Inverse-problem-based interdiffusion quantification with NMR

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Abstract. Nuclear magnetic resonance (NMR) is a non-invasive technique that can be used to measure concentration profiles and diffusion coefficient during an interdiffusion process of liquids. Due to their different permeabilities, the liquids induce inhomogeneities in the magnetic field. In the case where the inhomogeneities are of the same order as the difference of their chemical shift, the line-width increases lead to important overlapping effect. Moreover, the line broadening is asymmetric relative to its peak and the line shape is unknown. Since classical deconvolution techniques cannot resolve this overlapping, an inverse-problem-based approach is proposed. A constrained nonlinear least-squares optimization problem with respect to concentration emerges from the error minimization between the simulated and measured spectra. For the spectra calculation, the magnetic field distribution is neccessary, which is described by an elliptic PDE and solved with the finite element method. The representation of the concentration is implemented using parametric curves.

1. Introduction

The objective of this work is to present a new methodology that will increase the accuracy of NMR measurements when used to determine concentration profiles in a liquid mixture. Nuclear magnetic resonance is used in applications ranging from medicine to structural analysis of molecules and solid state. Here we are dealing with diffusion processes that arise in a broad range of industrial applications in chemical engineering, such as absorption, extraction and chemical reactions. Knowledge about the diffusion coefficients, and therefore the concentration profiles, is necessary in order to model and optimize these processes.

The experimental setup consists of a tube with two initially-separated liquids inside the NMR magnet. The concentration of the mixing components is resolved along the tube by means of a chemical shift imaging method. This technique provides the NMR spectrum at each slice perpendicular to the tube axis as a function of time. The application of the inverse Fourier transform as well as other generalized transforms are used for reconstructing the distribution of chemical shift in spatially inhomogeneous samples [1]. However, reconstruction techniques based on chemical shift imaging do not take into account the susceptibility-induced magnetic field inhomogeneities. It has been shown that even small differences in the susceptibility of the sample liquids can induce distortions in the magnetic field in the order of magnitude of the chemical shift difference [2]. These field distortions affect the shape and width of the NMR spectra in an a priori unknown way, leading to possible overlapping of the NMR spectra. In the inverse-problem-based approach these distortions have been taken into account by solving
the stationary Maxwell partial differential equations (PDE) as a constraint of the optimization problem.

2. Formulation of the Problem

2.1. Direct Problem

In this section, the direct problem will be briefly discussed. For a detailed discussion and numerical results of the direct problem see [2]. The permeability-induced magnetic field inhomogeneities are described by an axisymmetric model of the time-independent Maxwell equations without sources as follows:

\[-\nabla \cdot (\mu \nabla u) = 0 \quad \text{in } \Omega, \tag{1}\]
\[B = -\mu \nabla u \quad \text{in } \Omega, \tag{2}\]

where \(u\) is the scalar potential and \(B\) the magnetic field. The spatially-dependent magnetic permeability of \(n_{\text{mat}}\) materials inside the magnet is given by \(\mu(x) = \sum_{A=1}^{n_{\text{mat}}} c_A(x) \mu_A\), where \(c_A\) and \(\mu_A\) are the concentration and permeability of the substance \(A\) respectively. The region of magnet is defined as \(\Omega \subset \mathbb{R}^{3\text{D}}, n_{\text{sd}} = 2, 3\). The equations are closed with the following inhomogeneous Dirichlet (\(\Gamma_D\)) and homogeneous Neumann (\(\Gamma_N\)) boundary conditions over the whole boundary \(\partial \Omega := \Gamma = \Gamma_D \cup \Gamma_N:\)

\[u = U \quad \text{on } \Gamma_D, \tag{3}\]
\[\mathbf{n} \cdot \nabla u = 0 \quad \text{on } \Gamma_N. \tag{4}\]

The above problem is discretized with the finite element method [3]. The computational domain is discretized into subdomains (elements) \(\Omega_e\), where piecewise linear polynomials are used as interpolation functions for both the potential and the magnetic field:

\[V^h := \{ w^h \in H^1(\Omega) | w^h|_{\Gamma_e} \in P_m(\Omega^e) \text{ and } w^h = 0 \text{ on } \Gamma_D \}, \tag{5}\]
\[V^h := \{ w^h \in H^1(\Omega) | w^h|_{\Gamma_e} \in P_m(\Omega^e) \}, \tag{6}\]
\[S^h := \{ u^h \in H^1(\Omega) | u^h|_{\Omega_e} \in P_m(\Omega^e) \text{ and } u^h = u_D \text{ on } \Gamma_D \}, \tag{7}\]
\[S^h := \{ B^h \in H^1(\Omega) | B^h|_{\Gamma_e} \in P_m(\Omega^e) \}, \tag{8}\]

where \(V^h\) and \(V^h\) are the spaces of test functions and \(S^h\) and \(S^h\) are the collection of trial functions. Equations (1)–(2) are then written in their discrete form as:

\[-\int_\Omega \mu \nabla w^h \cdot \nabla u^h d\Omega = 0, \tag{9}\]
\[\int_\Omega w^h \cdot B^h d\Omega = -\int_\Omega \mu w^h \cdot \nabla u^h d\Omega. \tag{10}\]

For the solution of the linear equation system formed by the finite element discretization, the iterative algorithm GMRES [4] was implemented, which minimizes the norm of the residual over a Krylov subspace.

The signal evolution is governed by the time-dependent motion of macroscopic magnetization vector and given by the Bloch equation [5]:

\[\frac{dM}{dt} = \gamma M \times B - \frac{M_x i + M_y j}{T_2} - \frac{(M_z - M_0)k}{T_1}, \tag{11}\]

where \(M = M(t, x)\) is the macroscopic magnetisation, \(T_1, T_2\) the relaxation parameters, and \(i, j, k\) the unit vectors with \(k\) parallel to the principal NMR field. A spectrum \(S_k(\omega)\), for \(k = 1, \ldots, n_{\text{sle}}\), where \(n_{\text{sle}}\) is the number of slices across the \(z\)-direction and \(\omega\) the frequency, averaged over the \(x\)-, \(y\)-directions, is obtained after a Fourier transform of the magnetisation \(M\).
2.2. Inverse Problem

The inverse problem is formulated as a constrained optimization problem where the objective function is the error between the measured spectrum and the simulated one over all slices, and the control variables are the concentration distribution of the liquids:

\[
\min_{c_A(z)} J = \frac{1}{2} \sum_{k=1}^{n_{slice}} \int (S_k(\omega) - \tilde{S}_k(\omega))^2 d\omega,
\]

where \(\tilde{S}_k(\omega)\) are the \(k\)th measured slice spectra. The minimization is subject to the direct NMR problem as constraint (see eqs. (1)–(2)) and the concentrations act as the control variables. The minimization problem consists a nonlinear least-squares problem, which is solved with an optimization algorithm, using the Pantoja-Mayne update for the Hessian of the Lagrangian \([6, 7]\).

The calculation of the gradients is done with forward differences.

In order to reduce the number of unknowns entering the minimization problem, instead of using the finite element grid as representation medium for the concentration profile a parametric curve is used with fewer control points than the original grid. For a binary diffusion (\(A = 1, 2\)) where the sum concentrations of all substances everywhere should be equal to one, the number of unknowns is reduced to one i.e., \(c(z)\). It is also assumed that the diffusion takes place only in one direction, leading to one-dimensional concentration profiles. For this purpose, Bézier curves with Bernstein polynomials as basis functions \([8]\) are being used with uniform parametrization:

\[
c(z) = \sum_{i=1}^{n_{cp}} b_i B^n_i(z),
\]

where \(b_i\) are the control values, \(n_{cp}\) are the number of control points used, and \(B^n_i(z)\) are the Bernstein polynomials defined as:

\[
B^n_i(z) = \binom{n}{i} \cdot z^i \cdot (1 - z)^{n-i}.
\]

The above parametric curves interpolate the concentration at the quadrature points of the finite element grid at each optimization iteration.

Composite Beziér curves have been used in order to capture discontinuous profiles in the case when the discontinuity position is known a priori at some accuracy, due to the initial conditions. They consist of more Beziér curves whose end control points are coupled with an equality constraint to guarantee continuity. More strict conditions may be used between the end points of neighbouring curves if differentiability is needed at these points.

A degree of regularization is introduced by spatial (Galerkin) discretization of the PDE \([9]\). Additional regularization is introduced by the use of the parametric curves, since the number of degrees of freedom for the concentration is being reduced. The space of solutions is further reduced by setting bound constraints on the control values.

3. Results and Discussion

In this section some numerical results are presented for a binary diffusion experiment. Three different cases of profiles are studied here; a homogeneous mixture, a smooth profile at some time during the diffusion process and a steep profile when the two liquids are still separated. In all cases as initial solution has been taken as the homogeneous case.
3.1. Error-free measurements
Firstly, cases with no noise are shown. The recovery of a $c(z) = 0.5$ curve from a homogeneous mixture is trivial and therefore not shown. For the recovery of the smooth profile the optimization algorithm has converged after 400 iterations. The exact smooth profile, the initial homogeneous one as well as the solution of the inverse problem at different optimization steps are shown in Fig. 1. It has been observed that increasing the number of slices $n_{slc}$ leads to better results even when using a weaker optimization criterion of the gradient norm.

![Figure 1](image1.png)

**Figure 1.** Concentration profiles and control values at different iterations $n_{opt}$; original ($\circ$); initial ($\triangle$); $n_{opt} = 120$ (+); $n_{opt} = 250$ (×); $n_{opt} = 370$ (□).

If unconstrained optimization was used — that is the control points were unbounded — then the recovery of the steep profiles would exhibit known overshoot and undershoot effects. In Fig. 2 recovered steep profiles are shown with the use of three composite Bezié curves. The use of only one Bezié curve with 20 control points results in an overly-smooth solution.

3.2. Noisy measurements
To better represent experimental conditions, we perturb the measured spectrum with zero-mean and unit-variance Gaussian noise as follows:

$$\tilde{S}_k = S_k + \sigma \cdot N,$$

where $\sigma$ is the standard deviation of the measurement error and controls the amount of noise added to the exact data. In Table 1, the effect of the increase in the objective function with increasing noise levels can be seen. Although the objective function was increased, the recovered

| $\sigma$  | objective function | gradient norm |
|----------|--------------------|---------------|
| 0.2      | 0.3156E-04         | 0.4542E-01    |
| 0.3      | 0.1536E-03         | 0.2653E-01    |
| 0.4      | 0.4937E-03         | 0.3240E-01    |

**Table 1.** Objective function and gradient norm at optimum in presence of noise at the output data for a smooth profile.
concentration profiles with the given values of noise could not be distinguished from the original profile. However, with further increase of the noise level the concentration profiles could not be recovered. The fact that the concentration profiles were perfectly recovered, even in the presence of noise, shows the stability of the proposed approach.

Apart from the addition of noise at the output data (spectrum), other kind of errors can occur. In the above cases, all of the invariant parameters that enter the inverse problem, such as permeabilities, relaxation times, chemical shifts and boundary conditions, are considered to be exactly known. However, there can appear cases where they are not known with needed accuracy. For example, the air inside the magnet or a liquid can contain impurities, thus changing the physical properties of the substance. In Fig. 3 a collection of three such cases is shown. The first case represents a recovered profile where the relative error in the permeabilities of the bottom and top liquids ($\Delta r_{\mu_b}, \Delta r_{\mu_t}$) was 1.0E-10 and the relative error in the permeability of air ($\Delta r_{\mu_{air}}$) is 1.0E-6. It should be noted that the difference in the permeabilities of the liquids and the air are of the order of $10^{-6}$. The second case represents a relative error in the relaxation time ($\Delta r T_2 = 3.0$) and the third one a relative error in the chemical shift ($\Delta r \delta_1 = 0.03$) of one substance. These uncertainties affect the magnetic field distribution as well as the generated signal and spectrum. Therefore, errors in such parameters can change the recovered profiles and even small errors in the permeabilities can have a significant effect.

4. Conclusions
In this work, an inverse problem has been solved in order to calculate concentration profiles from NMR spectra. The problem has been formulated as an optimization problem where the direct problem of calculating the NMR spectra from a given material distribution is solved as a constraint. For further increasing the efficiency the concentration variables are represented by parametric Beziér curves and interpolated onto the finite element grid. The control points of these curves entered the optimization problem as control variables with bounds. Some numerical results are presented without and with noise.

A different way of solving this inverse problem would be to invert each transform separately, that is first calculate the inverse Fourier transform to find the magnetization, then the Bloch equation for the magnetic field and lastly solve the inverse “conductivity” problem. This
incremental approach would be more attractive, if at some stage different models should be chosen. However, this approach was not followed because it involves the solution of many inverse problems and all the models were a priori given.

For the identification of the diffusion coefficient from the concentration profiles [10], a second optimization problem needs to be solved. It is shown that during the initial phase of interdiffusion most information is contained for the recovery of the diffusion coefficient. The concentration profiles are then steep, leading to overshoot and undershoot problems when interpolated with continuous functions, such as Bézier curves. For this reason, the control points of the parametric curve would not be placed on a uniform grid, but their position would enter the optimization problem as additional variables.

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