Bayesian Analysis of QENS data: From parameter determination to model selection

L.C. Pardo1, M. Rovira-Esteva1, S. Busch2, M.D. Ruiz-Martin1, J.Ll. Tamarit1, T. Unruh2

1 Grup de Caracterització de Materials, Departament de Física i Enginyeria Nuclear, ETSEIB, Universitat Politècnica de Catalunya, Diagonal 647, 08028 Barcelona, Catalonia,Spain and
2 Physik Department E13 and Forschungszentrum Jülich (FZJ), Technische Universität München, Lichtenbergstr. 1, 85748 Garching, Germany

The extraction of any physical information from quasielastic neutron scattering spectra is generally done by fitting a model to the data by means of $\chi^2$ minimization procedure. However, as pointed out by the pioneering work of D.S. Sivia et al. [1], also another probabilistic approach based on Bayes theorem [2] can be employed. In a nutshell, the main difference between the classical $\chi^2$ minimization and the Bayesian approach is the way of expressing the final results: In the first case, the result is a set of values of parameters with a symmetric error ($P_i \pm \varepsilon_i$) and a figure of merit such as $\chi^2$, whereas in the second case the results are presented as probability distribution functions (PDF) of both, parameters and merit figure. In this contribution, we demonstrate how final PDFs are obtained by exploring all possible combinations of parameters that are compatible with the experimental error. This is achieved by allowing the fitting procedure to wander in the parameter space with a probability of visiting a certain point $P = \exp(-\chi^2/2)$, the so called Gibbs sampling. Three advantages of this method will be emphasized: First, correlations between parameters are automatically taken into account, which implies, for example, that parameter errors are correctly calculated, correlations show up in a natural way and ill defined parameters (i.e. parameters for which data only support the calculation of lower or upper bounds) are immediately recognized from their PDF. Second, it is possible to calculate the likelihood of a determined physical model, and therefore to select the one among many that fits the data best with a minimal number of parameters, in a correctly defined probabilistic way. Finally, in the case of a low count rate where the Gaussian approximation to the Poisson statistics fails, this method can also be used by simply redefining $\chi^2$.

INTRODUCTION

Science is based on the success of an hypothesis to describe experimental results, i.e. is based on the amount of "truth" and "falsity" of an hypothesis when contrasted with experimental results [3]. In order to find a quantitative method to determine this "amount of truth", hypotheses in science should at the end be reduced to a mathematical expression depending on a set of parameters with some physical meaning. The "amount of truth" is then determined by fitting the mathematical model to some experimental data. The general method to do so is to minimize the squared distance between experimental data and the points generated by the mathematical model. Furthermore, taking also into account the error associated with experimental data, a figure of merit $\chi^2$ can be defined

$$\chi^2 = \sum_{k=1}^{n} \frac{(H_k(P_i) - D_k)^2}{\sigma_k}$$

where $n$ is the number of experimental points and $m$ is the number of parameters, $D_k$ ($k=1,...,n$) are the experimental data, $H_k\{P_i\}$ ($k=1,...,n$) are the values obtained from our hypothesis (the mathematical model) using the $\{P_i\}$ ($i=1,...,m$) set of parameters contained in the model, and $\sigma_k$ ($k=1,...,n$) are the experimental errors associated with the respective $D_k$. Therefore, the fitting procedure has a twofold goal: first, to find the set of parameters $\{P_i\}$ which describes the experimental data best, and second, using this set of parameters, to define a figure of merit which quantifies the "amount of truth" of the proposed hypothesis. In order to be able to compare different hypotheses with different numbers of parameters it is reasonable to define a figure of merit which penalizes additional parameters such as the reduced $\chi^2$ defined as:

$$\chi^2_{\nu} = \frac{\chi^2}{n-m}$$

where $n$ is the number of experimental points and $m$ is the number of parameters, so $n-m$ is the number of degrees of freedom. The aforementioned way to quantify how good experimental data are described by a hypothesis is based on what is called a "frequentist" approximation to the problem [4], and has many drawbacks associated with both the fitting procedure and the way to quantify the correctness of the hypothesis describing experimental data.

Data fitting is usually done by minimizing the aforementioned $\chi^2$ (equation 1) using the Levenberg-Marquardt algorithm, which aims to find the minimum of the $\chi^2\{P_i\}$ hypersurface. Unfortunately, usually local minima make the algorithm unable to find the absolute minimum. For this reason, this method can find a final solution only when the algorithm is initialized with parameters near the global minimum. The final solution is then characterized by a set of parameters with an associated error ($P_k \pm \varepsilon_k$) and the figure of merit $\chi^2_P$. This way of quantifying the best fit to the data is based on the supposition that there is only one minimum in the $\chi^2(P_k)$
hypersurface compatible with data error, and that the functional dependence of $\chi^2(P_k)$ is quadratic on each parameter (i.e., one can stop at the second term of a Taylor expansion of the obtained minimum), and thus allowing only symmetric errors. Moreover, errors are usually calculated disregarding possible correlations between them and are thus generally underestimated.

We present in this work a method both to perform fittings and to analyze results based exclusively on probability by using what is called Bayesian inference. The main difference with the previously exposed frequentist method is the absence of any supposition on the $\chi^2(P_i)$ landscape which will rather be explored using the probabilities determined from experimental data. The method results in a different way to express fitted parameters and the figure of merit showing all the complexity of the final solution: they become Probability Distribution Functions (PDFs) obtained directly from exploring the $\chi^2(P_i)$ hypersurface.

The paper will be organized as follows: first the ubiquitous $\chi^2$ will be defined using exclusively probability theory, and on this basis a method to sample the $\chi^2(P_i)$ hypersurface will be presented: the Gibbs sampling. We will then refer on how both the frequentist and Bayesian methods select an hypotheses among others, stressing the hypersurface compatible with data error, and that the hypothesis is represented by $H_k$, we can relate the aforementioned probabilities using the Bayes theorem [5]:

$$
P(H_k | D_k) = \frac{P(D_k | H_k)P(H_k)}{P(D_k)} 
$$

where $P(H_k | D_k)$ is called the posterior, the probability that the hypothesis is in fact describing the data. $P(D_k | H_k)$ is named the likelihood, the probability that our data is well described by our hypothesis. $P(H_k)$ is called the prior, the knowledge we have beforehand about the hypothesis, and $P(D_k)$ is a normalization factor to assure that the integrated posterior probability is unity. In the method here presented we will assume no prior knowledge (maximum ignorance prior [2]), and in this special case Bayes theorem takes the simple form:

$$
P(H_k | D_k) \propto P(D_k | H_k) \equiv L 
$$

where $L$ is a short notation for likelihood.

We need first to find the likelihood that one data point $D_k$ is described by the mathematically modeled hypothesis $H_k$. In a counting experiment such as those related to neutron scattering this probability follows a Poisson distribution

$$
P(D_k | H_k) = \frac{H_k^{D_k} e^{-H_k}}{D_k!}. 
$$

Nevertheless, for a high enough number of counts, the Poisson distribution can be approximated by a Gaussian function (points) with $\sigma = \sqrt{n}$, being $n$ the number of counts.

![FIG. 1: Poisson statistics followed by a counting experiment such as a neutron scattering experiment (lines). For an increasing number of counts, the Poisson distribution can be approximated by a Gaussian function (points) with $\sigma = \sqrt{n}$, being $n$ the number of counts.](image-url)
Therefore, we have found the meaning of the ubiquitous \( \chi^2 \) based only on probabilistic grounds: it is related to the probability that a certain set of data is well described by an hypothesis, and hence the goal of minimizing \( \chi^2 \) is finding a set of parameters that maximizes the likelihood associated with the proposed mathematical model. The probability theory behind \( \chi^2 \) allows therefore also to deal with the case of experiments with only few counts where the Gaussian approximation is not valid anymore and the Poisson distribution must be employed simply by redefining \( \chi^2 \) as

\[
\chi^2 = -2 \sum_{k=1}^{n} \ln \left( \frac{H_k D_k e^{-H_k}}{D_k!} \right)
\]  

(6)

THE BAYESIAN METHOD: GIBBS SAMPLING OF PARAMETER SPACE

The probabilistic understanding of \( \chi^2 \) makes it possible to define a unique method, first to fit the experimental data, and then to analyze the obtained results, using a Markov Chain Monte Carlo (MCMC) technique. A set of parameters \( P_{i}^{\text{new}} \) is generated from an old set \( P_{i}^{\text{old}} \) by randomly changing one of the parameters \[8\]. The probability to accept the new set of parameters is given by

\[
\frac{P(H(P_{i}^{\text{new}}) \mid D_k)}{P(H(P_{i}^{\text{old}}) \mid D_k)} = \exp \left( -\frac{\chi_{\text{new}}^2 - \chi_{\text{old}}^2}{2} \right)
\]  

(7)

where \( \chi_{\text{new}}^2 \) and \( \chi_{\text{old}}^2 \) correspond to the \( \chi^2 \) (as defined in equation \[1\]) for the new and old set of parameters. This way of exploring the parameter space (called Gibbs sampling) is similar to the way used to find the possible molecular configurations of a determined system at a given temperature using the classical Monte Carlo method: the values of physical constants such as the potential energy will in fact be a PDF related to all the configurations explored by the Monte Carlo method. It is therefore possible to relate energy to \( \sum (H_k - D_k)^2 \), the magnitude giving information about the fit quality of the hypothesis with respect to the data, and temperature to the error associated with the data \( (T \sim \sigma^2) \). This way of exploring the parameter space has two main advantages:

- In the fitting process, the Bayesian method is able to accept a new set of parameters that do not decrease \( \chi^2 \), if this change is compatible with the experimental error and therefore does not get stuck in local minima as the Levenberg-Marquardt algorithm. In other words, the presented method is able to go "uphill" in the \( \chi^2 \{P_i\} \) hypersurface if the barrier is compatible with the error. Nevertheless, in order to avoid the presented algorithm to get stuck even in the case when barriers are greater than those associated to experimental error a simulated annealing can be used. This algorithm calculates a fictitious \( \chi^2 = \sum_{k=1}^{n} \frac{(H_k - D_k)^2}{T \sigma^2} \) where \( T \) is a constant defined to artificially increase the experimental error, and by similitude with classical Montecarlo simulation is named as "temperature". Fittings are then started at high temperature, and the system is relaxed by lowering the temperature up to \( T=1 \).

- Concerning the analysis of the results obtained by the fitting, the exploration of the whole parameter space compatible with data using the MCMC method allows both to find the PDF associated with the likelihood directly related the figure of merit \( \chi^2 \) (see equation \[4\]), and the parameters, taking into account possible correlations between them, or minima not describable by a quadratic approximation.

MODEL SELECTION

Data can usually be described by more than one hypothesis, each implying a different physical mechanism to explain experimental results. Albeit the importance to perform model selection accurately, vague arguments are usually given to prefer a model among others and usually no quantitative arguments are given to justify why an hypothesis is preferred, although it is possible to do so using both the frequentist and Bayesian methods. Model selection can be performed using the frequentist approach by using the \( \chi_{\nu}^2 \) figure of merit (see equation \[4\]) which takes into account the addition of parameters to a model by dividing \( \chi^2 \) by the degrees of freedom. Therefore, if two models fit the data with equal success, i.e. with the same \( \chi^2 \), the model with less parameters (with the smallest \( \chi_{\nu}^2 \)) will be favored. In some sense this is nothing but quantifying the Ockham’s razor principle: it is necessary to shave away unnecessary assumptions (parameters). Model selection performed by using \( \chi_{\nu}^2 \) has the same drawbacks as the determination of parameter errors: we suppose that there is a single minimum in \( \chi^2 \{P_i\} \), that this minimum parabolic depends on all parameters and that there are no correlations between parameters. In fact, if these three suppositions are accomplished, then the PDF of the \( \chi^2 \) reads \[2\]

\[
P(\chi^2) \propto (\chi^2)^{N/2-1} \exp(-\chi^2/2)
\]  

(8)

\( N \) is, in this simple case, the number of parameters. In figure \[2\] the chi-square distribution for increasing degrees of freedom (number of parameters) is shown. As can be seen in the inset from figure \[2\] this distribution has a term which is independent from the number of parameters, \( \exp(-\chi^2/2) \), and that decreases together with the quality of the fitting, or when the error associated with
EXAMPLES

Determining the intramolecular structure of CCl₄

Molecular structure can be calculated from diffraction experiments by fitting the high q-range of the scattering function \( S(q) \) to the following equation (see [4]):

\[
S(q) = h \sum_{i,j} b_{ij}^{\text{coh}} \frac{\sin(qr_{ij})}{qr_{ij}} \exp\left(-\frac{\langle l_{ij}^2 q^2 \rangle}{2}\right) \tag{9}
\]

where \( b_{ij}^{\text{coh}} \) are the coherent cross sections for each element, \( r_{ij} \) are the intramolecular distances and \( \langle l_{ij}^2 \rangle \) are the vibrational Mean Square Displacements (MSD) between elements \( i \) and \( j \), and \( h \) is a scaling factor.

In the proposed example, our objective is to calculate the intramolecular structure of carbon tetrachloride (one of the first molecular liquids studied by diffraction methods). The determination of its molecular structure implies to obtain the distance between carbon and chlorine atoms, the Cl-Cl distance is fixed by the tetrahedral symmetry, and the MSD between chlorine atoms and carbon and chlorine atoms.

Experiments were performed at the diffractometer D1b in the Institute Laue Langevin (Grenoble, France) using a wavelength of \( \lambda = 2.52\AA \) (see [10]). Figure 3 shows a good agreement between experimental data and two fittings of equation 9, one with a fixed scale factor \( h \), and the other with \( h \) as a free parameter. Figures 3b,c show the PDF from parameters \( r_{\text{CCl}} \) and \( l_{\text{CCl}} \) obtained through the two aforementioned fittings. Concerning the \( r_{\text{CCl}} \) PDF, we can immediately see that its determination is robust since both fixed and free scale factor \( h \) lead to the same PDF. On the contrary, the PDF associated with \( l_{\text{CCl}} \) is sensible to the way we have performed the fitting: if the scale factor is fixed we obtain a most probable value for this parameter (\( l_{\text{CCl}} = 0.066\AA \)), but for a free scale factor \( h \) only a maximum value for \( l_{\text{CCl}} \) can be obtained due to the correlation between both parameters (\( h \) and \( l_{\text{CCl}} \)). Defining the upper limit as that for which the integrated probability is 0.682 (as errors are usually defined in the frequentist approach [11]) the upper limit \( l_{\text{CCl}} = 0.02\AA \) can be determined from the cumulative distribution function (see fig. 8).

This example shows the main difference compared to the frequentist approximation: the results are presented as PDF. This has the advantage that, as it happens with the determination of \( l_{\text{CCl}} \) leaving \( h \) free, the result to our parameter determination can be expressed as a limit for the parameter, which is impossible with the frequentist approximation.

Parameter estimation: isotropic rotation

Quasi Elastic Neutron Scattering (QENS) is perfectly suited to determine the molecular dynamics in the liquid phase. Usually this dynamics is studied by splitting the spectra into diffusion and rotation contributions

\[
S(q, \omega) = S(q, \omega)_{\text{trans}} \otimes S(q, \omega)_{\text{rot}} \tag{10}
\]

where \( S(q, \omega)_{\text{trans}} \) is the translational contribution and \( S(q, \omega)_{\text{rot}} \) is associated with the rotation of the molecule, assuming that both movements are independent from each other. If we assume that the translation is described by a diffusion mechanism and, therefore, described by the Fick equation, and that rotation is isotropic [12]:

\[
S(q, \omega)_{\text{trans}} = \frac{1}{\pi} \frac{Dq^2}{\omega^2 + (Dq^2)^2} \tag{11}
\]
FIG. 3: (a) High momentum transfer scattering function for CCl₄, where the main contribution to S(q) is that related to the molecular structure. Lines are the best fits to S(q) setting the scale factor fixed and free in the fitting procedure. (b) Probability distribution functions obtained for the distances between carbon and chlorine atoms r_{CCl}, and Mean Square Displacement between carbon and chlorine atom (l_{CCl}) for both cases (fixed h, points, and free h, line). PDF(l_{CCl}) has been represented in logarithmic scale to show the different scale factor fixed and free in the fitting procedure. (b) Differences and equalities of fitting the whole data set together. A fitting using the Bayesian algorithm has also been performed to a spectrum for q = 0.4 Å⁻¹ and T = 300K in order to compare the error bars obtained by both methods. The Error bar using the Bayesian approach was calculated by obtaining the PDF for the radius of rotation and then fitting a Gaussian function with σ = ε, being ε the frequentist parameter error. This error bar is plotted in figure 3, together with that determined by the frequentist method. As it can be seen in the figure the error obtained by the presented method is much bigger that that estimated by the frequentist method. The presented Bayesian method is therefore able to deal with simultaneous fitting of various curves, obtaining the PDF of physical parameters as a function of temperature (see figures 3a,d,e).

Model selection: Diffusion in phospholipid membranes

Phospholipids are the main component of cell walls and can also be used in technological applications as for example drug delivery or food industry. Their dynamics is studied on many time- and length-scales with different techniques, among them quasielastic time-of-flight neutron scattering which probes the motions that dominate on times of about 100 ps.

As will be discussed in detail elsewhere [15], the question arose from previous neutron scattering experiments...
whether the long-range motion of phospholipids is visible on these times or if the motion appears rather localized, trapped in a cage of neighbours. This difference can be seen in the line shape of $S(q, \omega)$: Motions that are localized during the observation time cause a central line that is not broadened beyond the resolution of the instrument but cause a foot in the spectrum. In contrast, long-range motions do broaden the central line.

The neutron scattering experiments were performed with the phospholipid DMPC (1,2-Dimyristoyl-sn-Glycero-3-Phosphocholine) in a liquid crystal fully hydrated with $D_2O$ at the neutron time-of-flight spectrometer TOFTOF at the FRM II (Munich). A typical spectrum is shown in figure 5a after standard corrections including self absorption and subtraction of the $D_2O$ spectra, obtained with the program FRIDA [14]. It is possible to fit the data “satisfactorily” with both, a broadened and a delta-shaped central line.

As stated before, Bayesian analysis is able to quantify how “satisfactorily” the fits are, taking into account the whole $\chi^2\{P_i\}$ landscape and avoiding assumptions about it. In figure 5b, the PDFs associated with $\chi^2$ for the two models are displayed. The normal Levenberg-Marquardt algorithm would simply return the parameters at the minimal reachable value of $\chi^2$ together with this quantity. It is obvious that introducing an additional parameter, the nonzero width of the central line, reduces the $\chi^2$. The question that needs to be answered is if this reduction is significant enough to justify the additional parameter.

The $\chi^2$ gives this answer, however relying on the assumptions discussed above. Employing the Bayesian Analysis, no assumptions are made as the $\chi^2\{P_i\}$ landscape is rendered explicitly. One can see in figure 5b that the model incorporating a broadened central line does not only yield the smaller $\chi^2$ minimum but also the PDF associated with $\chi^2$ is for any combination of parameters smaller than the one of the delta model.

Therefore, the model comparison between the two possibilities of broadened and non-broadened central line favours the model with a broadened line.

**SUMMARY**

We have proposed a general Bayesian method to fit data, analyze results from the fit, and from these results to perform model selection between competing hypotheses. In contrast to the classical frequentist approach, where some assumptions are done concerning the $\chi^2$ landscape (there is only a minimum of $\chi^2\{P_i\}$ able to describe data within its error, this minimum has a square dependence on the parameters, and parameters are not correlated), the proposed method samples the parameter space with the only guide of probability, thus having the following advantages:

- In the fitting procedure, the Bayesian method will not get stuck in local minima if its barrier is smaller than the error associated with the experimental data set.

- Parameters are obtained as PDFs and, because the whole parameter space is sampled, correlations between parameters are naturally taken into account. Moreover, a natural way to define errors based on the PDF of parameters is obtained within this method, which following the frequentist approximations would be the 68% confidence interval around the most probable parameter value, i.e. the parameter is inside these limits with a probability $P=0.68$. PDFs may take an arbitrary form, for example indicating that only a superior limit to the parameter can be extracted from the experimental data.

- The likelihood (which as we have seen is directly related to $\chi^2$) obtained with this method is also a PDF hence revealing the whole complexity of the parameter landscape. Model selection is then performed taking into account all parameter combinations compatible with the experiment.

- The presented method is flexible enough to deal with low counts experiments where the Poisson distribution cannot be approximated by a Gaussian function, by simply redefining $\chi^2$ in the Gibbs sampling algorithm.

This work was supported by the Spanish Ministry of Science and Technology (FIS2008-00837) and by the Catalonia government (2005SGR-00535).
The "frequentist" description defines probability of a certain event $A (P(A))$ as the limiting frequency with which the event $A$ is observed when a great number of events $A$ is taken into account.

In fact it is possible to calculate errors taking into account the correlation between parameters using the frequentist approach (still supposing a parabolic dependence of parameters on $\chi^2 \{ P \}$). This could be done diagonalizing the covariant matrix. This procedure is nevertheless not usually found in the literature resulting in an underestimation of errors.

FABADA software (Fitting Algorithm for Bayesian Analysis of DAta) can be found in http://fisicaetseib.upc.es/gcm/members/lcpardo/software

Bayes, T.: An Essay towards solving a problem in the doctrine of chances, Phil. trans. Roy. Soc. London 53 (1764) 370.

Parameters are changed randomly, but their maximum change is restricted. A new parameter is therefore generated following $P_i^{\text{new}} = P_i^{\text{old}} + (\text{RND} - 0.5) \cdot 2P_i^{\text{max}}$ where RND is a random number between 0 and 1, and $P_i^{\text{max}}$ is the maximum change allowed.

Errors are defined supposing that parameter PDFs follow a Gaussian distribution $P(\text{parameter}) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left(-\frac{x^2}{2\sigma^2}\right)$. The probability that a parameter is within the interval $\pm \sigma$ is 0.683.