case  $x$  refers to the first column and  $y$  takes the value assigned in the data section using the statement format '#DATA y=...'. The experimental data is introduced in two DATA blocks using the following arrangement:

```
# DATA y=100e6
333      2.08333      0.104167
329      2.1978      0.10989
.         .           .
.         .           .
```

```
# DATA y=313
      1e+08      2.65957      0.132978
      1.79991e+07      7.42497      0.371249
      .          .          .
      .          .          .
```

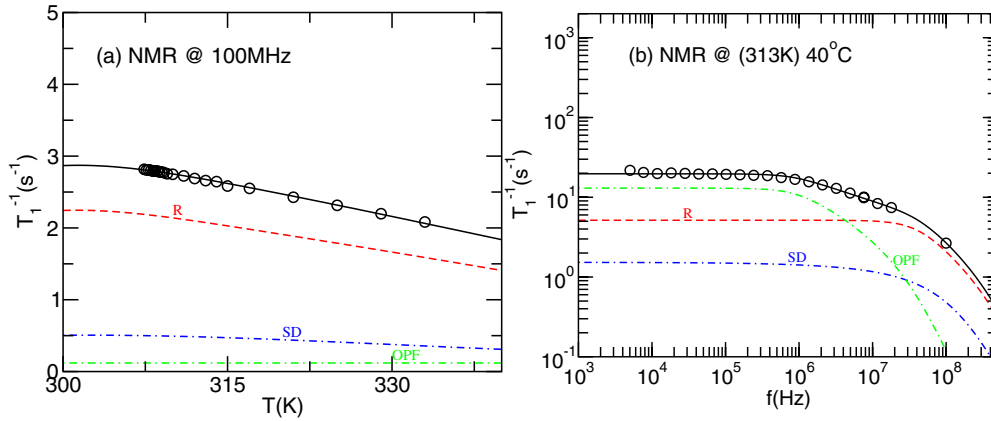
The frequency is always larger than the temperature and is never lower than 1 kHz. It is clear that when  $y > 500$ ,  $y \equiv \text{temperature}$  and  $x$  is the frequency and when  $y < 500$ ,  $y \equiv \text{frequency}$  and  $x$  is the temperature. In this way additional DATA can be introduced for different temperatures and different frequency dependences (see Sebastião *et al* [17]). Assuming that  $(T_1^{-1})_R$  is the sum of two ‘BPP’ contributions ( $(T_1^{-1})_R \equiv \text{BPP}(\tau_S) + \text{BPP}(\tau_L)$ ),  $(T_1^{-1})_{SD}$  is calculated using ‘Torrey1’ function ( $(T_1^{-1})_{SD} \equiv \text{Torrey1}$ ), and  $(T_1^{-1})_{OPF} \equiv \text{OPF}$  (additional information is available in the ESI, available from [stacks.iop.org/EJP/35/015017/mmedia](http://stacks.iop.org/EJP/35/015017/mmedia))

```
z=(
  (y>500.0) ? BPP(y,Arot,tauL*exp(EL/8.31*(1.0/x-1.0/Tref))) :
              BPP(x,Arot,tauL*exp(EL/8.31*(1.0/y-1.0/Tref)))
) + (
  (y>500.0) ? BPP(y,Arot,tauS*exp(ES/8.31*(1.0/x-1.0/Tref))) :
              BPP(x,Arot,tauS*exp(ES/8.31*(1.0/y-1.0/Tref)))
)
\+
(
  (y>500.0) ?
  Torrey1(y,d,r,n,r*r*1e-20/(6*Dref*exp(-ED/8.31*(1.0/x-1.0/Tref)))) :
  Torrey1(x,d,r,n,r*r*1e-20/(6*Dref*exp(-ED/8.31*(1.0/y-1.0/Tref))))
)
\+
(
  (y>500.0) ? OPF(y, Aopf, f0, fcm, fcM, np) :
              OPF(x, Aopf, f0, fcm, fcM, np)
)
```

A close analysis of the above expression shows that, according to the number of ‘\+’ symbols, three contributing curves will be plotted separately. The first curve will correspond to the sum of two ‘BPP’ functions, the second will be ‘Torrey1’ and ‘OPF’ the third. This is a second example of the independent plot of the model contributions presented previously for the x-ray fit. In addition, it can be observed that each contribution includes a conditional test ‘ $y > 500$ ’ that changes the meaning of  $x$  and  $y$ . ‘ $\text{BPP}(f, A, \tau)$ ’ is a function of frequency  $f$ , a pre-factor  $A$ , and a characteristic time  $\tau(T)$ . Since  $\tau(T)$  depends on the temperature  $T$ , ‘BPP’ depends on a frequency and a temperature. According to the data coding used  $x$  and  $y$  alternate meanings and if  $y > 500$  it is for sure a frequency, as the experimental results were obtained for temperatures below 500 K.

The model parameters obtained for the best fit are presented in table 3 and the model-fitting curves are presented in figure 6.

The plots presented in figures 1–6 were produced using the *fitter* and *plotter* interface modules available on <http://fitteia.org> [18]. In the ESI (available from [stacks.iop.org/EJP/35/015017/mmedia](http://stacks.iop.org/EJP/35/015017/mmedia)) additional information can be found concerning the use of *fitteia*’s web service.



**Figure 6.** Model fit to the experimental  $^1\text{H}$  spin-lattice relaxation rates: (a) fitting curves plotted as a function of temperature, for the fixed Larmor resonance frequency of 100 MHz; (b) fitting curves plotted as a function of the Larmor frequency, for the fixed temperature  $T = 40^\circ\text{C}$  as explained in the text.

**Table 3.** Fitting parameters (as presented in the ESI fit report generated by *fitteia*, available from [stacks.iop.org/EJP/35/015017/mmedia](http://stacks.iop.org/EJP/35/015017/mmedia)) obtained from the fit of model equation (8) to the experimental results as explained in the text.  $\chi^2[313\text{ K}] = 8.819\,02$ ,  $\chi^2[100\text{ MHz}] = 0.184\,23$ ,  $\chi^2_i = 9.003\,25$ .

$A_{\text{rot}} = 5.7688 \times 10^{+08} \pm 8.45 \times 10^{+06}$	$D_{\text{ref}} = 5.44 \times 10^{-11}$ (fixed)
$\tau_{\text{auS}} = 1.45 \times 10^{-09}$ (fixed)	$ED = 32\,800$ (fixed)
$ES = 294\,12$ (fixed)	$T_{\text{ref}} = 313$ (fixed)
$\tau_{\text{auL}} = 3.36 \times 10^{-10}$ (fixed)	$A_{\text{opf}} = 17438 \pm 1017.9$
$EL = 468\,28 \pm 6860.6$	$f_0 = 1 \times 10^{+05}$ (fixed)
$d = 5$ (fixed)	$f_{\text{cm}} = 4.25 \times 10^{+07}$ (fixed)
$n = 4.59 \times 10^{+22}$ (fixed)	$f_{\text{cm}} = 6.8381 \times 10^{+05} \pm 998\,54$
$r = 4$ (fixed)	$np = 10$ (fixed)

## 5. Conclusions

It is shown that when analysing experimental results in terms of theoretical models the concept of best fit is not only related to the numerical quality of the model fit but also connected with the physical coherence between the model parameters obtained. This is particularly true in the case of experimental observables that depend on different experimental variables known prior to the experiment and that can be used to better describe the studied system. Multidimensional fits require not only additional computation skills but also a method to easily understand the details of the minimization process. A web-based interface to a software package is presented that allows users to perform online model fits, data plots and report writing using models with different degrees of complexity. The details of the methods used to fit models to experimental data with one, two,  $\dots$ ,  $n$  dimensions were presented here. The methods used can be implemented in a relatively simple way using the interface but they can also be used to develop solutions using other numerical software packages. One important difference between the presented web-solution for the model fitting with respect to other solutions is the possibility of sharing working folders with other users involved in the project, no matter where they are physically or what type of computer system they use. The efficiency thus achieved is worth

noticing. Both graduate and post-graduate students find this solution quite useful during the learning stage, where they obtain the basic skills to independently perform model analysis and fitting to experimental data. Later, former students find the system also useful to perform more complex data analysis during their MSc and/or PhD research work.

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# The art of model fitting to experimental results (Supplementary Information)

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## 1. Notes on the use of *fitteia* interfaces

*fitteia* (Fitting Environment Interfaces for All) provides a set of graphic user interfaces accessible through the internet using any web browser (e.g. IE, Opera, Firefox, Mozilla, Safari, Chrome). *fitteia* is presently available on the site <http://fitteia.org>.

*fitteia* platform allows for:

- 1 The graphical representation of experimental results and/or mathematical functions;
- 2 The numerical fit of arbitrary user defined linear and/or non-linear functions dependent on M fitting parameters and n-experimental variables to experimental data
- 3 The data treatment using an integrated programmable calculator
- 4 The use of a integrated Matlab-like calculator
- 5 The writing of professional-quality reports using LaTeX
- 6 The production of documents in PDF, PNG, JPG, EPS formats using the fit results
- 7 The user registration through a email/password security process to assure the user's privacy
- 8 The sharing of working areas with other select users
- 9 The sharing of user defined fitting functions/fitting models, documents/projects with other select users
- 10 The possibility to use three different expertise levels (e.g. Basic, Advanced, Expert)
- 11 The saving/recovery of important results
- 12 The download/upload of the configuration/setup files
- 13 The assignment of two levels of user privileges

### 1.1. Registration

The *fitteia* login webpage (<http://fitteia.org>) presents some basic information about the service and presents a "login" link that users must follow to login the system. New users must first register accessing the "sign up" page. A valid email address is required to "sign up" *fitteia*. The user receives an email with a new password after answering a security question. This password is required to proceed to the second step of the registration process. The user is invited to change the password and to introduce his name in the system.

Registered users may reset their passwords following the same procedure.

### 1.2. Logging in

Logging in the system requires typing the email used for the registration and the password. When logging in for the first time the user is directed to a webpage as presented in the print screen of Fig. 1. Some links will conduct to actions that are more

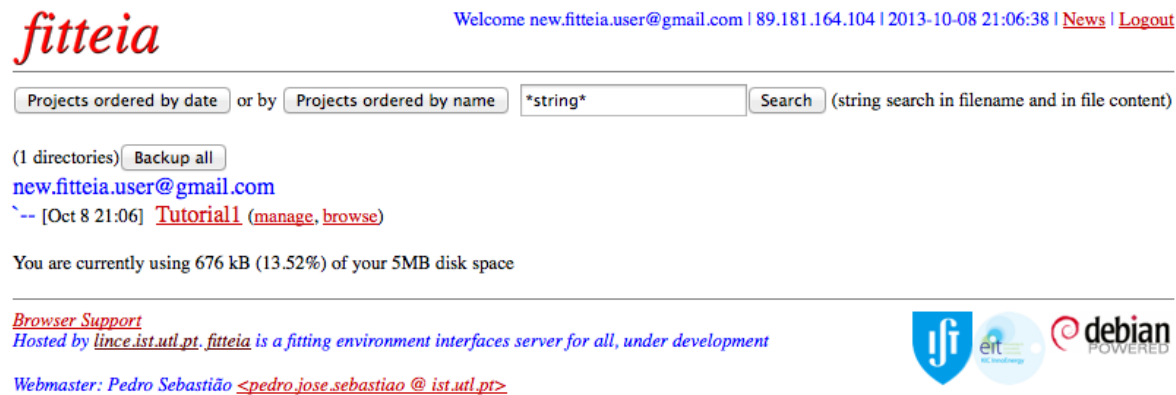


Figure 1. *fitteia* webpage after logging in.

or less self-explaining. The user should check the information concerning the "Browser Support".

"**Tutorial1**" is the name of a default folder that contains some self-explaining fit and plot examples.

"**browser**" allows for a vista to the users home folder tree using the web browser.

"**manage**" links to a webpage where the user can delete files or include emails of other users with whom the folder will be shared provided that the folder's name is not a duplicate of a pre-existing folder of the guest user.

"Tutorial1" links to *fitteia*'s *fitter* module that opens with some pre-recorded data loaded, as partially presented in Fig. 2.

### 1.3. The *fitter* module

#### 1.3.1. Header



Figure 2. *fitteia*'s *fitter* webpage header.

Besides the self-evident links the following links deserve some additional comments.

"**News**" links to a page where new *fitteia* features are presented after being included in the system.

"**Basic**", "**Advance**", and "**Expert**" link to *fitter* module interface with different layouts according to the level of expertise required by the system to tackle the user's data analysis problem.

**"Calculator"** links to a programable calculator that receives the fitting parameters of the last fit performed and helps the user to perform additional calculus.

**"Plotter"** links to *fitteia's* *plotter* module.

**Report Editor** links to a web form filled with the last fit results and can be used to prepare L<sup>A</sup>T<sub>E</sub>X reports

**"Upload"** links to a upload web form that allows the user to upload a file to the system. usually a previous downloaded *fitter* or *plotter* environment file.

**"MyFits"** links to the list of user folders (included folder shared with him).

In Fig. 2 a pair of text boxes can be found between buttons "Overwrite" and "Archive". The text box filled with "Tutorial1" shows the folder's name where the user is working. Additional folders can be created by changing this name. Next to it a text box filled with "file\_name" shows the environment name given to file where all the web page information will be saved.

**"Overwrite"** saves the web form in a file named "file\_name.sav" in folder "Tutorial1"  
This file can be overwritten repeatedly.

**"Archive"** saves the web form in a file named "file\_name-YYYY-MM-DD\_hh:mm:ss.sav" in folder "Tutorial1". This file can not be overwritten and can only be deleted in "MyFits->Folder\_name->manage".

On the bottom right side of Fig. 2 it is possible to see a button to select a previous saved environment fit data file to "Recover" or "Download". The list of files can be filtered using the "list" button.

### 1.3.2. Data, Plot Settings and Fitting Function

The core of the *fitter* module webpage is composed by the sections with following characteristics:

**"1°-Data"** The main text box allows the user to type (or copy and paste) values of  $x$ ,  $y$ , and  $\epsilon_y$ , where  $x$  is the independent variable,  $y$  is the dependent variable, and  $\epsilon_y$  is expected to be the uncertainty of  $y$ . The numbers must be written in three columns and separated by white spaces. The values  $x$ ,  $y$ , and  $\epsilon_y$  form column vectors, named "c1", "c2", ..., "cn", where 1,...,n is the order of the column

Below the main "Data" text box a second box allows users to perform arithmetic operations with the column vectors of the "Data" text box. The syntax for the arithmetic calculations is that of PERL but it is quite simple to write expressions to perform basic calculations. Both "^" and "\*\*" can be used in power expressions (e.g.  $c1^p$  or  $c1^{**p}$ ).

**abs(c1)** – absolute values of column vector c1;

**sqrt(c1)** – square root function of column vector c1;

**exp(c1)** – exponential function,  $e^{c1}$ ;

**sin(c1), cos(c1), tan(c1), asin(c1), acos(c1), atan(c1)** – trigonometric functions of column vector c1;

**sinh(c1), cosh(c1), tanh(c1), asinh(c1), acosh(c1), atanh(c1)** – hyperbolic functions of column vector c1;

Button "Calculate" when be used evaluates these expressions in sequence and generates a new Data table.

Button "Data Plot" generates a new layout of the *fitter* webpage where a graph with a data plot is presented according to the "Plot Parameters" introduced.

**"2°-Plot Parameters"** Axis names, limits, tick names, etc.. can be defined in this section. Both  $x$  and  $y$  autoscaling is possible.

**"3°-Function and Parameters"** The function to be fitted to the experimental results must be written in language C. The names of the independent and dependent variables must be introduced and they will have the corresponding values of the first and second columns of the "Data" table when performing the least-squares' minimization. For the large majority of cases the only language C specific mathematical functions that users must be aware of are:

$fabs(x)$  – absolute value of a floating point number  $x$ ;

$pow(x, y)$  –  $x^y$ ;

$sqrt(x)$  – square root function,  $\sqrt{x}$ ;

$exp(x)$  – exponential function,  $e^x$ ;

$sin(x)$ ,  $cos(x)$ ,  $tan(x)$ ,  $asin(x)$ ,  $acos(x)$ ,  $atan(x)$  – trigonometric functions;

$sinh(x)$ ,  $cosh(x)$ ,  $tanh(x)$ ,  $asinh(x)$ ,  $acosh(x)$ ,  $atanh(x)$  – hyperbolic functions;

For conditional calculations the syntax "(condition) ? if\_true\_this : if\_false\_this" can be used. When calculating ratios between integers, like in the case of "1/2" it is required to write "1.0/2.0" to obtain the expected value 0.5 as the result, otherwise an integer division is performed and the result is 0.

If the fitting function is composed of different terms, *fitteia's fitter* specific syntax character "\+" can be used to allow for the independent plotting of each one of the terms of the fitting function. The "Plot Parameters" section layout is changed according to the number of terms of the fitting function to allow for the setting of lines types, colors and labels of each curve.

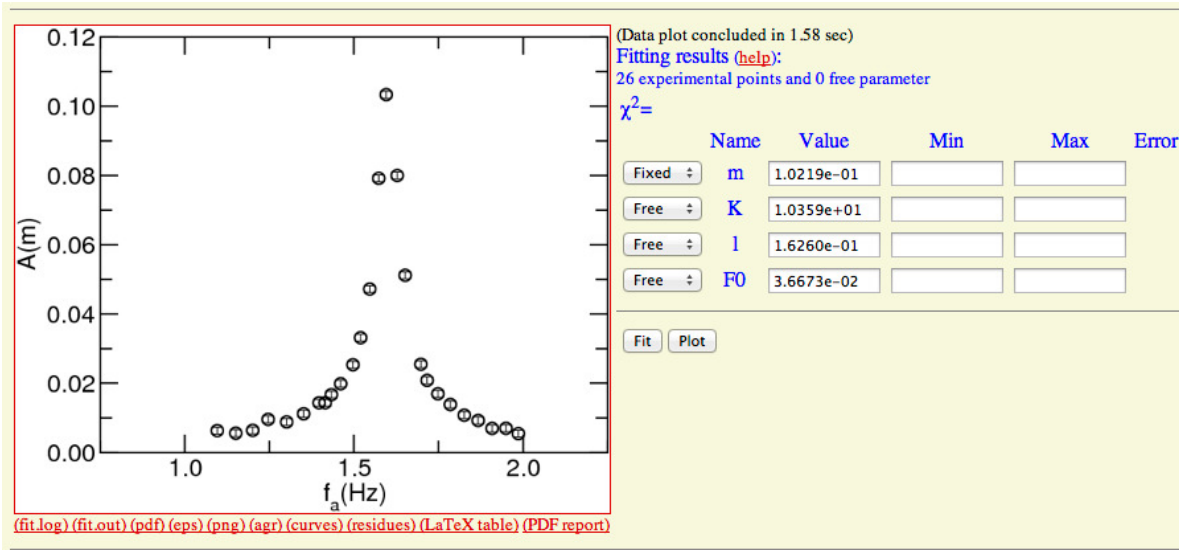
Button "Compile" will compile the function and link it with the *fitteia's fitter* kernel. A link to a log file might help to debug the function in case compilation errors occur. The *fitter* webpage layout changes in the case of a successful compilation and below the page header a graph and the function parameters' table are shown next to each other.

In the Data tex box and in the text boxes containing the plot settings addition arithmetic expressions can be included and will be evaluated when the web form is submitted to the *fitteia* server.

### 1.3.3. Recovering a previous fit

After selecting the name and recovering the fit the *fitter* webpage layout shows the graph with the data and the function parameters' table as illustrated in Fig. 3 for the

fit file "Basic-EJP-Resonance-const-err-2013-08-09\_19-13-54".



**Figure 3.** *fitteia*'s *fitter* graph and function parameters' table after "Recover" a previously saved fit.

If the the user has still storage space in his account buttons "Fit" and "Plot" are seen below the function parameters' table. They allow for two different actions:

**"Fit"** starts the fitting procedure using the values of the fitting parameters in the table as initial values. If a fitting parameter status is "Free" the minimization procedure tries to find the minimum of  $\chi^2$  in the parameter's space defined by the user. If "Min" and "Max" have finite values for a given parameter the minimization is restricted to that particular region of the parameter's space, otherwise the region extends  $[-\infty; \infty]$ . The graph is updated with both data points and the fitting curves calculated using the fitting output values.

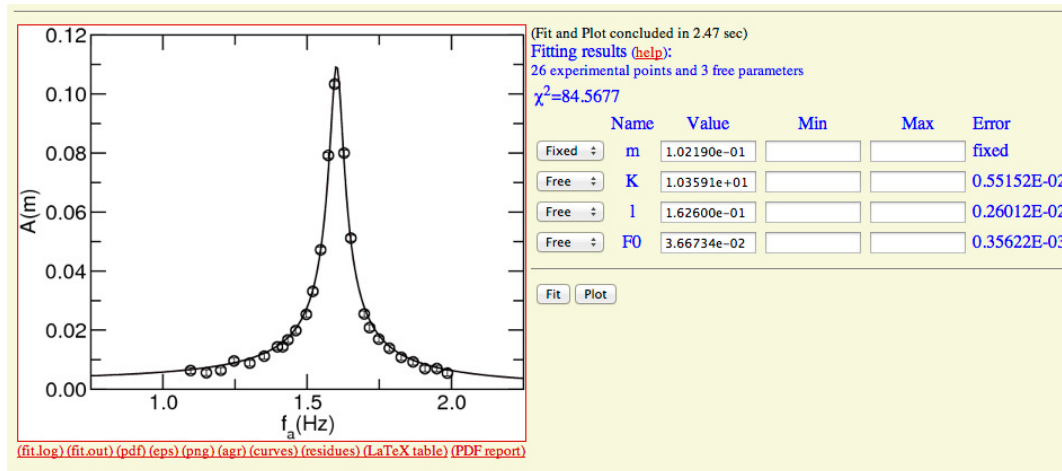
**"Plot"** generates a graph with the data points and the curves calculated using the values of the parameters without performing a fitting procedure. It can be used to generate curves calculated with different parameters.

When the fitting ends an additional column is added to the function parameters' table with either the error estimates of the "Free" parameters, or the word "Fixed" stating the status of that parameter during the minimization procedure, as illustrated in Fig. 4

Below the graph several links become handy when exporting the graph in different file formats, getting an automatic PDF report of the fit, obtaining a table with the values of the theoretical curves, or a  $\text{\LaTeX}$  table with the fitting results.

"fit.log" deserves a comment as it contains a log report of the MINUIT actions during the fitting procedure plus some information from the *fitteia*'s *fitter* module.

”PDF Report” links to the ”Report Editor” previously referred and returns a PDF report that contains the graph and fitting results obtained (check below some examples).



**Figure 4.** *fitteia*’s *fitter* graph and function parameters’ table after a fitting procedure.

#### 1.4. Using 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 *Calculator* starts with a list of examples that can be studied as a tutorial text. In Fig. 5 part of *Calculator* webpage is illustrated after opening the ”example” operations’ set previously saved. The fitting parameters obtained in the fit of Fig. 4 were loaded and simple calculations using those parameters are presented.

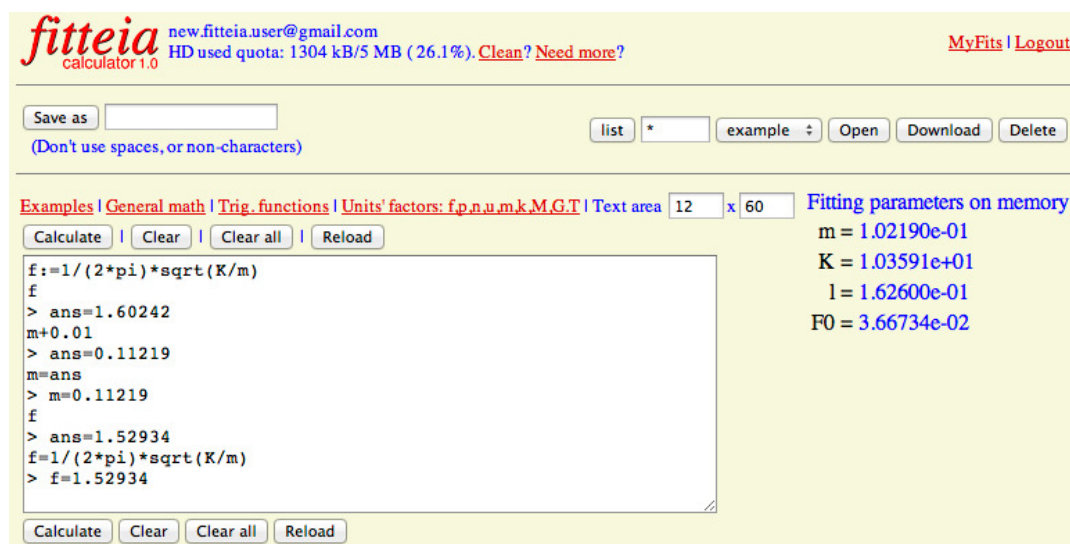
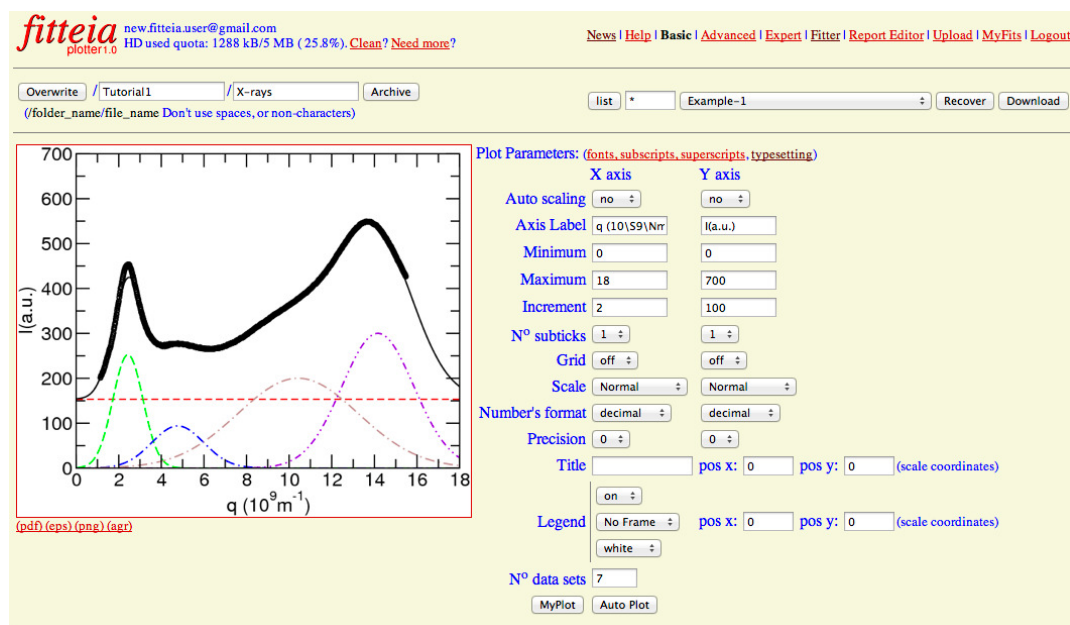
#### 1.5. Plotter module

Producing more elaborated graphs can be achieved using *fitteia*’s *Plotter* module. When opened it presents a basic layout. After ”recovering” a previous save example its layout is modified as illustrated in Fig. 6.

The particular example illustrated in Fig. 6 presents 7 data sets where one data set is shown with black circles and the reaming data sets are represented by lines. The settings of each data set are of the type shown in Fig. 7 for Data set 1.

#### 1.6. Advanced and Expert modes

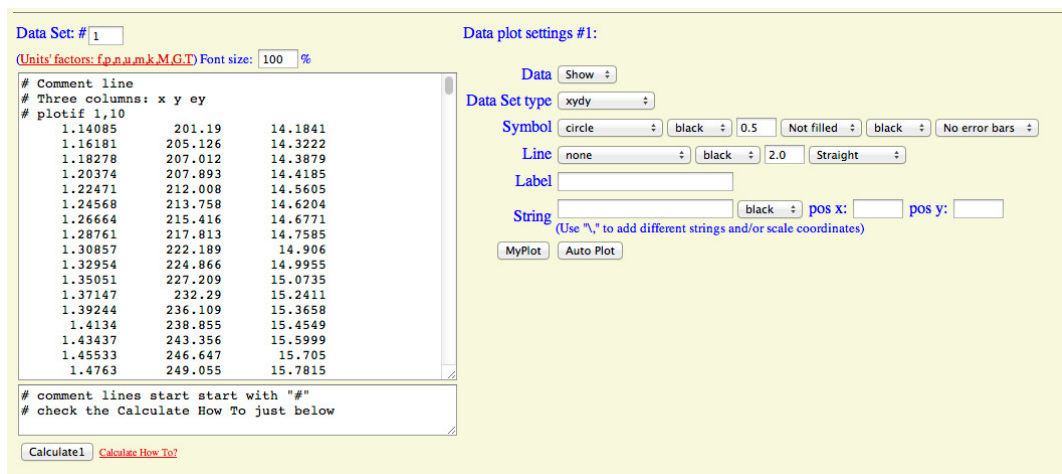
Using the notes presented above for the *fitteia*’s Basic user mode the behavior of the *fitter* module for the remaining user modes can be followed using the examples illustrated in the ”Tutorial1” folder.

Figure 5. *fitteia*'s Calculator layout example.Figure 6. *fitteia*'s Plotter layout example.

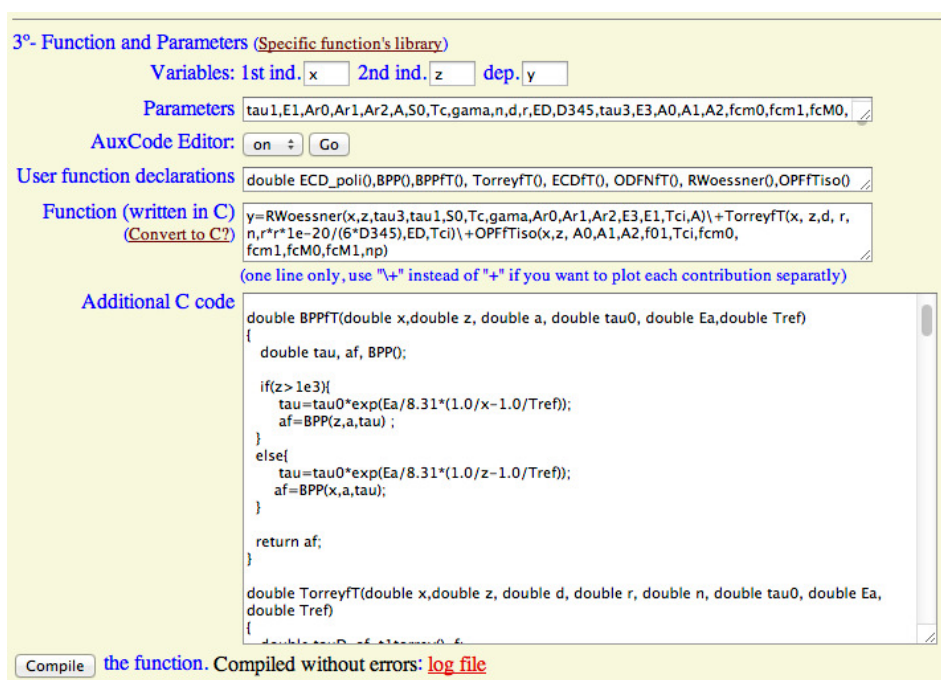
### 1.7. Use of fitteia with increased privileges

For advanced model fitting the basic functions writing is, some times, not enough as 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 additional user's C code. In Fig. 7 is presented one example of the *fitter* web age layout of section "Function and



Figure 7. *fitteia*'s Plotter layout example of plot setting for one data set.

Parameters".

Figure 8. *fitteia*'s fitter layout example of section "Function and Parameters" for a privileged user.

## 2. Notes on the NMR relaxation models

### 2.1. Translational self-diffusion

The relaxation model used to fit spin-lattice relaxation results of a liquid crystal compound is in many cases that developed by H. C. Torrey [1] and can be expressed as

$$(T_1^{-1})_{SD} = \frac{9}{8} \gamma^4 \hbar^2 \left( \frac{\mu_0}{4\pi} \right)^2 \frac{n\tau_D}{d^3} [\mathcal{T}(\alpha, \omega\tau_D) + 4\mathcal{T}(\alpha, 2\omega\tau_D)], \quad (1)$$

with  $\mathcal{T}(\alpha, x)$  given by

$$\begin{aligned} \mathcal{T}(\alpha, x) = & \frac{32\pi\alpha}{15x^2} \left[ \left( u_+ \left( 1 + \frac{1}{u_-^2 + u_+^2} \right) + 2 \right) e^{-2u_+} \cos u_- \right. \\ & \left. + u_+ \left( 1 - \frac{1}{u_-^2 + u_+^2} \right) + u_- \left( 1 - \frac{1}{u_-^2 + u_+^2} \right) e^{-2u_+} \sin 2u_- \right] \end{aligned} \quad (2)$$

where

$$u_{\pm} = \frac{1}{2} \left( \frac{q(1 \pm q)}{\alpha} \right)^{1/2} \quad (3)$$

$$q = \frac{x}{(4 + x^2)^{1/2}} \quad (4)$$

and  $\alpha = \langle r^2 \rangle / (12d^2)$ . In this model  $n$  is the density of spins,  $d$  is distance between neighborhood molecules,  $\langle r^2 \rangle$  is the mean square jump distance, and  $\tau_D$  is the average time between molecular translational jumps.

### 2.2. Order parameter fluctuations

In the isotropic phase of a liquid crystal compound, close to the phase transition into the nematic phase, fluctuations of the order parameters are some times observed [2] when analyzing spin-lattice relaxation results. The relaxation mechanism can be expressed by

$$(T_1^{-1})_{OPF} = \frac{A_{OPF}}{\omega^{1/2}} \int_{\omega_{Cl}/\omega}^{\omega_{Ch}/\omega} \frac{\sqrt{x}}{1 + (x + \omega_0/\omega)^2} dx \quad (5)$$

with  $A_{OF} = (9/8)(\mu_0/4\pi)^2 \gamma^4 \hbar^2 k_B T \eta_{iso}^{1/2} / (4\pi^2 K_{iso}^{3/2} a_{eff}^6)$ .  $\omega_{Cl}$  and  $\omega_{Ch}$  are the low and high cut-off frequencies that correspond to the largest and smallest wave length modes, respectively.  $\omega_0 \sim K_{iso}/\eta\xi^2$  depends on the coherence length associated with the size of nematic cybothatic domains in the isotropic phase and acts also as a cut-off frequency [2].

## References

- [1] H. C. Torrey. Nuclear spin relaxation by translational diffusion. *Physical Review*, 92(4):962–969, 1953.
- [2] R.Y. Dong. *Nuclear magnetic resonance of liquid crystals*. Springer New York, 1997.

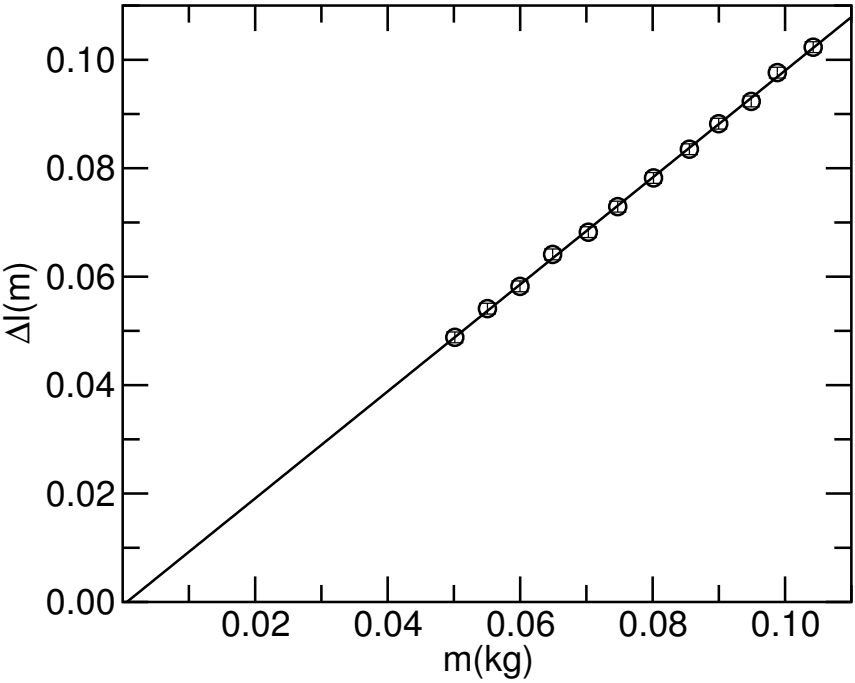
**3. *fitteia*'s *fitter* reports corresponding to the examples presented in the paper**

*fitteia* Report  
(internet based fitter service)

Subject	Tutorial1, Basic-EJP-Elastic-Constant
Date	Friday 9 <sup>th</sup> August, 2013, 20:30
Affiliation	pj.sebastiao@gmail.com 77.54.10.14
Abstract	Fit report produced with the fit results of function: $y = g/K \cdot x + d0$ to the 12 experimental points, considering 2 free parameters.

$g = 9.8$ (fixed)	$d0 = -0.00062389 \pm 0.001344$
$K = 9.9356 \pm 0.17085$	

$\chi^2[1] = 2.22217 \qquad \chi^2_t = 2.22217$



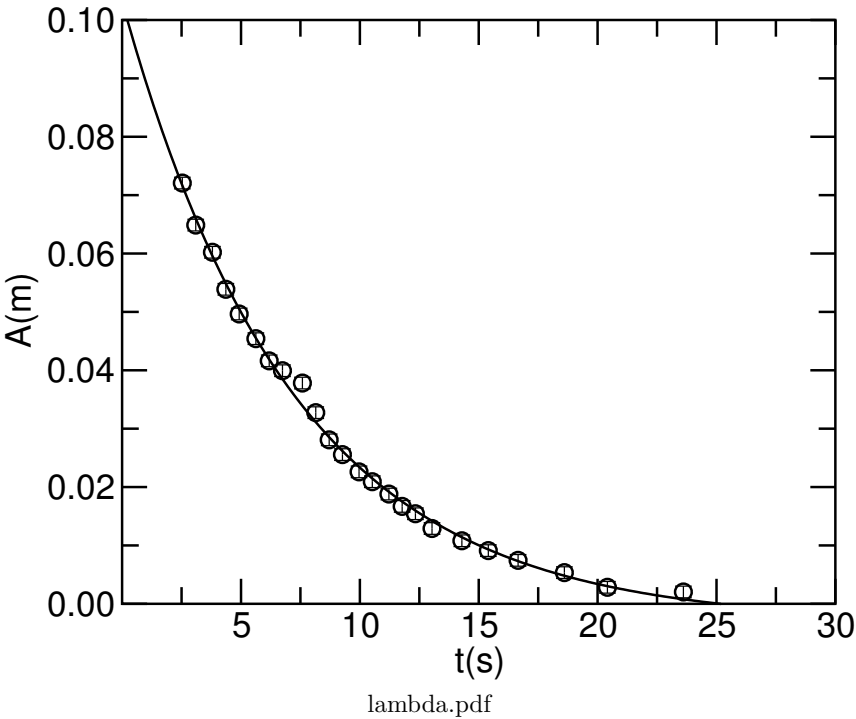
recta.pdf

*fitteia* Report  
(internet based fitter service)

Subject	Tutorial1, Basic-EJP-Damped-oscillator
Date	Friday 9 <sup>th</sup> August, 2013, 20:30
Affiliation	pj.sebastiao@gmail.com 77.54.10.14
Abstract	Fit report produced with the fit results of function: $Z=(Zt0-Zinf)*exp(-l*t) + Zinf$ to the 24 experimental points, considering 3 free parameters.

$l = 0.13878 \pm 0.0044065$	$Zinf = -0.0032395 \pm 0.00093744$
$Zt0 = 0.10319 \pm 0.0015956$	

$\chi^2[1] = 30.1509$	$\chi^2_t = 30.1509$
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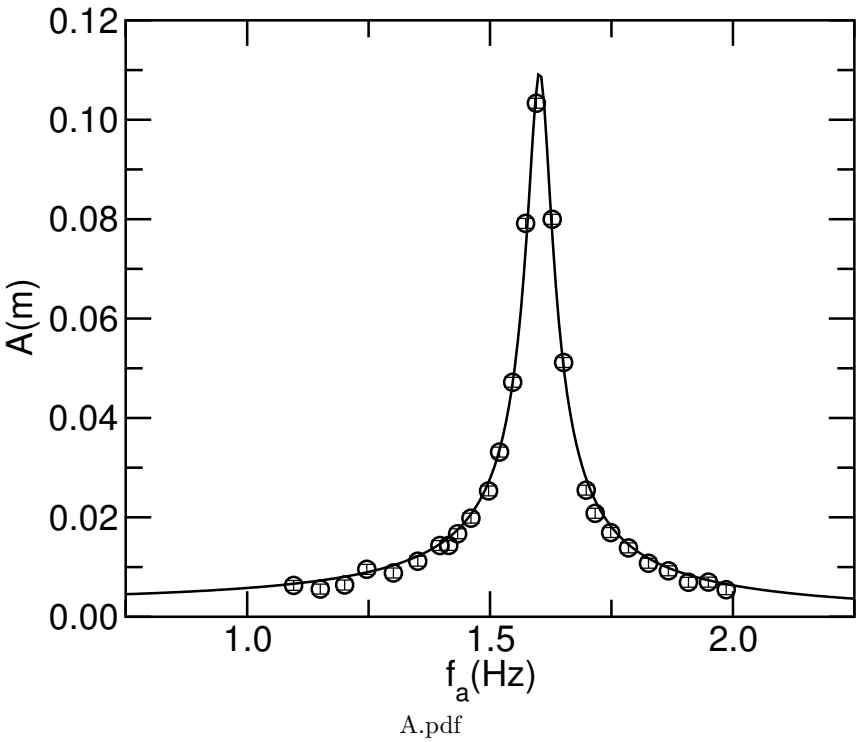


*fitteia* Report  
(internet based fitter service)

Subject	Tutorial1, Basic-EJP-Resonance-const-err
Date	Friday 9 <sup>th</sup> August, 2013, 20:31
Affiliation	pj.sebastiao@gmail.com 77.54.10.14
Abstract	Fit report produced with the fit results of function: $A=F0/(m*\sqrt{\text{pow}(K/m-4*\pi*\pi*fa*fa, 2.0) + 16*\pi*\pi*l*fa*fa}))$ to the 26 experimental points, considering 3 free parameters.

$m = 0.10219$ (fixed)	$l = 0.1626 \pm 0.0026012$
$K = 10.359 \pm 0.0055152$	$F0 = 0.036673 \pm 0.00035622$

$\chi^2[1] = 84.5677 \qquad \chi^2_t = 84.5677$

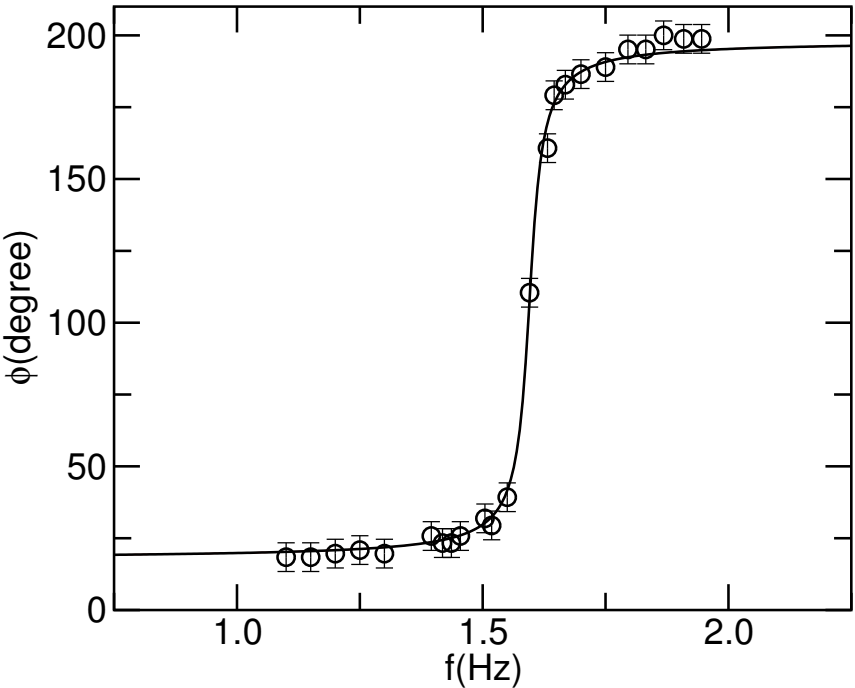


*fitteia* Report  
(internet based fitter service)

Subject	Tutorial1, Basic-EJP-Phase-const-err
Date	Friday 9 <sup>th</sup> August, 2013, 20:40
Affiliation	pj.sebastiao@gmail.com 93.108.109.5
Abstract	Fit report produced with the fit results of function: $y=(x>\sqrt{K/m}/(2\pi)) ? \left( \arctan\left(\frac{2l^2\pi x}{K/m-4\pi^2 x^2}\right) + \pi + b\right)180/\pi :$ $\left( \arctan\left(\frac{2l^2\pi x}{K/m-4\pi^2 x^2}\right) + b\right)180/\pi$ to the 23 experimental points, considering 3 free parameters.

$m = 0.10219$ (fixed)	$l = 0.12442 \pm 0.012487$
$K = 10.269 \pm 0.022925$	$b = 0.32068 \pm 0.019616$

$\chi^2[1] = 8.5947$	$\chi^2_t = 8.5947$
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recta.pdf

***fitteia* Report**  
(internet based fitter service)

Subject	Tutorial1, Expert-EJP-spring-mass
Date	Friday 9 <sup>th</sup> August, 2013, 20:24
Affiliation	pj.sebastiao@gmail.com 77.54.10.14
Abstract	Fit report produced with the fit results of function: $y = (\text{flag} == 1) ? g/K * x + d0 : (\text{flag} == 2) ? (Zt0 - Zinf) * \exp(-l * x) + Zinf : (\text{flag} == 3) ? F0/m / \sqrt{\text{pow}(K/m - 4 * \pi * \pi * x * x, 2.0) + 16 * \pi * \pi * l * x * x)} : (x > \sqrt{K/m} / (2 * \pi)) ? (\text{atan}(2 * l * 2 * \pi * x / (K/m - 4 * \pi * \pi * x * x)) + \pi + a0) * 180 / \pi : (\text{atan}(2 * l * 2 * \pi * x / (K/m - 4 * \pi * \pi * x * x)) + a0) * 180 / \pi$ to the 85 experimental points, considering 8 free parameters.

$$g = 9.8 \text{ (fixed)}$$

$$m = 0.10219 \text{ (fixed)}$$

$$K = 10.392 \pm 0.0076501$$

$$d0 = 0.0027261 \pm 0.00028868$$

$$l = 0.14291 \pm 0.00077868$$

$$A = 0.64014 \pm 0.09051$$

$$Zt0 = 0.1045 \pm 0.00058394$$

$$Zinf = -0.0024616 \pm 0.0002795$$

$$a0 = 0.33976 \pm 0.019833$$

$$F0 = 0.032986 \pm 0.00029406$$

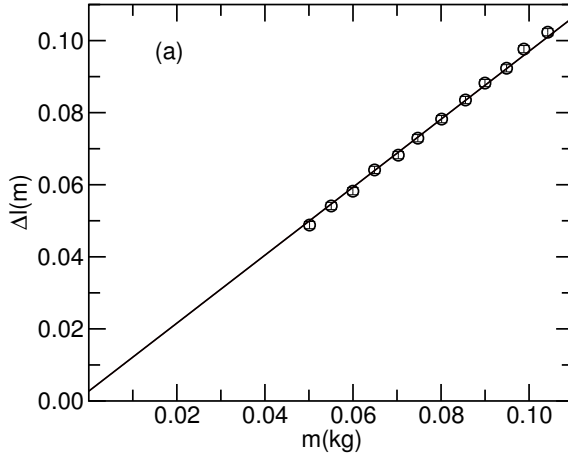
$$\chi^2[2] = 31.0108$$

$$\chi^2[4] = 10.327$$

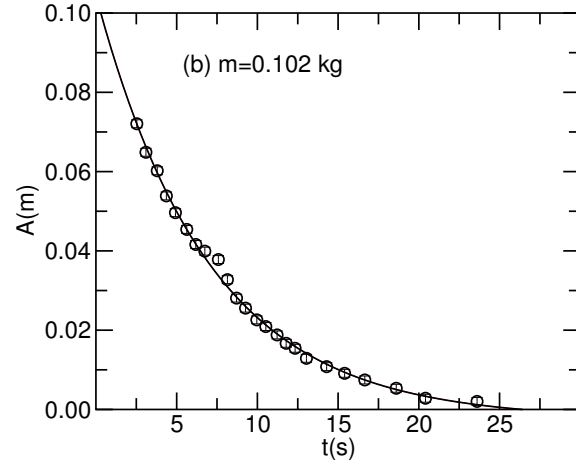
$$\chi^2_t = 60.8831$$

$$\chi^2[1] = 8.73329$$

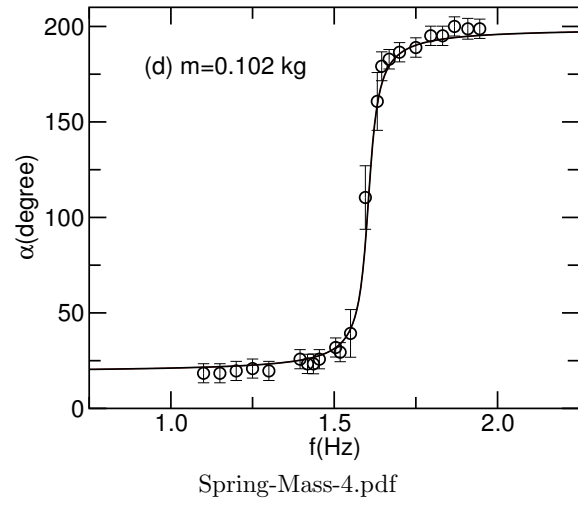
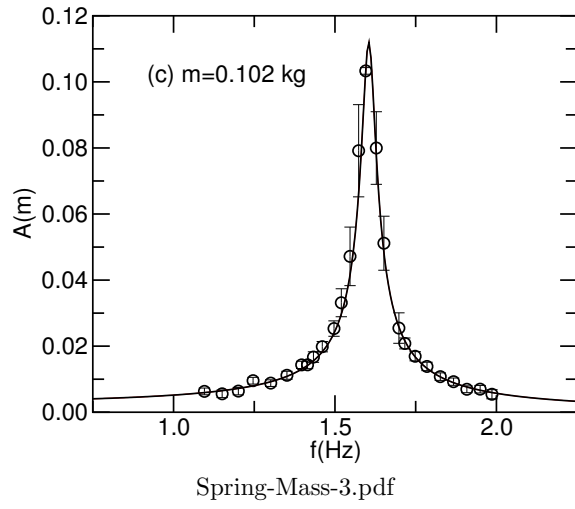
$$\chi^2[3] = 10.8119$$



Spring-Mass-1.pdf



Spring-Mass-2.pdf



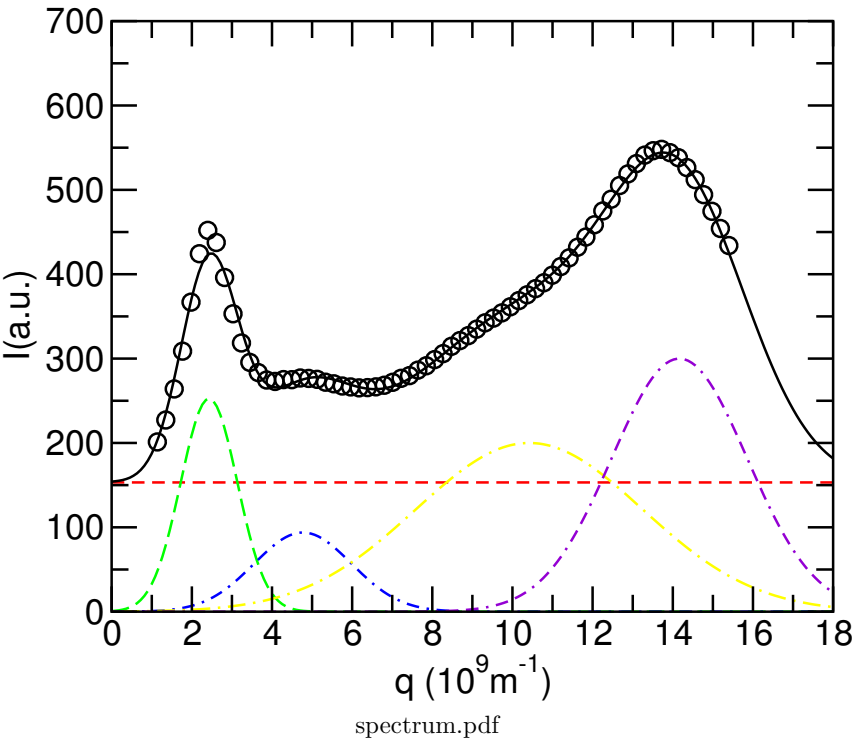


*fitteia* Report  
(internet based fitter service)

Subject	Tutorial1, Basic-EJP-x-rays
Date	Friday 9 <sup>th</sup> August, 2013, 20:21
Affiliation	pj.sebastiao@gmail.com 77.54.10.14
Abstract	Fit report produced with the fit results of function: $y=a + a0*\exp(-\text{pow}((q-q0)/b0, 2.0)) + a1*\exp(-\text{pow}((q-q1)/b1, 2.0)) + a2*\exp(-\text{pow}((q-q2)/b2, 2.0)) + a3*\exp(-\text{pow}((q-q3)/b3, 2.0))$ to the 69 experimental points, considering 13 free parameters.

$a = 153.21 \pm 5.4086$	$a2 = 200 \pm 29.723$
$a0 = 252.52 \pm 15.052$	$b2 = 4 \pm 0.12931$
$b0 = 1 \pm 0.014206$	$q2 = 10.419 \pm 0.12791$
$q0 = 2.4294 \pm 0.040112$	$a3 = 300 \pm 9.6683$
$a1 = 93.836 \pm 7.8405$	$b3 = 2.3904 \pm 0.14258$
$b1 = 1.7183 \pm 0.29467$	$q3 = 14.164 \pm 0.080498$
$q1 = 4.7695 \pm 0.14836$	

$\chi^2[1] = 8.78204$        $\chi^2_t = 8.78204$



***fitteia* Report**  
(internet based fitter service)

Subject	Tutorial1, Expert-EJP-5CB-Iso
Date	Friday 9 <sup>th</sup> August, 2013, 20:26
Affiliation	pj.sebastiao@gmail.com 77.54.10.14
Abstract	Fit report produced with the fit results of function: $z = ( (y > 500.0) ? \text{BPP}(y, \text{Arot}, \text{tauL} * \exp(\text{EL}/8.31 * (1.0/x - 1.0/\text{Tref}))) : \text{BPP}(x, \text{Arot}, \text{tauL} * \exp(\text{EL}/8.31 * (1.0/y - 1.0/\text{Tref}))) ) + ( (y > 500.0) ? \text{BPP}(y, \text{Arot}, \text{tauS} * \exp(\text{ES}/8.31 * (1.0/x - 1.0/\text{Tref}))) : \text{BPP}(x, \text{Arot}, \text{tauS} * \exp(\text{ES}/8.31 * (1.0/y - 1.0/\text{Tref}))) ) + ( (y > 500.0) ? \text{Torrey1}(y, d, r, n, r * r * 1e-20 / (6 * \text{Dref} * \exp(-\text{ED}/8.31 * (1.0/x - 1.0/\text{Tref})))) : \text{Torrey1}(x, d, r, n, r * r * 1e-20 / (6 * \text{Dref} * \exp(-\text{ED}/8.31 * (1.0/y - 1.0/\text{Tref})))) ) + ( (y > 500.0) ? \text{OPF}(y, \text{Aopf}, f0, fcm, fcM, np) : \text{OPF}(x, \text{Aopf}, f0, fcm, fcM, np) )$ to the 44 experimental points, considering 4 free parameters.

$\text{Arot} = 5.7688 \times 10^{+08} \pm 8.45 \times 10^{+06}$	$\text{Dref} = 5.44 \times 10^{-11}$ (fixed)
$\text{tauS} = 1.45 \times 10^{-09}$ (fixed)	$\text{ED} = 32800$ (fixed)
$\text{ES} = 29412$ (fixed)	$\text{Tref} = 313$ (fixed)
$\text{tauL} = 3.36 \times 10^{-10}$ (fixed)	$\text{Aopf} = 17438 \pm 1017.9$
$\text{EL} = 46828 \pm 6860.6$	$f0 = 1 \times 10^{+05}$ (fixed)
$d = 5$ (fixed)	$fcM = 4.25 \times 10^{+07}$ (fixed)
$n = 4.59 \times 10^{+22}$ (fixed)	$fcm = 6.838 \times 10^{+05} \pm 99853$
$r = 4$ (fixed)	$np = 10$ (fixed)

$$\chi^2[313] = 8.81902 \quad \chi^2[1 \times 10^{+08}] = 0.184233$$

$$\chi^2_t = 9.00325$$

