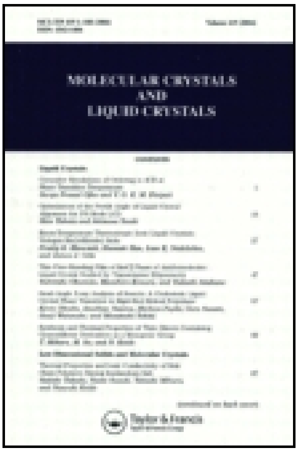

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The Structural Fingerprint in Lyotropic Mesophases by the Use of Inverse Laplace Transform Applied to PGSE NMR Data

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Abstract: We present a theoretical study of the potentialities of the Inverse Laplace Transform when applied to Pulsed Gradient Spin Echo NMR data from water in lyotropic liquid crystalline mesophases. This mathematical application should be able to produce structural information about the studied systems by the determination of the self-diffusion coefficient distribution, giving in this way a significant fingerprint of the molecular organisation in lamellar and reverse hexagonal phases. The critical point of finding the best algorithm to treat the data has been faced: several numerical methods have been tested comparing the performances of the different algorithms with results predictable by theory.

Keywords: NMR; PGSE; Diffusion; Inverse Laplace Transform; Lyotropic Mesophases.

INTRODUCTION

The measurement of the translational self-diffusion requires a method that allows the labelling and tracing of individual molecules without perturbation of the motional process. Pulsed field Gradient Spin Echo (PGSE) NMR methods provide one of the most attractive techniques for investigation of molecular transport in biological cells, lipid membranes and anisotropic fluid systems. In heterogeneous systems, NMR measurements on restricted translational diffusion may be used to determine microgeometry and cell size.

One of the most successful applications of the PGSE technique is found in the field of "complex" liquids. Self-diffusion studies are frequently used for structural investigations on micellar and other isotropic phases [1], lamellar liquid crystalline phases [2,3], cubic liquid crystalline phases [4], and of the adsorption of surfactant to polymers and surfaces [5].

Recently, the Inverse Laplace Transform (ILT) has been successfully applied to PGSE-NMR experiments in isotropic systems to obtain a distribution of self-diffusion coefficients. This mathematical application was used to characterise molecular weight distributions of poly(ethylene oxide) in D_2O [6] and polypropylene and polystyrene samples and mixtures, to study adsorption fractionation of two model systems consisting of bimodal poly(ethylene oxide) (PEO) solutions with and without silica particles [7] and to analyse self-diffusion coefficients distribution as a function of both associative polymer and surfactant concentration [8].

In the present paper, for the first time in our knowledge, the possibility of applying the ILT to PGSE-NMR experiments in restricted systems of powder samples is investigated: the distribution functions of the self-diffusion coefficient for molecules confined in bilayers and capillaries are obtained by a theoretical way and used to test the performances of different Laplace Tranform inversion algorithms. The spirit of the work is to suggest an alternative point of view to analyse a well known phenomenon, effectively studied by well established traditional techniques of fitting [2-5]. Actually, any fitting procedure is in principle affected by the basic problem of the preventive choices of the user (the form of the regression used to describe the physics of the problem, the number of parameters to be optimized etc.) and by the subjective evaluation of the goodness of the fitting; the ILT application is, on the contrary, an automatic, user-independent approach only connected to the quality of the algorithm used to do the inversion.

THEORETICAL CONSIDERATIONS

The Laplace transform inversion is a well known mathematical problem and a large number of studies exist in literature about this argument [9-12]. The use of the ILT can give the answers required in several fields (spectroscopic techniques, digital electronics and so on), where it needs to face the inverse problem of estimating the desired function from the noisy measurements of experimental data. Anyway, for convenience, we will recall shortly the definition of the problem.

Let f(t) be a function defined for $t \geq 0$; the function F(s), introduced by means of the expression,

$$F(s) = \int_{0}^{\infty} f(t)\exp(-st)\,dt \tag{1}$$

is termed the real Laplace Transform of f(t).

In order to indicate both the linear dependence on the function f(t) and to honour Laplace, we will use henceforth the notation $F(s) = L[f(t)]$. The inverse process, indicated by the notation $f(t)=L^{-1}[F(s)]$, is termed Inverse Laplace Transform.

As an integration, the Laplace transform is a highly stable operation, in the sense that small fluctuations (or errors) in f(t) are averaged out in the determination of the area under a curve. Furthermore, the exponential factor, exp(-st), means that the behaviour of f(t) at large t is in practice unimportant, unless s is very small. As a result of these two aspects, a large change in f(t) at large t indicates a small (perhaps insignificant) change in F(s). On the contrary, the inverse transformation from F(s) to f(t) is a highly unstable process: a tiny change in F(s) may result in an uncontrolled variation of f(t) and all significant trends may disappear [13].

Initially, we will consider the ILT of the echo attenuation function in the PGSE-NMR experiments for three-dimensional unrestricted system, where the particles are subject to a completely free Brownian motion. In this case the phenomenon is governed by the following equation:

$$I(\delta,G,\Delta) = I_0 \exp\left(-\frac{2\tau}{T_2}\right)\exp\left(-(\gamma\delta G)^2(\Delta-\frac{\delta}{3})D_0\right) \tag{2}$$

where the measured peak intensity I is a function of field gradient pulse duration δ, intensity G and separation time Δ [14], γ being the magnetogyric ratio and τ the rf pulse interval. The I_0 term is determined by the number of protons in the sample and the first exponential term gives the attenuation deriving from spin-spin relaxation during the experiment duration, 2τ. The translational self diffusion coefficient D_0 is extracted by the fit of experimental data by means of Equation (2). When both duration and intensity of the field gradients are varied in a single experiment (at a constant value of τ), Equation (2) can be are rewritten as:

$$R(k) = I(\delta, G, \Delta)/[I_0 \exp(-2\tau/T_2)] = \exp(-kD_0) \qquad (3)$$

where $k=(\delta\gamma G)^2(\Delta-\delta/3)$. R(k) represents the measured echo attenuation function: its plot vs. k should give an exponential function with a time constant proportional to the self-diffusion coefficient. The ILT of the Equation (3) is, as commonly recognized, a Dirac δ-function, centred on the D_0 value.

When more diffusing species, in a low resolution experiment, give their signals at about the same frequency, the function R(k) contains a sum of exponential decays. Each of them is characterised by a time constant corresponding to the self-diffusion coefficient of each single species. The echo attenuation is then given by:

$$R(k) = \int_0^\infty P(D) \exp(-kD)\, dD \qquad (4)$$

where P(D) is the probability density function of the self-diffusion coefficients.

The equation can be expressed by using the inverse Laplace notation:

$$P(D) = L^{-1}[R(k)] \qquad (5)$$

The ILT of R(k) in isotropic unrestricted systems, where different diffusion components were present, has been already used to determine the probability density P(D) from a set of n experimentally measured values of limited accuracy and it was possible to obtain a representation of the self-diffusion coefficients [7]. In this work, for the first time, we extend, by analogy, the same mathematical treatment to PGSE-NMR experiments in systems restricted by reflecting barriers, organized in randomly oriented arrays, as it occurs in several lyotropic liquid crystals. Following this approach, the self-diffusion of water in a reverse hexagonal phase, composed by hexagonal arrays of thin capillaries, results to be equivalent to one-dimensional diffusion, and the echo attenuation of water protons signal, $R_{1d}(k)$, is given by [15-17]:

$$R_{1d}(k) = \int_0^1 \exp(-kD_w x^2)\,dx \qquad (6)$$

where D_w is the water self-diffusion coefficient within the structure.

This trend of the echo attenuation by PGSE-NMR technique is found in the lyotropic liquid crystals with reverse hexagonal structure [16], where the only diffusional free direction is along the axis of the structures.

On the other hand, lyotropic lamellar systems show free diffusion in the two directions parallel to the surfactant planes. Therefore the self-diffusion of the solvent is defined as two-dimensional and the echo attenuation, $R_{2d}(k)$, is [15-17]:

$$R_{2d}(k) = \int_0^1 \exp(-kD_w(1-x^2))\,dx \qquad (7)$$

It is worthwhile to emphasize that the Equations (6) and (7) have respectively the following analytical solutions, through the error function:

$$R_{1d}(k) = \frac{\sqrt{\pi}}{2}\,\frac{erf(\sqrt{kD})}{(\sqrt{kD})} \qquad (8)$$

$$R_{2d}(k) = \frac{\sqrt{\pi}}{2}\exp[-kD]\,\frac{erf(i\sqrt{kD})}{(i\sqrt{kD})} \qquad (9)$$

The two echo attenuation trends, $R_{1d}(k)$ and $R_{2d}(k)$, can be interpreted as a continuous sum of exponential functions, similar to Equation (4), each one with a different constant corresponding to the self-diffusion coefficient within the arrays oriented in the same direction. According to this hypothesis, by application of the ILT to the Equations (6) and (7), it should be possible to determine the probability spectrum P(D), peculiar of molecules moving in ideal structures of bilayers and capillaries, respectively. The results of these mathematical treatments show indeed well defined behaviours, giving a fingerprint of the structural organisation.

The theoretical trends for self-diffusion distribution in capillary and lamellar structures, i. e. one and two-dimensional diffusion, have been derived to test the ILT application results.

In systems of capillaries, the molecular motion is free in only one dimension and restricted in the other dimensions by the reflecting cylindrical wall, forming the capillary. In a system where water is confined to several capillaries randomly oriented over the sample, the longitudinal and transverse (respect to the axis of cylindrical symmetry) diffusion coefficients have to be considered. Capillary behaviour (where one dimension extends much more then the mean square displacement during the measurement time) would be described by setting $D_{\|} = D_W$ and $D_{\perp}=0$ [15].

The following equation [18]:

$$W(z') = \frac{1}{2\sqrt{\pi D_w t}} \exp\left[-\frac{z'^2}{4D_w t}\right] \qquad (10)$$

gives the probability density W(z') to find a water molecule at distance z' after a time t, along the cylindrical axis direction with $-\infty \leq z' \leq \infty$. Since the PGSE-NMR experiment is influenced only by $<z^2>$, the mean square displacement along the z direction corresponding to the field gradient axis, it is possible to obtain, for the differently oriented arrays of capillaries in the sample, the following expression:

$$\langle z^2(\theta)\rangle = 2tD(\theta) = \frac{1}{2\cos\theta\sqrt{\pi D_w t}} \int_{-\infty}^{\infty} z^2 \exp\left[-\frac{z^2}{4D_w t\cos^2\theta}\right] dz \qquad (11)$$

(with $0 \leq \theta \leq \pi/2$) where the Equation (10) has been taken into account.

$D(\theta)$ is an apparent self-diffusion coefficient for molecules moving in capillaries where the axis of symmetry makes an angle θ respect to the gradient.

The probability density function of self-diffusion coefficients, equivalent to the dN fraction of water molecules having a self-diffusion coefficient contained in the range between D and D+dD in a sample composed by randomly oriented capillaries, will be given by the function:

$$P_{1d}(D) = \frac{dN}{dD} = \frac{dN}{d\theta}\frac{d\theta}{dD} = \frac{1}{2}(D_w D)^{-1/2} \qquad (12)$$

for $0 \le D \le D_w$ and $P_{1d}(D)=0$ for $D > D_w$.

The Equation (12) is similar to the uniaxial symmetry NMR powder pattern spectrum of only one line, whose frequency varies with the orientation of the crystal [19, 20].

Introducing the Equation (12) in Equation (4), it is possible to write:

$$R_{1d}(k) = \int_0^1 \exp(-kD_w x^2)\,dx = \frac{1}{2}\int_0^{D_w} (D_w D)^{-1/2} \exp(-kD)\,dD \qquad (13)$$

An *a posteriori* analytical checking of the last equality is immediately obtained by putting $x^2=D/D_w$.

About the Equation (12), it is very interesting to notice that the mean value of D gives exactly $D_w/3$, the apparent diffusion coefficient of such a powder sample with ideal capillary structure [17].

A lamellar structure (where two dimensions are extended infinitely respect to the mean square displacement in the measurement time) can be described by $D_{\|}= 0$ and $D_{\perp}= D_w$. So, it is immediate to obtain the self-diffusion probability function in a lamellar structure from the cylindrical one, only by exchanging the $D_{\|}$ and $D_{\perp}$ values:

$$P_{2d}(D) = \frac{1}{2}(D_w(D_w - D))^{-1/2} \qquad (14)$$

for $0 \le D \le D_w$ and $P_{2d}(D)=0$ for $D > D_w$.

Again, we obtain the equality:

$$R_{2d}(k) = \int_0^1 \exp\left(-kD_w(1-x^2)\right)dx = \frac{1}{2}\int_0^{Dw} (D_w(D_w - D))^{-1/2} \exp(-kD)\, dD \qquad (15)$$

promptly verified for $x^2 = 1 - D/D_w$.

In this powder sample with ideal two-dimensional structure, the mean value of D, obtained by Equation (14), is $2D_w/3$ as expected for such a situation [21]. In Figure 1 the plots of Equations (12) and (14) (one- and two-dimensional case, respectively) are showed.

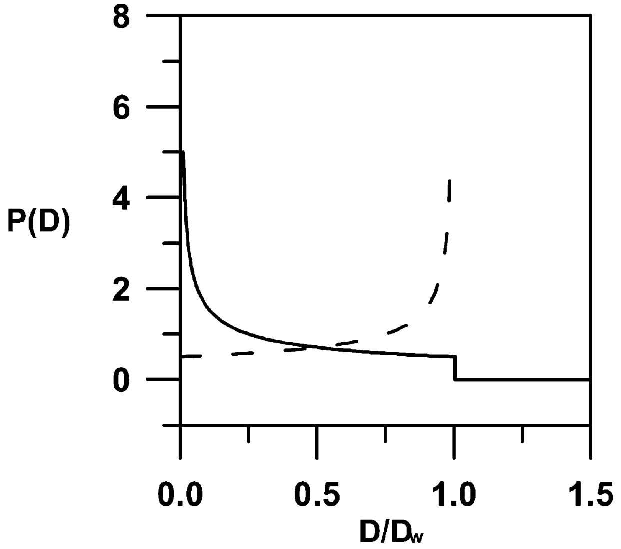

FIGURE 1: The expected probability density functions of self-diffusion coefficient. Solid and dashed lines refer to one and two-dimensional diffusion, respectively.

TESTS OF NUMERICAL ILT PROCEDURES

It is important to emphasise that "the Inverse of the Laplace Transform is not stable under reasonable perturbations" [22]. In our particular case, the situation is made more difficult by the presence of asymptotes and discontinuity in the expected Laplace inverted functions. In a preliminary screening, several algorithms were investigated and analysed: the ILT procedures contained in the *Contin*, *Mathematica* and *Gifa* packages proved to be the most promising, so in this paper we have limited our attention to these procedures.

Contin [22] is a well known general Fortran IV package for inverting noisy linear operator equations. It uses "parsimony" principle as an evaluation of the quality of the resultant distribution: the simplest solution is selected where other more complicated solutions are also possible. *Contin* is very flexible, consisting of a core of several subprograms that the user can customise. The application of *Contin* method allows to perceive the correct trend of the expected solutions in both cases (one and two-dimensional), but unfortunately, as it is shown in Figure 2, it is strongly affected by physiological oscillations that make it unusable for the enunciated problem.

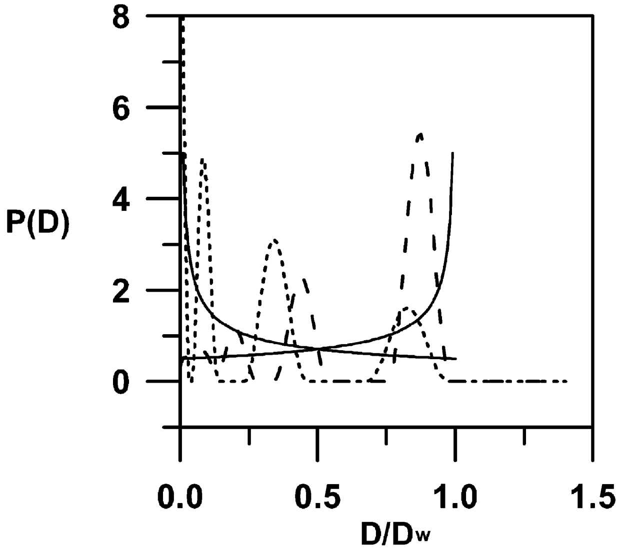

FIGURE 2: The probability density function of self-diffusion coefficient obtained by *Contin*. The solid lines represent the expected functions; dotted and dashed lines refer to one and two-dimensional diffusion, respectively.

The Stehfest ILT method [23], included in the *Mathematica*™ [24] package (NlaplaceInversion.m) is a popular numerical inversion technique used in groundwater flow and petroleum reservoir engineering applications. The inversion formula is based on computing a sample of the time function using a delta-convergent series. As it is shown in the plot (Figure 3), the Stehfest method reproduces very well the mono-dimensional case, whereas it shows serious limitations in the two-dimensional case. Furthermore, its use is restricted only to analytical functions, so it is not applicable to a discrete set of n experimental values of R(k) to be inverted.

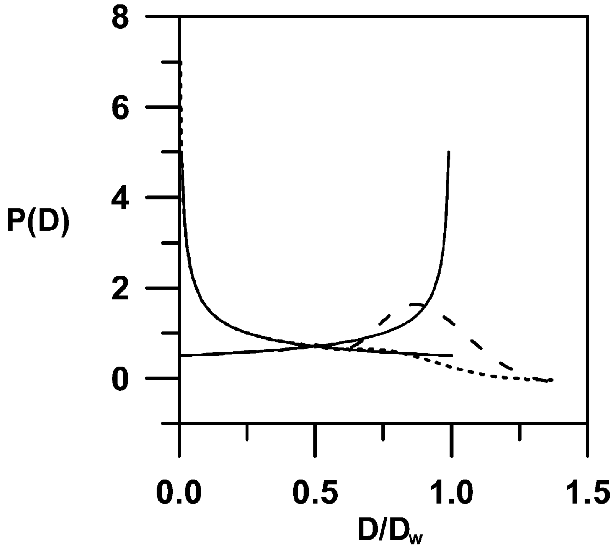

Fig.3: The probability density function of self-diffusion coefficient obtained by Stehfest method. The solid lines represent the expected functions; dotted and dashed lines refer to one and two-dimensional diffusion, respectively.

The *Gifa* [25] is a complete package for NMR data set processing. The inversion algorithm, based on the Maximum Entropy (M. E.)

principle and implemented in the DOSY processing [26], shows in general a higher stability with respect to the oscillations. The program yields an acceptable solution for the two-dimensional case, but it is scarce in the reproduction of the mono-dimensional case (Figure 4).

It is worthwhile to observe that the Stehfest and M. E. methods seem to be complementary in reproducing very well a situation (one- and two-dimensional case, respectively) and badly the other one; on the contrary, *Contin* appears to be a more "general-purpose" procedure, but it fails in reproducing both cases at an acceptable level, being strongly affected by oscillations. These differences are probably to be ascribed to the qualities and flaws hidden in the inmost nature of the algorithms, but these kind of very interesting technical considerations are out of the purposes of this paper.

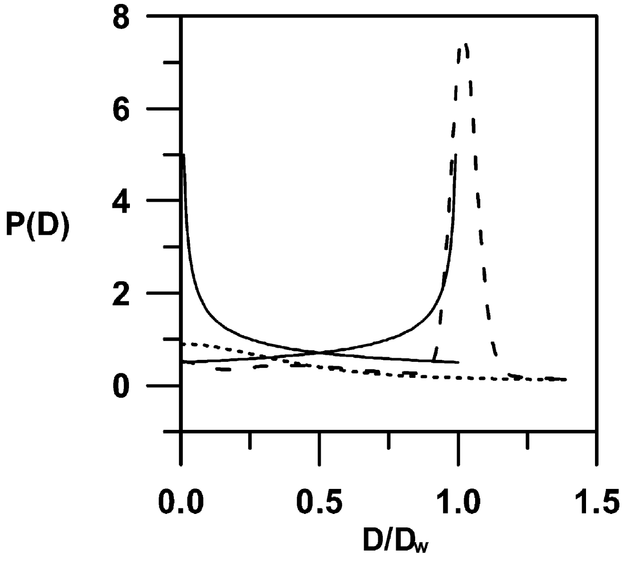

Fig.4: The probability density function of self-diffusion coefficient obtained by Gifa. The solid lines represent the expected functions; dotted and dashed lines refer to one and two-dimensional diffusion, respectively.

CONCLUSIONS

The proposed ILT method can be viewed as an alternative way to the standard fitting method of treatment and interpretation of PGSE-NMR experiments in one- and two-dimensional diffusion: the two approaches (ILT and fitting) can give in principle the same information but they are very different conceptually. In the "classical" approach to the problem, based on the fitting of the data by the use of Equations (6) and (7), the crucial point is represented by a subjective evaluation of the goodness of the fitting; on the contrary, the ILT procedure, being a mere mathematical transformation, is an unpiloted method where the main difficulty is to find a powerful algorithm able to treat restricted diffusion problems.

The availability of a general method, able to determine the ILT from a large set of experimental data of R(k), could allow to obtain in a simple manner important information about, for example, possible structural defects hidden in the signal. Unfortunately, the three ILT methods tested in this work, the best in our knowledge, were not able to solve satisfactorily the exposed problem: intrinsic oscillations and other limitations make them in point of fact inapplicable, even if we cannot exclude that the unsatisfactory results are due to our limited experience in the use of the packages. Finally, being ILT algorithms continuously developed, our further efforts will be focused on their study to find the *optimum* for our purposes.

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