

Lifetime distribution of multiexponential recovery processes

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Multiexponential recovery is a process where a transient signal recovers through multiple relaxation pathways to a nonzero steady-state value. Such processes are ubiquitous in science and technology—for example in longitudinal (T_1) relaxation in nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI). Existing schemes for extracting lifetime distributions from multiexponential recovery data are inaccurate or inefficient. They either impose unrealistic initial-condition constraints or require extensive late-time sampling. We present a robust inversion method that overcomes both limitations. The devised method determines the lifetime distribution by solving explicitly for the steady-state value and implicitly for the recovery factor—where the recovery factor defines the arbitrary starting point of the signal relative to the steady-state value. The method provides unprecedented accuracy even at shorter time windows and opens up new possibilities in research and industry. Several examples show the features of the method especially in nuclear magnetic resonance, food science, geoscience, and climate science.

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I. INTRODUCTION

Nuclear magnetic resonance (NMR) relaxation techniques are applied in various applications, such as medical imaging [1], exploration and production of energy resources [2], industrial process monitoring [3], quality control of materials [3], monitoring underground aquifers [4], and analytical chemistry [5]. Lifetimes of NMR relaxation processes inform us of health and disease in biological tissue [1], size of pores in technological materials [6], and how batteries work [7]—among many other applications. Relaxation techniques especially enable industrial applications of NMR using inexpensive low-field permanent magnets with inhomogeneous static magnetic fields [3]. Several relaxation dimensions are available in NMR methods, each monitoring the time evolution of nuclear magnetization in a different frame.

The longitudinal T_1 relaxation measures the recovery of a nonequilibrium nuclear magnetization $m_z(t)$ in the longitudinal dimension—relative to that of the static magnetic field—until its full recovery to a nonzero steady state. The dynamics of m_z are commonly measured by the *inversion recovery* and *saturation recovery* methods [8,

pp. 139–145]. In saturation recovery,

$$[\text{saturation}] - t - \frac{\pi}{2} - \text{Acq}, \quad (1)$$

the longitudinal magnetization is first zeroed using one or a series of 90° rf pulses, marked [saturation] above. The inversion recovery method inverts the magnetization in the z direction with a single 180° rf pulse, as

$$\pi - t - \frac{\pi}{2} - \text{Acq}. \quad (2)$$

The longitudinal magnetization is then allowed to recover for a variable delay time t . In both methods, the recovery may be monitored directly (for example in ^1H) by a 90° rf pulse—or indirectly by transferring the magnetization to a coupled nuclei (for example, by a ^1H to ^{13}C transfer) [9]. By varying the recovery time t , a signal $s(t)$ is recorded to produce the recovery curve.

T_1 relaxation is usually governed by multiexponential processes, such as those of mass diffusion [10] or spin diffusion [11,12], where magnetization moves to sites where it relaxes faster. For example, the Bloch-Torrey partial differential equation describes the evolution of longitudinal nuclear magnetization M_z for liquids in confined domains [6,13] by

$$\frac{\partial M_z}{\partial t} = D \nabla^2 M_z - \frac{M_z - M_0}{T_{1b}}, \quad (3)$$

where T_{1b} is the bulk longitudinal relaxation-time constant, D is mass diffusivity, and M_0 is the equilibrium magnetization. In porous materials, Eq. (3) describes the diffusion of

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longitudinal magnetization to surfaces that enhance relaxation and is solved in terms of normal modes that recover to a steady-state value with distinct lifetimes [6,13]. It is usually not possible to directly measure the spatial distribution of $M_z(r, t)$. Instead, one can measure the total nuclear magnetization in the longitudinal plane $m_z(t) = \int_V M_z(r, t) dr$ that would be a multiexponential recovery signal $m_z(t) = s(t)$, where

$$s(t) = \int_0^\infty f(\tau) \left(1 - \alpha e^{-\frac{t}{\tau}}\right) d\tau. \quad (4)$$

α is the *recovery factor*, a scalar constant that depends on the measurement method: $\alpha = 1$ for saturation recovery and $\alpha = 2$ for inversion recovery. $f(\tau)$ is the distribution of recovery time constants, the lifetime distribution, where in this case $\tau \equiv T_1$.

The multiexponential time evolution of Eq. (4) is common in science and technology with examples such as the longitudinal T_1 recovery in NMR and MRI [1,6], fluorescence recovery after photobleaching (FRAP) in confocal laser scanning microscopy [14], charge transfer in semiconductors [15], chemical reactions, and stability of carbon sinks in climate research [16]. These processes exhibit a complex behavior—reflecting processes like relaxation diffusion, reaction diffusion, cross relaxation, and exchange—that is better represented by a probability distribution function $f(\tau)$ of lifetimes, rather than a mono- or biexponential. The position, width, and integral of peaks in the lifetime distribution carry information about the properties of a sample, parameters of a process, quality of a product, or health of biological tissue. For example, in rocks, the position and width of a dominant peak in the T_1 distribution approximately correlate with the absolute size and the pore size spread, respectively [6].

Multiexponential analysis methods find a discretized distribution $f(\tau)$ that reproduces the signal $s(t)$ in the presence of measurement noise [17]. A spectrum of decay lifetimes $f(\tau)$ is produced for a given vector τ , preferably at a high resolution. The common approach to compute $f(\tau)$ is by discretizing τ over N_τ points, typically $N_\tau = 32$ to 512, using a logarithmic distribution from $\tau_{\min}$ to $\tau_{\max}$ and finding a sum-of-exponential solutions to the multiexponential recovery problem

$$s(t) = \sum_{i=1}^{N_\tau} f_i \left(1 - \alpha e^{-\frac{t}{\tau_i}}\right) \quad (5)$$

for predetermined constant recovery factors, $\alpha = 1$ for saturation recovery and $\alpha = 2$ for inversion recovery. Such a logarithmic discretization has the possibility to reveal multiscale processes involving recovery lifetimes differing by several orders of magnitude. Inverting this equation to determine f_i contrasts with the Fourier transformation

and may be considered as a special case of a more general inverse Laplace transformation [18]. The inversion represents an ill-posed inverse problem—as the kernel $(1 - \alpha e^{-t/\tau_i})$ is not orthogonal with respect to τ_i . Although the inversion may seem similar to that of the multiexponential decay [19], the difference is significant enough that it requires its own treatment.

Equation (5) is commonly solved for a recovery time constant distribution f_i by two schemes by either (a, first scheme) fitting the data to a predefined mathematical model with assuming a fixed value of $\alpha = 2$ or $\alpha = 1$, or (b, second scheme) normalizing the signal in the positive real space and employing methods designed for multiexponential decay. The first scheme is implemented in many NMR data analysis software programs. The second scheme is more flexible, but needs sampling at very long times (t) with high precision to precisely measure the recovery level of the signal [6]. Both of these schemes fail to properly capture the full complexity of the data, particularly for multiexponential features that exhibit both dominant and nondominant lifetime components. Such solutions therefore may introduce inaccuracies especially in industrial or nonideal experimental settings. We would like to emphasize that the discretized recovery time constant distribution f_i —addressed in the first and second schemes above, and in more detail with a devised method—is in contrast to the variable projection method that first finds several optimal τ values and then uses the optimal values for τ to solve for the corresponding f [20,21].

We recognized that the common schemes employed in computing the relaxation-time distributions of multiexponential recovery processes are not appropriate or efficient, because they disregard prior information available on the physics of the problem. We provide a robust alternative solution to finding $f(\tau)$ in multiexponential *recovery* processes with *unknown recovery factor* α and without extended measurement windows. By recasting the recovery signal as a linear system that includes the unknown steady-state value explicitly, and the recovery factor implicitly, our approach adopts the prior information about the recovery problem and robustly solves the ill-posed inverse problem. Regularization techniques are then applied to ensure a numerically stable solution. The alternative solution finds $f(\tau)$ in any one- or multidimensional datasets with at least one multiexponential recovery dimension such as in longitudinal relaxation recovery in heterogeneous materials and dynamic nuclear polarization build-up curves. The devised method can recover components of recovery signals that may constitute useful but nondominant fractions of the total signal.

In the past few decades, innovation in the relaxation inversion methods has been mostly focused on the type of applied regularization methods and expansion to multiple dimensions, see Refs. [18,22,23] for examples. Our method is *transforming the formulation*

of multiexponential recovery analysis and distinguishes it from decay analysis with removing the restrictive assumptions commonly imposed on the recovery factor.

The devised method addresses key practical barriers in using recovery NMR methods. Firstly, it reduces the need for extensive data acquisition at long times (t), which are expensive time wise but normally needed to accurately pin down the final steady-state value. Second, it considers possible deviations from an expected recovery factor due to instrumental imperfections or physics of the sample under study that may cause imperfect inversion or saturation of nuclear magnetization. This is especially relevant when (a) the rf field is not completely homogeneous (for example, in heterogeneous materials) [24], (b) quadrupolar nuclei with non-negligible quadrupole couplings are probed [25], or (c) experimental parameters slightly deviate from their expected values [26]. Third, it removes systematic error inherent in current multiexponential recovery models such that the remaining problems in acquiring T_1 relaxation-time distributions would be limited to the availability and precision of data.

In addition to time savings, the correct modeling of recovery signals produces accurate position, width, and integrals of peaks in $f(\tau)$ that improve the sensitivity of T_1 dimension to physical and chemical properties of a sample. Calculating and correcting for the recovery factor can remove instrument-specific measurements and enable multisensor fusion of data, enable high-field measurement features of longitudinal relaxation-time distribution in heterogeneous materials [6], and permit more accurate processing of fast two-dimensional (2D) time-domain data [18,27]. The developed method has broad applicability and impact on NMR instruments such as high-field NMR spectroscopy [28], low-field NMR with permanent magnets for quality control and process monitoring [3], magnetic resonance imaging [24], fast field cycling [29], magnetic resonance sounding with surface coils [4], NMR well-logging [30], electron paramagnetic resonance [31], and dynamic nuclear polarization [9]. In addition, the same method can be applied to fluorescence recovery after photobleaching (FRAP) in fluorescence microscopy [32], reaction kinetics [33], and monitoring electron transfer in semiconductors [34].

The method may broaden applications in magnetic resonance of complex materials, especially at high and ultra-high static magnetic fields with magic angle spinning, where transverse relaxation and diffusion dimensions may be inaccessible. Many advanced applications require finer resolution of individual relaxation components, especially for nonideal experimental conditions, such as *in situ* analysis [35]. The devised method provides more accuracy and sensitivity to material properties, such as those in catalysis, geoscience, polymer science, biophysics, and medical imaging—potentially enabling the observation of other

phenomena and the measurement of alternative material properties.

II. THEORY

In magnetic resonance, Eq. (5) is commonly solved for the time constant distribution f_i by two schemes. The first scheme assumes a known value for α consistent with the physics of the problem: $\alpha = 2$ for the inversion recovery method where an experiment starts with inverted signal $s(0) = -s(\infty)$ following a perfect inversion—where $s(\infty)$ is the steady-state signal at equilibrium; or $\alpha = 1$ for the saturation recovery method where the experiments starts with zeroed signal $s(0) = 0$. In the first scheme, methods employed in the recovery of $f(\tau)$ are nearly identical to those of multiexponential decay [36]; for example,

$$s(t) = \sum_{i=1}^{N_\tau} f_i \left(1 - 2 e^{-\frac{t}{\tau_i}} \right) \quad (6)$$

for inversion recovery, where the only difference with multiexponential decay is the recovery kernel $1 - 2 \exp(-t/\tau_i)$ used instead of the decay kernel $\exp(-t/\tau_i)$. We will later show that this scheme produces inaccurate results in the location and intensity of peaks in the lifetime distribution. Even variations of this scheme (see Ref. [37] and its Supplemental Material; Ref. [38] and its Appendix; as well as Refs. [39,40]) that collect and discard the deviation between the ideal formulation and real signal may lead to inaccurate results for large deviations from a complete inversion.

The second scheme normalizes Eq. (5) to a multiexponential *decay* problem by transformation

$$s'(t) = \left(\frac{s(\infty) - s(t)}{s(\infty) - s(0)} \right) s(\infty), \quad (7)$$

or similar, where $s(\infty)$ is the total magnetization at equilibrium, acquired from measurements *at sufficiently long times*. This scheme produces more accurate results than the first scheme—at the expense of significant increase in experimental time required for measuring a *precise* $s(\infty)$. Normalizing the time-domain data in this scheme does require $s(\infty)$ that is precise enough to enable the accurate computation of the intensity and lifetime of fast recovering components [6,41]. In addition, Eq. (7) adds a dependency of $s(0)$ to all points, which means that the noise of this data point is amplified in the total dataset. One way to circumvent this is to use only the transformation $s'(t) = s(\infty) - s(t)$ in which the amplitudes need to be corrected afterwards. For accurate measurements of the lifetime distribution, this scheme requires such long measurement times that makes it impossible to use in routine applications.

The present method reformulates the discrete form of the multiexponential recovery problem, Eq. (5), to the linear form

$$s(t) = f_\infty - \sum_{i=1}^{N_\tau} f'_i \exp(-t/\tau_i). \quad (8)$$

where f_∞ is defined by

$$f_\infty = s(\infty) = \sum_{i=1}^{N_\tau} f_i, \quad (9)$$

and the recovery factor α and f_i are collected into the unadjusted discrete values of the lifetime distribution f'_i , as

$$f'_i \equiv \alpha f_i. \quad (10)$$

Equations (8)–(10) describe how an unknown α and f_∞ in a multiexponential recovery can be recast into a system of linear equations—the core innovation of this work and a clear distinction from multiexponential decay formulations. τ_i are N_τ elements of a vector of decay lifetimes distributed between $\tau_{\min}$ and $\tau_{\max}$; and f_i are the adjusted discrete values of the lifetime distribution, intensity corresponding to each τ_i .

Equation (8) needs to be recast in a matrix form for solution. It may be expressed in the familiar linear form

$$Ax \cong b \quad (11)$$

to be solved as an inverse problem. Matrix $A \in N_t \times (N_\tau + 1)$ represents the forward mapping; vector

$$b \equiv s \in N_t \times 1 \quad (12)$$

represents experimental data with noise; and vector

$$x \equiv [f_\infty \ f'_i]^T \in (N_\tau + 1) \times 1 \quad (13)$$

contains the desired distribution f'_i .

Finally, after finding $x \equiv [f_\infty \ f'_i]^T$ as the solution to Eq. (11), α and f_i are obtained in two steps from

$$\alpha = \frac{\sum f'_i}{f_\infty}, \quad (14)$$

and f'_i are adjusted to obtain

$$f_i = \frac{f'_i}{\alpha}. \quad (15)$$

Adjusting the lifetime distribution based on the recovery factor ensures that the extracted lifetime components

more accurately reflect the physical properties of the system under study, and compensates for variations in signal intensity and initial perturbations that might otherwise distort the lifetime distribution. This is particularly useful in experimental setups where instrument conditions introduce inconsistencies in signal magnitude, such as differences in inversion efficiency in NMR experiments. Alternatively, the adjustment can also use the first discrete point of the recovery as $\alpha = (f_\infty - s(0))/f_\infty$.

The significant difference between our method for *recovery* to a nonzero steady state and methods employed for *decay* to zero lies in the definition of matrix A and solution x . Matrix A corresponds to the operation performed in Eq. (8) that samples the signal from $f(\tau)$ at N_t discrete times t , for a total of N_τ time constants τ . Matrix A is defined as

$$A = \begin{bmatrix} \mathbb{I} & -\mathbb{A} \end{bmatrix} = \begin{bmatrix} 1 & -e^{-\frac{t_1}{\tau_1}} & -e^{-\frac{t_1}{\tau_2}} & \dots & -e^{-\frac{t_1}{\tau_{N_\tau}}} \\ 1 & -e^{-\frac{t_2}{\tau_1}} & -e^{-\frac{t_2}{\tau_2}} & \dots & -e^{-\frac{t_2}{\tau_{N_\tau}}} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 1 & -e^{-\frac{t_{N_t}}{\tau_1}} & -e^{-\frac{t_{N_t}}{\tau_2}} & \dots & -e^{-\frac{t_{N_t}}{\tau_{N_\tau}}} \end{bmatrix} \quad (16)$$

and is a composite matrix produced from two matrices $\mathbb{I} \in N_t \times 1$ and $\mathbb{A} \in N_t \times N_\tau$; where $\mathbb{I}$ is a vector of ones. Matrix $\mathbb{A}$ is computed by

$$\mathbb{A} = \exp^\circ(-\mathbf{t}(\boldsymbol{\tau}^{(-1)})^T) \quad (17)$$

where $\exp^\circ$ and $^\circ(-1)$ are Hadamard (elementwise) exponential and inverse operations, respectively. T shows transpose. In the analogy of Eqs. (8) and (16), matrix $\mathbb{I}$ represents multiplication by 1 of f_∞ ; $\mathbb{A}$ represents multiplication by $\exp(-t/\tau_i)$ of $f'_i \equiv \alpha f_i$;

$$\begin{bmatrix} \mathbb{I} & -\mathbb{A} \end{bmatrix} \begin{bmatrix} f_\infty \\ f'_1 \\ f'_2 \\ \vdots \\ f'_{N_\tau} \end{bmatrix} = b. \quad (18)$$

Regularization methods solve Eq. (11) in the form of

$$\min_{x \geq 0} \{ \|Ax - b\|_2^2 + \lambda^2 \Omega(x) \}, \quad (19)$$

where the penalty term $\Omega(x)$ determines the type of regularization. For example, a special case of Tikhonov regularization corresponds to $\Omega(x) = \|x\|_2^2$ with the condition $x \geq 0$ and is implemented by solving $\min_{x \geq 0} \|Cx - d\|_2^2$

with $C = [A^T \ \lambda I]^T$, and $d = [b^T \ 0]^T$, where I is a square identity matrix of size N_τ and 0 is a zero vector

of size $N_\tau \times 1$. Tikhonov regularization incorporates a penalty term that suppresses extreme variations in the solution and improves robustness in the presence of noise [42]. Other methods that may be employed in solving Eqs. (8)–(19) include, but are not limited to, singular value decomposition, iterative regularization, maximum entropy, spline regularization, adaptive regularization, and Bayesian methods—or a combination of them [23,43–46]. We do not provide an exhaustive list of such methods, but for the purpose of experimentation, our method may be implemented as a general case for numerical experiments with a combination of RMERA [19] and IR Tools [47] toolboxes in MATLAB or Python. We do not pursue such an avenue here.

Regularization finds a combination of f_∞ and αf_i that minimizes the residual error without overfitting the data. The regularization parameter λ determines the smoothness of the solution by filtering out components of noise [42], that is Gaussian in most time-domain magnetic resonance data [48]. We employ the non-negative linear least-squares method of Lawson and Hanson [49] with $\Omega(x) = Lx_2^2$ where $L = I$, and determine the optimal value of λ from the L curve: $\|x\|_2$ versus $\|Ax - b\|_2$ in log–log form [42]. It should be noted that when using non-negative least-squares fitting, the present form of the method is strictly for recovery to a positive nonzero value. In some cases, steady-state decays are observed, e.g., CPMG experiments decaying to a steady-state value. Our method is also capable of handling such situations, where the exponential elements in matrix A [Eq. (16)] just need to be inverted, from $-e^{-t_1/\tau_1} \rightarrow +e^{-t_1/\tau_1}$.

Formulating the multiexponential recovery problem in terms of Eq. (18) corrects the pitfalls of the two common schemes discussed above by (a) computing the correct f_∞ , (b) removing the necessity for acquiring experimental data with very long delay times, and (c) removing the assumptions of a given value for α . We would like to emphasize that the proposed solution corrects the common model misspecification (or inadequacy) in multiexponential recovery [50]. However, it is not necessarily providing a more stable solution.

Similar methods can also be applied to any two- or multidimensional dataset that contains at least one multiexponential recovery dimension—such as in T_1 - T_2 relaxation correlation [19], or recovery MRI [24].

III. RESULTS

A. Test problem

The proposed method provides excellent inversion fidelity in test problems. As a test problem, we considered a model lifetime distribution with five peaks of different widths and intensities spread over 4 orders of magnitude in lifetimes. The properties of these lifetime peaks are shown in Table I. 1024 points were used in the discretization of the model. With a recovery factor of $\alpha = 1.9$, the time-domain data s_{sim} for the known $f_{\text{sim}}(\tau)$ was calculated in 64 points from $t = 10 \mu\text{s}$ to 10 s using Eq. (8) and with each of the five peaks adding to $f_{\text{sim}}(\tau)$ according to

$$f_i(\tau) = a_i \exp(-[(\log_{10} \tau) - b_i]/c_i)^2. \quad (20)$$

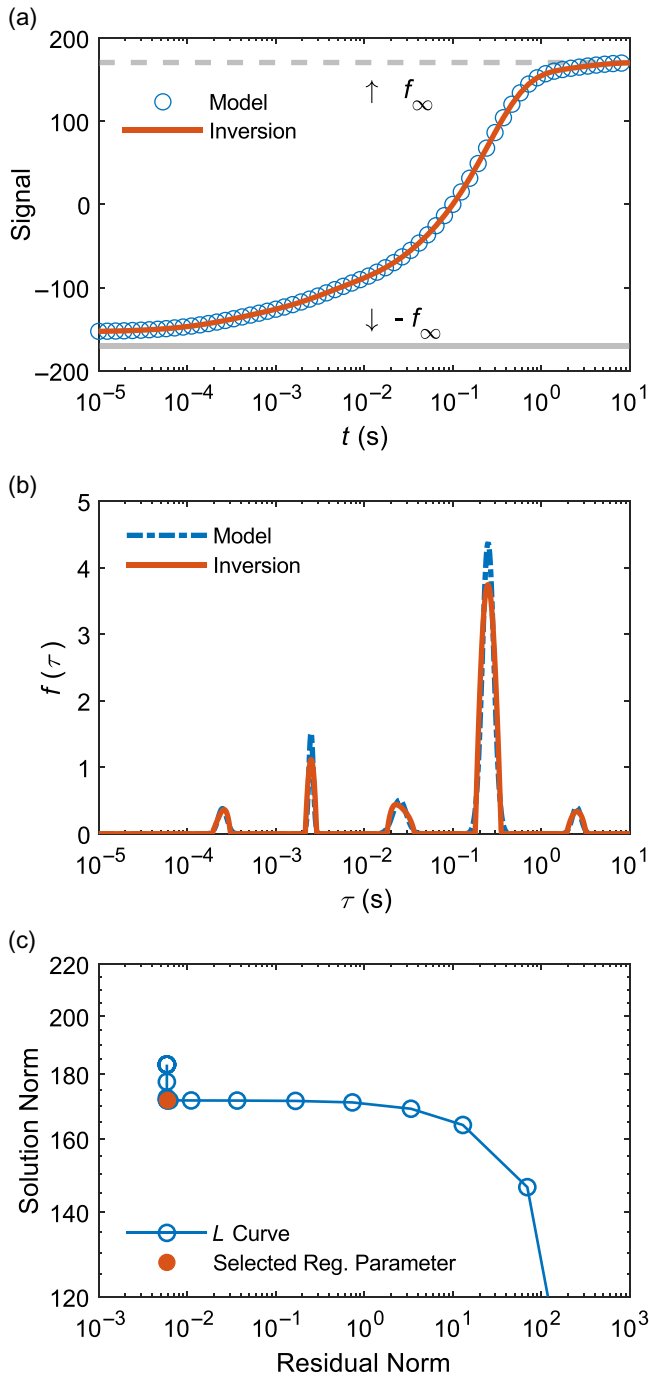
Gaussian noise was then added to simulate realistic conditions with a signal-to-noise ratio of 1000—see the test problem in the time domain shown in Fig. 1(a). The time axis is shown in the logarithmic scale to highlight signal especially at early times.

The parameters of the test problem were chosen according to common NMR recovery processes, where signal $s(t) = m_z(t)$ should be sampled at enough many time points t to determine f_i' with adequate precision— N_t is usually between 8 to 128, while N_τ is usually between 32 to 1024. In our laboratory, we usually acquire at least $N_t = 16$ time-domain points and have $N_\tau = 512$, 1024, or 2048 for a logarithmically distributed τ . The selection of t and N_t ensures a sufficient resolution for capturing the recovery behavior at multiple timescales while maintaining measurement and computational efficiency.

The devised method transformed $s_{\text{sim}}(t)$ into the lifetime distribution $f(\tau)$ with a similar discretization as that of the model lifetime distribution. The L curve determined the optimal $\lambda = 0.0005$ [51]. It is expected that $f(\tau)$ closely

TABLE I. Parameters of the function in Eq. (20) and the recovery factor α (a) used in producing the simulated $f_{\text{sim}}(\tau)$, and (b) of fitted peaks of inverted distribution. The center b_i , width c_i , and integral of simulated and fitted peaks closely match. See the distributions in Fig. 1 and correlations in Fig. 2.

Peak no.	(a) Log-normal function ground truth				(b) Log-normal fit to multiexponential analysis			
	a_i	b_i	c_i	Integral	a_i	b_i	c_i	Integral
1	0.399	0.398	0.0707	0.0500	0.361	0.399	0.0815	0.0521
2	4.37	−0.602	0.0919	0.712	3.98	−0.603	0.105	0.740
3	0.505	−1.60	0.106	0.0950	0.463	−1.61	0.120	0.0989
4	1.52	−2.60	0.0354	0.0951	1.193	−2.60	0.0468	0.0990
5	0.379	−3.60	0.0707	0.0475	0.379	−3.60	0.0730	0.0490
α			1.9				1.9000	



matches $f_{\text{sim}}(\tau)$. Figure 1(b) compares the inverted lifetime distribution with the model, where the reconstruction closely matches the model with the chosen regularization parameter [Fig. 1(c)]. This is in contrast to a perfect inversion—an impossible undertaking due to the ill-posed nature of the problem—that would result in an exactly similar distribution. Since each peak in the model was represented by Eq. (20), a similar functional form was used to fit the inverted distribution to assess the closeness of the inverted lifetime distribution. The location b_i , width c_i , and integral $\sqrt{\pi} a_i c_i$ of all five peaks fitted to the inverted $f(\tau)$

FIG. 1. The method devised in this work successfully inverts multiexponential recovery signals as shown in a test problem. Our method inverted the simulated signal with 64 points [blue circles in (a) and blue line in (b)] into a lifetime τ distribution of 1024 points [orange lines in (a) and (b)], that closely matches the model. The test problem has five peaks, each represented by Eq. (20) spanning over more than 4 orders of magnitude in τ . The centers b_i , widths c_i , and integrals $\sqrt{\pi} a_i c_i$ of simulated and fitted peaks are in excellent agreement (see Fig. 2). Note the two aspects of the time-domain data that make it difficult to be inverted with conventional multiexponential decay analysis methods: first, a signal that is still increasing with time at late times (see the slope of the signal at $t = 10^1$ s), and second, a starting point at early times that does not have a well-defined relationship to the signal at infinite time (notice the difference between the signal intensity at $t = 10^{-5}$ s and $-f_\infty$ where recovery factor is $\alpha = 1.9$). The time dimension in (a) is shown in logarithmic scale only to highlight the complexity of early time data. The model signal had a signal-to-noise ratio of 1000. An optimized regularization parameter of 0.0005 was used according to the L curve (c) and yielded $\alpha_{\text{inversion}} = 1.9$. All input parameters of the model are given in Table I.

excellently match model parameters. The correlation plot of Fig. 2 shows the agreement.

In another test problem (see Fig. S2 in the Supplemental Material), we varied the relative fraction of a lifetime model with two lognormal components ($b_1 = 0.01$ s and $b_2 = 0.1$ s, $c_1 = c_2 = 0.01$) in a discrete relaxation-time distribution of 1024 points between 0.001 and 1 s to determine the minimum detectable fraction. The method could distinguish components with at least 1% total intensity with up to 2% and 6% error for signal-to-noise ratios of 1000 and 100, respectively. For the lower signal-to-noise

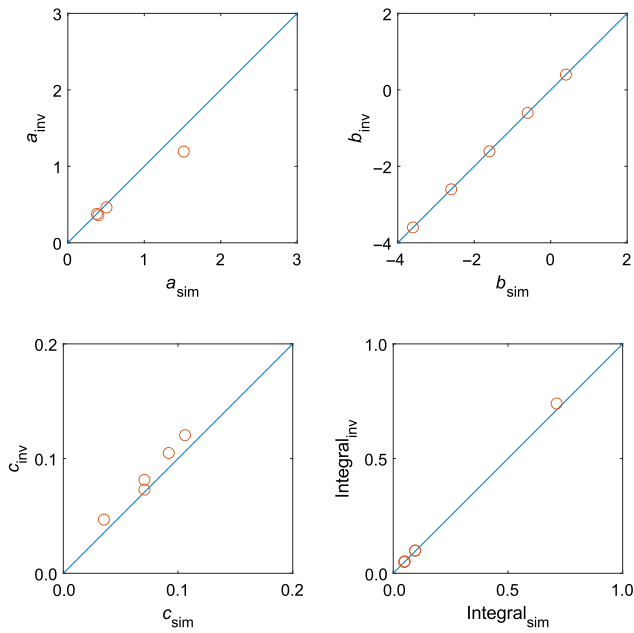


FIG. 2. The similarity between the parameters of the log-normal distributions given by Eq. (20) for the true model and fits to inverted peaks. An exact match is shown with the blue line as a guide. The position b , width c , and integral all show strong similarity for five peaks spanning 4 orders of magnitude in τ .

ratio of 10, the minimum detectable component became 10% with a precision of 10%; but even lower component fractions could also be detected depending on the noise realization. More details on these tests are provided in the Supplemental Material. Specifically see Figs. S2–S5 in the Supplemental Material. The present T_1 inversion method is examined for different signal-to-noise ratios in the Supplemental Material [52].

B. Comparison with common methods

The present method substantially outperforms common methods—schemes one and two discussed in Sec. II—where they either (a) assume a fixed α value (first scheme) or (b) normalize the signal in the positive real space and employ methods designed for multiexponential decay (second scheme). At long measurement times and very high signal-to-noise ratios—for example, at an exorbitantly large time window of up to $t = 30$ s with $\alpha = 1.9$ in the test problem above—our method and the second scheme are comparable and significantly outperform the first scheme with respect to the fidelity of the solution (results not shown).

Differences between the three methods become more pronounced at shorter measurement times that have relevance to laboratory and industrial settings with imperfect conditions, because the experiments recorded for large values of t are expensive time wise to record. Figure 3 displays the performance comparison where our method is compared against other schemes at measurement times

only up to $t = 2.7$ s, with $\alpha = 1.9$. This test problem is similar to that of Figs. 1 and 2 and Table I, but with a shorter observation window. Only 58 logarithmically distributed time-domain points were used between $t = 10$ μ s and $t = 2.7$ s. Our method provides superior fidelity in the location, width, and integral of lifetime distribution peaks, as shown in Fig. 3.

We realized that our method only needs measurements at observation times up to approximately the longest lifetimes of the signal to provide a reliable reconstruction. Such an improvement translates in approximately 50% reduction in experiment time in common low-field ^1H NMR measurements of water in dairy and rock samples in comparison to scheme two described above. In the test problem above, by reducing the observation time to $t = 0.17$ s for the same problem, we see that our method still provides an acceptable representation of the model signal, except for the longest lifetime, as shown in Fig. 4. At such a short measurement time, even our method cannot correctly predict the longest-lifetime component at $t = 2.5$ s. Our method shows more accurate positions, integrals, and widths for peaks in the lifetime distribution and much smaller residual norms. If the signal is sampled up to 10 s, our method outperforms schemes one and two with a residual norm that is an order of magnitude smaller—reflecting on how our method appreciates the correct form of the signal.

The method is still functional even at significant noise levels. Reconstructions of the test problem at the low signal-to-noise ratio of 10 exhibited several important features that are different from the low-noise regime: (1) the width and height of lifetime components become inaccurate, (2) the integral remains accurate but with less precision, (3) the position of computed peaks may shift compared to true positions, and (4) it would not be uncommon to observe peaks that break into several smaller ones centered around the expected center of mass of the true peak position. In such low SNR signals, even the how of manifestation of noise also becomes key; to the extent that different noise realizations may produce different lifetime distributions. Figure S1 in the Supplemental Material displays six lifetime distributions corresponding different noise realizations for the same model distribution as that of Fig. 1, but with a signal-to-noise ratio of 10. Figures S3–S5 in the Supplemental Material show the precision and limits of detection of components at different signal-to-noise ratios for the bimodal distribution of Fig. S2 in the Supplemental Material.

We would like to emphasize that in industrial applications, lifetime parameters like T_1 are employed as a surrogate measure for other physicochemical parameters. So, inaccuracy in T_1 measurements can reduce the sensitivity of NMR measurements to the parameter of interest—hence reducing or removing the efficacy of NMR as a sensor. Since long measurement times are not favorable in industry, T_1 is a less favorable dimension in industrial

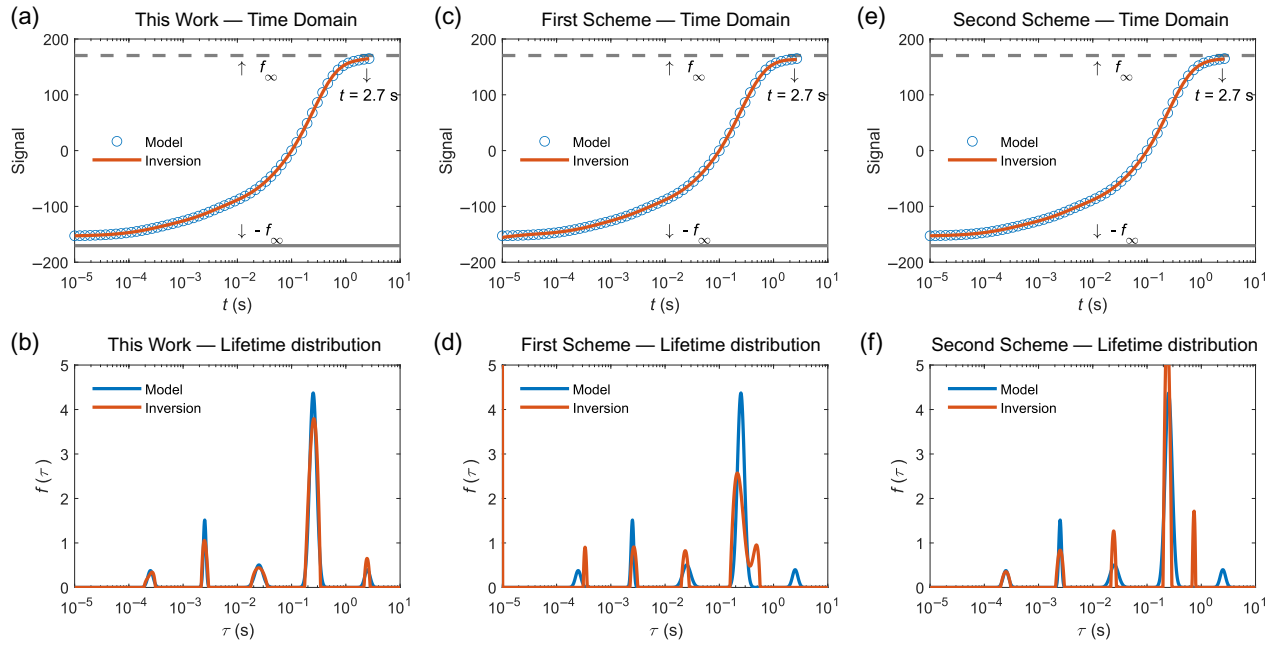


FIG. 3. The devised method substantially outperforms common existing methods in the inversion of multiexponential recovery signals. The comparison highlights differences between multiexponential recovery inversion of a complex signal with five peaks in its complex lifetime distribution (top) and its inversion to the lifetime distributions (bottom) using three different methods: (a),(b) this work, (c),(d) the first scheme that employs an inversion recovery kernel of $1 - 2 \exp(-t/\tau)$ with assumed recovery factor $\alpha = 2$, and (e),(f) the second scheme that normalizes the recovery curve to the positive real space before using multiexponential decay methods. All fits look fine in the time domain, although the first (d) and second (f) schemes fail to produce the model lifetime distribution with high fidelity. The first scheme is widely employed in the transformation of inversion recovery data in research and industry—without rigorous validation of its underlying assumptions. Our method predicted $\alpha_{\text{inversion}} = 1.9006$ in comparison to a model value of $\alpha_{\text{model}} = 1.9$. Regularization parameters were chosen using the L -curve method: $\lambda_{a,b} = 0.0005$, $\lambda_{c,d} = 0.05$, $\lambda_{e,f} = 0.007$.

NMR measurements and T_2 is favored. Improving the accuracy of T_1 peaks in measurements—especially at short times—can potentially shift the favorability of T_1 methods for process monitoring and quality control [3].

C. EXPERIMENTS

1. Water absorption in milk powders

In the first example, we provide an application in food science and technology where we measured the pseudo-2D ^1H longitudinal T_1 relaxation time—chemical shift $\delta_{1\text{H}}$ correlation of skim milk powder particles using the inversion recovery method. A commercial skim milk powder (Arla Foods, Viby, Denmark), composed of 54% lactose, 32% proteins (caseins and whey), 9% ash, 4% moisture, and 0.5–0.9% fat, was exposed to 53% relative humidity air (80% D_2O and 20% H_2O) for 3 days at room temperature. This hydration level simulates poor storage conditions that reduce a milk powder’s solubility in water [53]; the addition of D_2O was for other purposes.

The inversion recovery method used a 180° rf pulse of $9.8 \mu\text{s}$ (400 MHz ^1H frequency), and 64 delay times from $10 \mu\text{s}$ to 40 s, at 5-kHz magic angle spinning (MAS) rate with a sufficiently long repetition delay. The signal is

Fourier transformed to a chemical shift spectrum (frequencies) that informs of the functional groups of mobile ^1H in the milk powder. The chemical shift data, ranging from -2 to 10 ppm, was divided to 512 bins. For each bin, the multiexponential recovery method transformed data from the t dimension to a distribution of τ time constants, $f(\tau \equiv T_1)$, calculated for 1024 logarithmically distributed points from 10^{-6} to 10^2 s. An optimized regularization parameter of 0.01 was used based on the L -curve method [42,51].

Figure 5 presents the ^1H $T_1 - \delta_{1\text{H}}$ correlation map of milk powder exposed to humid air, where water constitutes 10.0% of the dry mass dominating the ^1H signal intensity with a broad peak centered at 4.8 ppm. Smaller signal fractions are associated with mobile lactose, appearing from $\delta_{1\text{H}} = 3.5$ to 4.0 ppm, and trace amounts of milk fat from $\delta_{1\text{H}} = 0$ to 3.5 ppm (see Fig. 5). Due to the low MAS rate of 5 kHz, solid proteins and solid lactose components resulted in very broad ^1H peaks, which do not separate from the baseline in this experiment, and thus with only mobile ^1H components visible in the correlation plot. Such solid components would only become sharper in the ^1H spectrum at spinning rates faster than 100–150 kHz [54]. The inversion was acceptable as assessed by residuals and the parameter α , which should be 2 for a perfect inversion

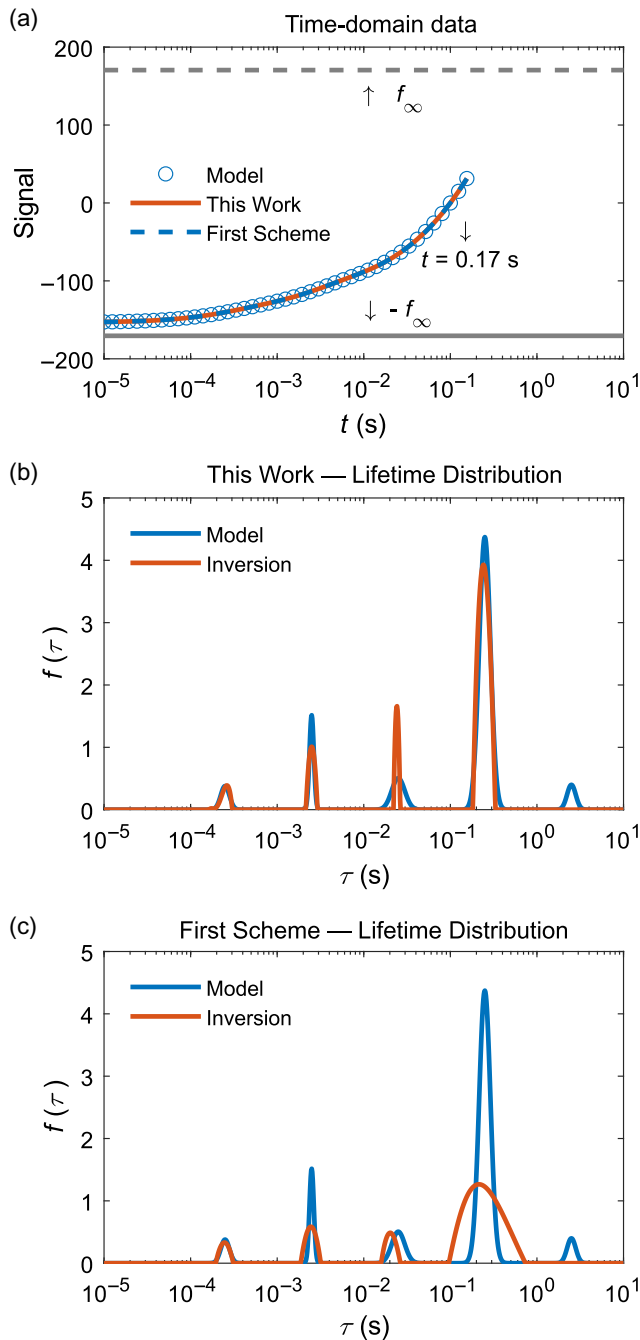


FIG. 4. The devised multiexponential recovery analysis method correctly detects the absolute value of recovery time constants up to the same order of magnitude as that of the longest observation time; here, $t = 0.17$ s. Time-domain data points are shown in (a). The lifetime distribution from our method is shown in (b) and inversion from the first scheme is shown in (c). The first scheme with an inversion recovery kernel of $1 - 2 \exp(-t/\tau)$ cannot correctly determine the center of mass of lifetime components. The peak at $\tau = 0.25$ s is correctly determined by our method, although its lifetime is longer than the maximum time window. Notice that even our method did not identify the longest lifetime of the model at 2.5 s. Our method clearly provides a superior fidelity in the position and integral of the peaks.

and was found to be 1.9–2.0 across the water peak and 1.8–1.9 for the lactose and fat peaks.

The most intense peak in the $T_1 - \delta$ correlation map is that of water associated with lactose appearing at maximum of $\delta_{\text{H}} = 4.8$ ppm and $T_1 = 2.2$ s (62% of the water signal). In comparison, the mobile lactose peak is most intense at $T_1 = 2.3$ s, which is partially overlapping that of water in the T_1 projection due to cross-relaxation. The lactose peak represents a fraction of lactose molecules that gain rotational mobility in the presence of water [54]. We ascribe the shorter relaxation times of water maxima—at $T_1 = 0.68$ s (22%), $T_1 = 0.22$ s (12%), and $T_1 = 0.007$ s (4%)—to the water associated with proteins and salts in the nanodomains of the milk powder nanostructure. This assignment is consistent with the simulated moisture sorption [55] of different components of skim milk powder at 20 °C: 60% absorbed by lactose, 8.5% by whey proteins, and 32% by micellar caseins; in total 9.9 g water per 100 g dry milk powder where the effect of ash is disregarded—in agreement with our measurements. To the best of our knowledge, this is the first time that it is possible to measure and assign absorbed water to a solid component of a complex food material in agreement with the simulated moisture sorption [55].

2. Surface NMR

The second experiment investigates the longitudinal relaxation-time distributions measured by surface NMR in a homogeneous sand aquifer in Skive, Denmark [4]. In surface NMR, the water content and magnetic resonance relaxation parameters of water-bearing sediments are measured as a function of depth using the Earth's magnetic field with large circular or square surface coils—with loops of up to 50–100 m in diameter, or edge length. The longitudinal relaxation-time constant T_1 is an NMR parameter well known to be correlated to the pore size and hydraulic conductivity of sediments and rocks, and less affected by the presence of magnetic materials [4]. The accurate measurement of T_1 using surface NMR methods enables non-invasive subsurface hydraulic conductivity measurements without expensive drilling and coring operations [56].

T_1 measurements using surface NMR equipment commonly employ the pulse sequence of Eq. (1a) with a single $\pi/2$ pulse for saturation. In the original pulse sequence termed pseudosaturation recovery (PSR), the two pulses have opposite phases [57]. A refined version, phase-cycled PSR (pcPSR), can correct the shortcomings of PSR where rf inhomogeneity and instrumental power limitations are significant [4]. pcPSR performs two experiments, one with in-phase pulses and another with 180°-out-of-phase pulses; the signals are then subtracted to remove the effects of deviation from imperfect conditions—similar to phase cycling in common NMR experiments. It has been argued that the pcPSR method is superior to PSR—supported with field measurements [57].

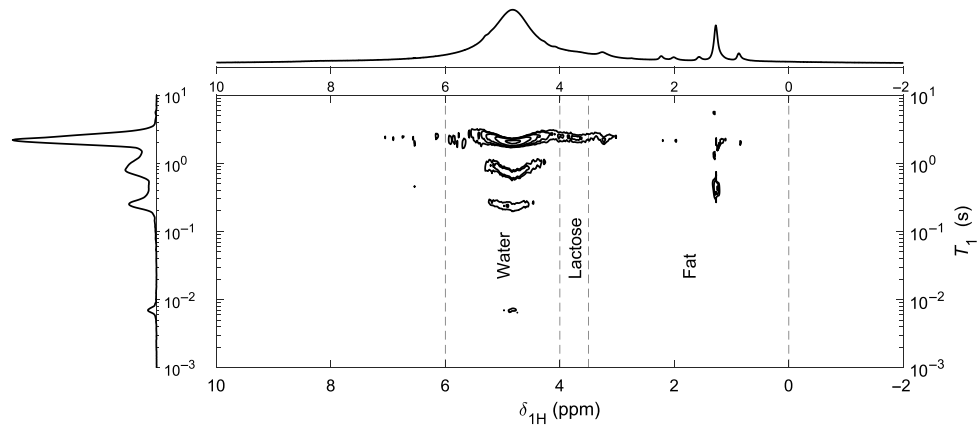


FIG. 5. NMR ^1H longitudinal relaxation time T_1 —chemical shift $\delta_{1\text{H}}$ correlation map of skim milk powder exposed to air with 53% relative humidity (80% D_2O , 20% H_2O) for 3 days. ^1H in water dominates the NMR signal with four peaks in the T_1 distribution from $\delta_{1\text{H}} = 4$ to 6 ppm. The most intense water peak is for water associated with lactose. MAS averages magnetic susceptibility differences between water and other components of milk powder particles (casein and whey proteins, lactose, oil) present in its nanodomains. The lactose signal is associated to molecules that have gained sufficient rotational mobility. Solid proteins and solid lactose are not visible in the spectra. NMR data were acquired at 400 MHz ^1H frequency with 5-kHz magic angle spinning.

Figure 6(a) shows the surface NMR recovery curves obtained by PSR and pcPSR methods for a site in Skive, Denmark—where we used data of Ref. [57] without further data collection. The site is known to be a homogeneous sandy aquifer in the top 30 m where the distribution of pore sizes do not vary significantly across the formation [57]. Dry sand extends to about 15 m below surface (3 m above sea level) overlaying a water aquifer with water content of 25% that extends from 3 m to above 27 m below sea level [57]. Geological records in the area confirm homogeneous fine sand in surrounding boreholes [58]. A square 50 m $\times$ 50 m loop was used as a transmitter and receiver with pulse durations of 40 ms at a static ^1H frequency of 2136 Hz (50 176 nT) [57]. Signals for 14 delay times from 0.2 to 4.0 s were measured with 8 number of scans per each delay, corresponding to a signal-to-noise ratio of approximately 10. T_2^* was 141 ± 9 ms [57]. Authors had assumed that because the pore size is reflected by the T_1 relaxation time, they can characterize the recovery using a single-exponential T_1 recovery: their monoexponential T_1 was 820 ± 38 ms for pcPSR, whereas the monoexponential T_1 varied between 530 and 750 ms for PSR depending on the pulse moment [57].

We use the field data of Ref. [57] for the homogeneous sand aquifer and argue that PSR and pcPSR methods can both measure the dominant component of T_1 correctly. It is this component that corresponds to the ground eigenvalue of the relaxation-diffusion equation and informs of the pore size in geological materials [6,13]. The dominant recovery time constant of the relaxation-time distribution is considerably different from the monoexponential recovery-time constants due to the multiexponential nature of the data. Our multiexponential analysis of data of Ref. [57]

indicates biexponential distributions in the T_1 distribution peaks for both methods—as shown in Fig. 6(b). In addition to a dominant relaxation-time constant, the PSR method displays an extra peak—likely an artifact—in the T_1 distribution that is not representative of a homogeneous sand aquifer. The presence of this peak skews the average monoexponential T_1 to a shorter time constant. Both PSR and pcPSR methods show a common dominant component—with a mode of 0.88 s. This dominant T_1 component corresponds to average particle sizes in the range of 100 to 400 μm [59] that agree with fine sand reported in nearby wells [58]. Brownstein-Tarr simulations yield a pore size of approximately 85 μm , which agrees with the particle size, with a surface relaxivity of 20 to 30 $\mu\text{m/s}$ using a planar pore model [6]. The calculated surface relaxivity would be smaller for spherical geometries and consistent with reported values for sand at kHz frequencies [6,59]. A monoexponential fit of the recovery data would have underpredicted the pore size and hydraulic conductivity of the aquifer.

In summary, our recovery inversion method correctly addresses the multiexponential behavior of the surface NMR recovery signals and yields the same dominant T_1 mode for both PSR and pcPSR methods; with a pore size estimate that agrees with independent geological evidence. Both pulse sequences generate short- T_1 peaks that distort any analysis using single-exponential fits and it appears that neither pulse sequence can properly saturate the magnetization. We showed that it is indeed possible to appropriately analyze existing PSR data by retrieving the dominant T_1 peak location and intensity—an impossible undertaking with commonly used methods.

3. Dynamic nuclear polarization

The third example investigates dynamic nuclear polarization (DNP), where spin polarization from unpaired electrons in a source doped with radicals is transferred to an NMR active nuclei by microwaves [60]. DNP studies provide orders of magnitude in sensitivity enhancement and have become invaluable for the measurements of nuclei with low abundance—with applications in complex pharmaceutical, catalyst, and micro-nano materials with special focus on their surface layers. DNP build-up curves—similar to the saturation curves of Eq. (1a)—measure the polarization on the target nucleus governed by diffusion of spin polarization inside particles as a function of time [9]. Nuclei at surface layers have a faster build-up in comparison to bulk nuclei. The build-up curve is usually modeled using simplified stretched-exponential functions [9,61] that are difficult to correlate to models of dynamic nuclear polarization that are suggested to follow kinetically constrained diffusion [62].

Here, we investigate the build-up curves of a DNP experiment with the present multiexponential recovery method and show that their DNP buildup time (T_{DNP}) distribution exhibits two dominant components with a strong dependency on the distance from the particle surface. We use data of Ref. [61] on the direct ^{17}O DNP NMR of CeO_2 nanoparticles where the chemical shift dimension distinguishes between ^{17}O signals at the first, second, and third layers of oxygen sites in the nanomaterial—as well as bulk sites. The nanoparticles had an average particle size of 11 ± 5 nm and were suspended in a TEKPOL biradical solution in 1,1,2,2-tetrachloroethane

then frozen in 3.2-mm sapphire rotors for measurements at 14.1 T at approximately 95-K temperature with magic angle spinning at $\nu_{\text{MAS}} = 10$ kHz [61]. Hope *et al.* [61] measured the ^{17}O build-up curves of different layers of these nanoparticles as shown in Fig. 7(a)—where we used their data as is, without further experimentation.

The application of the multiexponential recovery analysis method yields time constants and corresponding intensities that are sensitive to the depth of ^{17}O layers in the material. The T_{DNP} distributions are dominant in three regions of (a) larger than 200 s, (b) approximately 100 s, and (c) approximately 10 s or smaller. See Fig. 7(b) where we only show the data of the second and bulk layers to avoid a crowded lifetime distribution, and Fig. 8 where we provide a summary of T_{DNPs} and corresponding intensities for the two longest components. We focus on peaks in areas (a) and (b) where the quality of data is superior, and disregard data for peaks in the (c) region as they are associated with higher uncertainties due to digitization. T_{DNPs} (square markers), and their corresponding intensities (circle markers), have a significant correlation to the location within the nanomaterial. Figures 8(a) and 8(b) show the log-mean average T_1 and their corresponding intensity for long and intermediate T_{DNP} components of different layers, respectively.

These T_{DNPs} and corresponding intensities for polarization diffusion into nanoparticles represent eigenvalues of the reaction-diffusion equations [6,9]. A complete analysis of these systems is beyond the scope of this work and a subject of a future study. Our results however indicate that the devised method can clarify how high

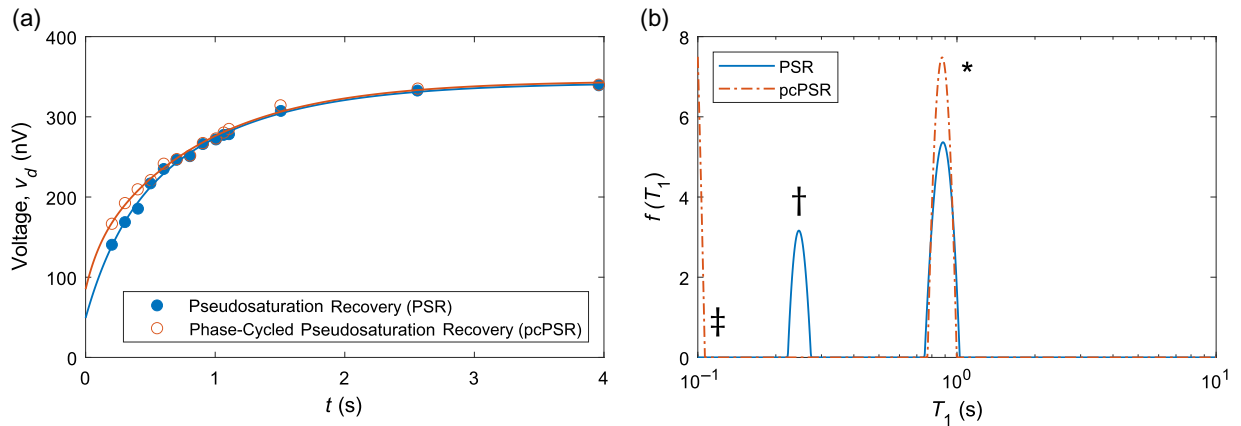


FIG. 6. Surface NMR longitudinal recovery data measured by two different methods (left) exhibit the same (*) dominant component in their T_1 relaxation-time distribution (right). This peak corresponds to the ground eigenvalue of the relaxation-diffusion equation for water in sediment pores and informs of the hydraulic conductivity in aquifers. The peak at (*) corresponds to a particle size in the range of 100 to 400 μm in agreement with reports of fine sand in adjacent wells [58]. It has previously been shown that phase-cycled pseudosaturation recovery (pcPSR) provides superior measurements, compared to the classical PSR method. We show that the PSR method produces an unrealistic peak (†) at $T_1 = 0.25$ s—potentially a measurement artifact. Accurately determining the shortest T_1 component (‡) of pcPSR signal is not possible as time-domain data was sampled only after $t = 0.2$ s. Regularization parameters are $\lambda_{\text{PSR}} = 0.0234$ and $\lambda_{\text{pcPSR}} = 0.0428$, and the calculated recovery factors are $\alpha_{\text{PSR}} = 0.856$, and $\alpha_{\text{pcPSR}} = 0.7535$. Data from Ref. [57].

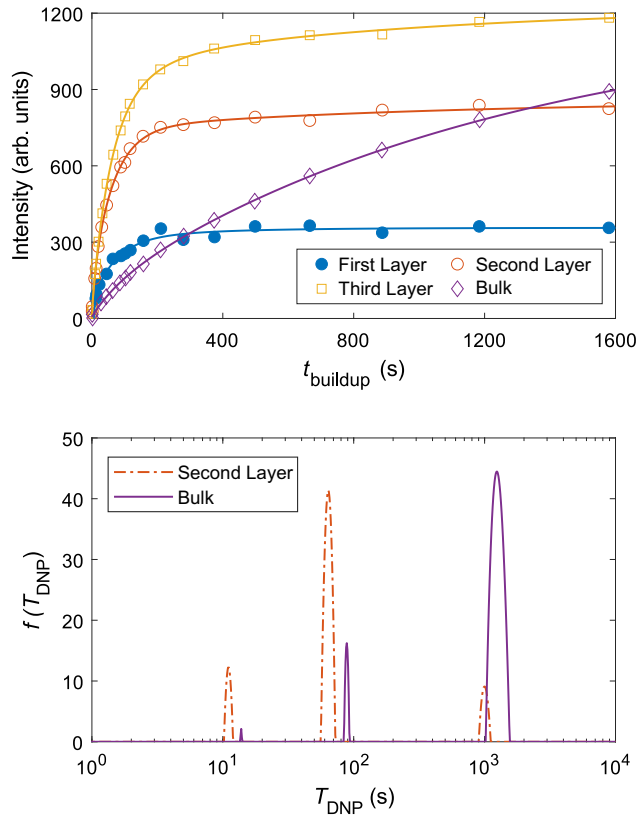


FIG. 7. ^{17}O DNP NMR build-up curves for different layers in CeO_2 nanoparticles (top) and their T_{DNP} distributions (bottom). The position and intensity of peaks in the T_{DNP} distribution is a strong function of location in the nanoparticles as shown in Fig. 8. Data (top) are from Ref. [61].

spin polarizations diffuse inside nanosized particles using DNP build-up curves. T_{DNP} values and their corresponding intensities from analysis with stretched exponentials do not display such level of sensitivity to the location of the nuclei [9,61]—see diamond markers in Fig. 8—and may not be easily related to mechanistic equations that describe the diffusion of polarization.

4. Stability of biochar in climate change mitigation

This example applies the present method to a non-NMR application—biochar stability in climate research. Biochar is produced by thermochemical conversion of biomass through pyrolysis processes that generate heat and fuels, besides the solid biochar [63]. It is an emerging vehicle for carbon dioxide removal due to its maturity and low cost [63]. In addition to carbon storage, adding biochar to soil improves its nutrient and water retention, among other benefits [64]. There is a debate about the permanence of carbon storage in biochar [65,66]. On the one hand, some research argues that biochar has coal-like properties that makes it possible to keep CO_2 out of the atmosphere for a long time [66]. On the other hand, others argue against

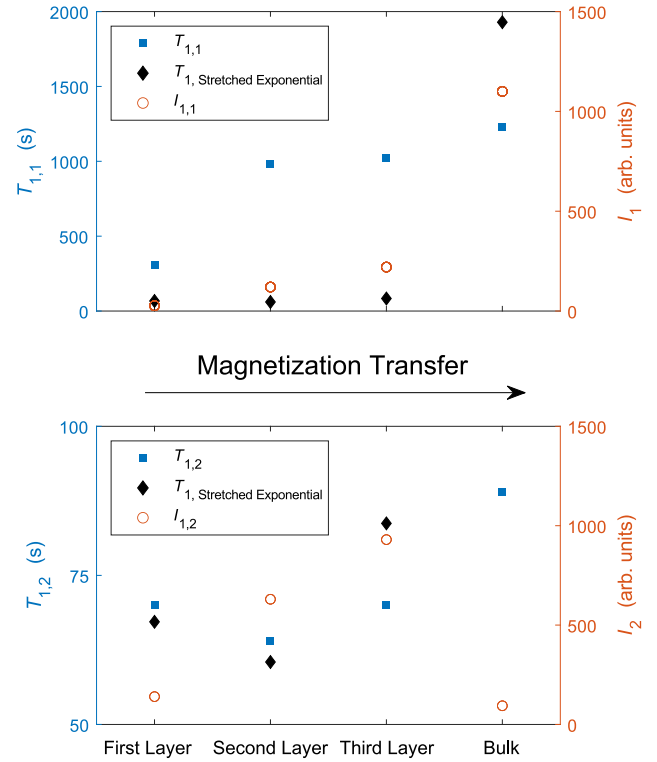


FIG. 8. The long $T_{\text{DNP},1}$ (top) and intermediate $T_{\text{DNP},2}$ (bottom) components of ^{17}O DNP NMR build-up curves in CeO_2 nanoparticles (square)—along with their corresponding intensities I_1 and I_2 (circle). The lifetime and intensity of the components are correlated to the location of the ^{17}O sites in the nanoparticles. Stretched exponential time constants $T_{\text{DNP,SE}}$ are shown in diamond markers: 67, 60, 84, and 1929 s for the first, second, third, and bulk layers, respectively; with corresponding stretching exponents of 0.747, 0.768, 0.794, and 0.757.

the long-term stability of biochar and indicate that different biochar types may act differently, and more research is needed to address their permanence [65]. The permanence of biochar significantly affects carbon dioxide removal credit markets.

Quantifying biochar permanence relies on experiments that monitor its released carbon [33]. These experiments, although short in duration, attempt to model permanence over 100–1000+ years. Biochar is often modeled with its released carbon accumulated in two pools that have different release lifetimes [67]. Not only does such a model appear too simplistic, but problems associated with kinetic fitting of incubation data are also well known, and the analysis is known to be difficult to address [16].

Our multiexponential recovery method can potentially address gaps in data analysis of biochar decomposition to find kinetic parameters at lifetimes up to the same order as that of the maximum measurement time. We applied the devised method to the biochar decomposition data of Ref. [68] as tabulated by Ref. [33] without further experimentation. The experimental data—shown

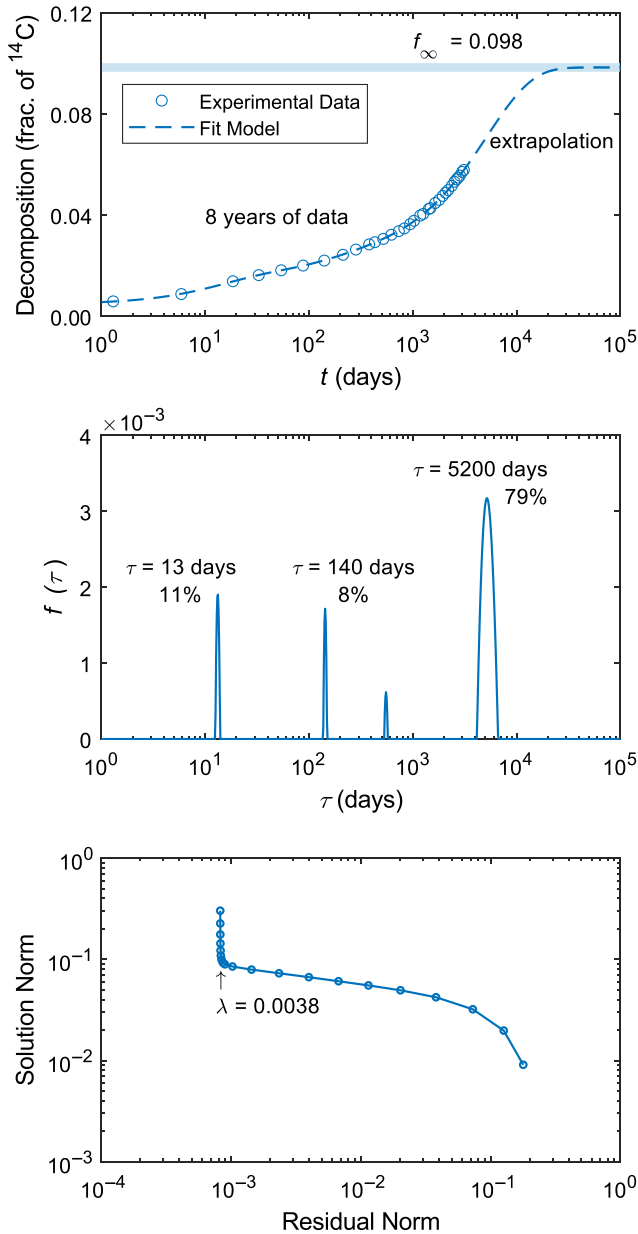


FIG. 9. Decomposition of ^{14}C in biochar as a function of input carbon (top) and its lifetime distribution (middle). The decomposition lifetime distribution demonstrates three dominant peaks representing timescales of 13 days (11%), 140 days (8%), and 5200 days (14 years, 79%). Extrapolation of the decomposition data according to the multiexponential recovery analysis determined a maximum decomposition fraction of 9.8% (f_∞ , top). The L -curve plot (bottom) determined the optimal regularization parameter of $\lambda = 0.0038$ that balances the residual norm (8.4×10^{-4}) against the solution norm (0.0994) and yielded the recovery factor $\alpha = 1.00$. Data from Refs. [33,68]. We observed similar multiexponential features in other data assembled from the literature [33].

in Fig. 9(a)—demonstrate biochar mineralization in soil and loess during 8.5 years (3102 days) acquired based on $^{14}\text{CO}_2$ efflux measurements [68]. The lifetime distribution

displays four lifetime components of 5200 days (14 years, 79%), 550 days (2%), 140 days (8%), and 13 days (11%). Given such a lifetime distribution, we find a simple mono- or biexponential pool model for carbon decomposition unlikely [67]—encouraging more research in the area. The model predicted a decomposition fraction of approximately 10% in approximately 50 years. Such a model would be valid only if longer lifetime components—that are significantly longer than 14 years—do not exist.

IV. DISCUSSION AND FUTURE PERSPECTIVES

The test problems and real applications presented above—as well as many other use cases we explored and did not show here—demonstrated that treating the recovery factor α as an unknown parameter is crucial for robust multiexponential recovery analysis. In comparison to the normalization scheme, the present method can reduce the acquisition window by 5 to 10 times in T_1 NMR measurements. Avoiding long sampling times is not only convenient in industrial measurements but also determines whether a measurement technology is viable or not. The devised method is a step forward in making the T_1 NMR relaxation dimension more accessible, and together with our alternative algorithm to automatically find the regularization parameter [51], this makes T_1 NMR more viable in monitoring food, polymers, and other industrial intermediate and final products—especially by enabling a chemometric analysis of lifetime distributions.

The recovery factor appropriately captures instrument and sample nonidealities—or in the case of biochar, just fits the problem—and folds these imperfections and characteristics into a fitting parameter with physical significance. Residual norms that are below those of other common schemes show that by incorporating our prior knowledge about the existence of an imperfect recovery factor, regularization methods no longer need to absorb a physics they do not know.

A possible limitation is that one could envisage different recovery factors for different components of recovery, hence different α_i may exist. However, it would not be possible—by any method—to determine independent values for all $[\alpha_i, f_i]$ sets from a single recovery curve. The milk powder experiment presented above is an example where different α values could be envisioned, as the inversion efficiency may vary with the chemical shift. Obtaining such information from complementary experiments could be used to refine the model by Eq. (15).

As mentioned above, the devised method may also be applied to determine the lifetimes of any multiexponential process that converges to a nonzero steady state—either in recovery or decay processes. Redefining Eq. (17) by $A = [\mathbb{I} \ \mathbb{A}]$ and $A = [-\mathbb{I} \ \mathbb{A}]$, respectively, simulate multiexponential decay to positive and negative constants without the need to remove the non-negative constraint

in optimization. These formulations ensure that the solution is positive and can be acquired from robust non-negative least-squares methods. Such multiexponential decay analysis methods with offset are well known [46], but also possible with our formulation.

Looking forward, we anticipate further applications in (a) multidimensional relaxation measurements, (b) magnetic resonance imaging, and (c) beyond magnetic resonance, where many other physical phenomena share the same mathematical structure and can use the same analysis.

V. CONCLUSION

We have recast the multiexponential recovery analysis as a problem that is distinctly different from multiexponential decay analysis. The introduction of the recovery factor and steady-state value into the problem yielded three advantages in (a) an improved accuracy in lifetime distributions under imperfect conditions, (2) reducing the acquisition window, and (3) directly computing the steady-state signal. By reducing barriers to accurate and efficient recovery lifetime distributions, the method enables quantitative and multidimensional T_1 relaxation processing for a variety of NMR applications in addition to other physical phenomena governed by multiexponential recovery processes.

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This method has been filed as a patent application by Armin Afrough and Thomas Vosegaard and all rights are assigned to Aarhus University.

DATA AND SOFTWARE AVAILABILITY

The data that support the findings of this article are openly available [69]. The software of the devised method can be accessed for academic research in EasyNMR [70, 71] through its seamless access to computations at the NMRbox [72].

- [1] N. Weiskopf, L. J. Edwards, G. Helms, S. Mohammadi, and E. Kirilina, Quantitative magnetic resonance imaging of brain anatomy and in vivo histology, *Nat. Rev. Phys.* **3**, 570 (2021).
- [2] K.-J. Dunn, D. J. Bergman, and G. A. Latorraca, *Nuclear Magnetic Resonance Petrophysical and Logging Applications* (Pergamon, Amsterdam, The Netherlands, 2002), Vol. 32.
- [3] J. Mitchell, L. F. Gladden, T. C. Chandrasekera, and E. J. Fordham, Low-field permanent magnets for industrial process and quality control, *Prog. Nucl. Magn. Reson. Spectrosc.* **76**, 1 (2014).
- [4] A. A. Behroozmand, K. Keating, and E. Auken, A review of the principles and applications of the NMR technique for near-surface characterization, *Surv. Geophys.* **36**, 27 (2015).
- [5] J. Keeler, *Understanding NMR Spectroscopy*, 2nd ed. (John Wiley & Sons, Ltd, Chichester, UK, 2010).
- [6] A. Afrough, F. Marica, B. Macmillan, and B. J. Balcom, Pore-size measurement from eigenvalues of magnetic resonance relaxation, *Phys. Rev. Appl.* **16**, 034040 (2021).
- [7] A. R. Aguilera, B. MacMillan, S. Krachkovskiy, K. J. Sanders, F. Alkhayri, C. Adam Dyker, G. R. Goward, and B. J. Balcom, A parallel-plate RF probe and battery cartridge for ^7Li ion battery studies, *J. Magn. Reson.* **325**, 106943 (2021).
- [8] J. Kowalewski and L. Maler, *Nuclear Spin Relaxation in Liquids* (CRC Press, Boca Raton, FL, USA, 2006).
- [9] A. C. Pinon, J. Schlagnitweit, P. Berruyer, A. J. Rossini, M. Lelli, E. Socie, M. Tang, T. Pham, A. Lesage, S. Schantz, and L. Emsley, Measuring nano- to microstructures from relayed dynamic nuclear polarization NMR, *J. Phys. Chem. C* **121**, 15993 (2017).
- [10] H. C. Torrey, Bloch equations with diffusion terms, *Phys. Rev.* **104**, 563 (1956).
- [11] T. Manolikas, T. Herrmann, and B. H. Meier, Protein structure determination from ^{13}C spin-diffusion solid-state NMR spectroscopy, *J. Am. Chem. Soc.* **130**, 3959 (2008).
- [12] A. Afrough, N. V. Christensen, R. W. M. Jensen, D. W. Juhl, and T. Vosegaard, Magic angle spinning effects on longitudinal NMR relaxation: ^{15}N in L-histidine, *AIP Adv.* **13**, 115123 (2023).
- [13] K. R. Brownstein and C. E. Tarr, Importance of classical diffusion in NMR studies of water in biological cells, *Phys. Rev. A* **19**, 2446 (1979).
- [14] B. Sprague and J. McNally, FRAP analysis of binding: Proper and fitting, *Trends Cell Biol.* **15**, 84 (2005).
- [15] G. Ramakrishna, D. A. Jose, D. K. Kumar, A. Das, D. K. Palit, and H. N. Ghosh, Strongly coupled ruthenium–polypyridyl complexes for efficient electron

- injection in dye-sensitized semiconductor nanoparticles, *J. Phys. Chem. B* **109**, 15445 (2005).
- [16] L. Weihermüller, A. Neuser, M. Herbst, and H. Vereecken, Problems associated to kinetic fitting of incubation data, *Soil Biol. Biochem.* **120**, 260 (2018).
- [17] D. Benjamini, in *Advanced Diffusion Encoding Methods in MRI*, edited by D. Topgaard (Royal Society of Chemistry, Cambridge, UK, 2020), pp. 278–316.
- [18] J. Mitchell, T. C. Chandrasekera, and L. F. Gladden, Numerical estimation of relaxation and diffusion distributions in two dimensions, *Prog. Nucl. Magn. Reson. Spectrosc.* **62**, 34 (2012).
- [19] A. Afrough, R. Mokhtari, and K. L. Feilberg, Simple MATLAB and Python scripts for multi-exponential analysis, *Magn. Reson. Chem.* **62**, 698 (2024).
- [20] G. Golub and V. Pereyra, Separable nonlinear least squares: the variable projection method and its applications, *Inverse Probl.* **19**, R1 (2003).
- [21] V. Pereyra and G. Scherer, *Exponential Data Fitting and Its Applications* (Bentham Science Publishers, Sharjah, United Arab Emirates, 2012).
- [22] J. Martin, A. Reymbaut, M. Schmidt, A. Doerfler, M. Uder, F. B. Laun, and D. Topgaard, Nonparametric D - R_1 - R_2 distribution MRI of the living human brain, *Neuroimage* **245**, 118753 (2021).
- [23] M. Urbańczyk, D. Bernin, W. Koźmiński, and K. Kazmierczuk, Iterative thresholding algorithm for multiexponential decay applied to PGSE NMR data, *Anal. Chem.* **85**, 1828 (2013).
- [24] P. A. Gowland and V. L. Stevenson, in *Quantitative MRI of the Brain*, edited by P. Tofts (Wiley, Chichester, UK, 2003), pp. 111–141.
- [25] M. Makrinich, R. Gupta, T. Polenova, and A. Goldbourt, Saturation capability of short phase modulated pulses facilitates the measurement of longitudinal relaxation times of quadrupolar nuclei, *Solid State Nucl. Magn. Reson.* **84**, 196 (2017).
- [26] A. Roscher, L. Emsley, and C. Roby, The effect of imperfect saturation in saturation-recovery T_1 measurements, *J. Magn. Reson. A* **118**, 108 (1996).
- [27] V.-V. Telkki, M. Urbańczyk, and V. Zhivonitko, Ultrafast methods for relaxation and diffusion, *Prog. Nucl. Magn. Reson. Spectrosc.* **126–127**, 101 (2021).
- [28] P. Schanda and M. Ernst, Studying dynamics by magic-angle spinning solid-state NMR spectroscopy: Principles and applications to biomolecules, *Prog. Nucl. Magn. Reson. Spectrosc.* **96**, 1 (2016).
- [29] J.-P. Korb, Multiscale nuclear magnetic relaxation dispersion of complex liquids in bulk and confinement, *Prog. Nucl. Magn. Reson. Spectrosc.* **104**, 12 (2018).
- [30] N. Heaton, H. N. Bachman, C. Cao Minh, E. Decoster, J. LaVigne, J. White, and R. Carmona, 4D NMR—applications of the radial dimension in magnetic resonance logging, *Petrophysics* **49**, 172 (2008).
- [31] A. J. Pell, G. Pintacuda, and C. P. Grey, Paramagnetic NMR in solution and the solid state, *Prog. Nucl. Magn. Reson. Spectrosc.* **111**, 1 (2019).
- [32] B. L. Sprague, R. L. Pego, D. A. Stavreva, and J. G. McNally, Analysis of binding reactions by fluorescence recovery after photobleaching, *Biophys. J.* **86**, 3473 (2004).
- [33] E. S. Azzi, H. Li, H. Cederlund, E. Karlton, and C. Sundberg, Modelling biochar long-term carbon storage in soil with harmonized analysis of decomposition data, *Geoderma* **441**, 116761 (2024).
- [34] B. Wenger, M. Grätzel, and J.-E. Moser, Rationale for kinetic heterogeneity of ultrafast light-induced electron transfer from Ru(II) complex sensitizers to nanocrystalline TiO_2 , *J. Am. Chem. Soc.* **127**, 12150 (2005).
- [35] Q. Zheng, J. Williams, L. R. van Thiel, S. V. Elgersma, M. D. Mantle, A. J. Sederman, T. A. Baart, G. L. Bezemer, C. M. Guédon, and L. F. Gladden, Operando magnetic resonance imaging of product distributions within the pores of catalyst pellets during Fischer–Tropsch synthesis, *Nat. Catal.* **6**, 185 (2023).
- [36] L. Venkataramanan, Yi-Qiao Song, and M. D. Hurlimann, Solving Fredholm integrals of the first kind with tensor product structure in 2 and 2.5 dimensions, *IEEE Trans. Signal Process.* **50**, 1017 (2002).
- [37] P. M. Singer, A. Arsenault, T. Imai, and M. Fujita, ^{139}La NMR investigation of the interplay between lattice, charge, and spin dynamics in the charge-ordered high- T_c cuprate $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$, *Phys. Rev. B* **101**, 174508 (2020).
- [38] A. Arsenault, T. Imai, P. M. Singer, K. M. Suzuki, and M. Fujita, Magnetic inhomogeneity in charge-ordered $\text{La}_{1.885}\text{Sr}_{0.115}\text{CuO}_4$ studied by NMR, *Phys. Rev. B* **101**, 184505 (2020).
- [39] J. Kikuchi, T. Kamoda, N. Mera, Y. Takahashi, K. Okumura, and Y. Yasui, Field evolution of magnetic phases and spin dynamics in the honeycomb lattice magnet $\text{Na}_2\text{Co}_2\text{TeO}_6$: ^{23}Na NMR study, *Phys. Rev. B* **106**, 224416 (2022).
- [40] J. Wang, W. Yuan, P. M. Singer, R. W. Smaha, W. He, J. Wen, Y. S. Lee, and T. Imai, Emergence of spin singlets with inhomogeneous gaps in the kagome lattice Heisenberg antiferromagnets Zn-barlowite and herbertsmithite , *Nat. Phys.* **17**, 1109 (2021).
- [41] A. Afrough, S. Vashaei, L. Romero Zerón, and B. Balcom, Absolute measurement of pore size based on nonground eigenstates in magnetic-resonance relaxation, *Phys. Rev. Appl.* **11**, 041002 (2019).
- [42] P. C. Hansen, *Discrete Inverse Problems* (Society for Industrial and Applied Mathematics, Philadelphia, PA, USA, 2010).
- [43] G. Demoment and J. Idier, in *Bayesian Approach to Inverse Problems*, edited by J. Idier (Wiley, Hoboken, NJ, USA, 2008), pp. 41–58.
- [44] G. Demoment and Y. Goussard, in *Bayesian Approach to Inverse Problems*, edited by J. Idier (Wiley, Hoboken, NJ, USA, 2008), pp. 59–78.
- [45] G. Frasso and P. H. C. Eilers, Smooth deconvolution of low-field NMR signals, *Anal. Chim. Acta* **1287**, 341808 (2024).
- [46] G. C. Borgia, R. J. S. Brown, and P. Fantazzini, Uniform-Penalty Inversion of Multiexponential Decay Data, *J. Magn. Reson.* **147**, 273 (2000).
- [47] S. Gazzola, P. C. Hansen, and J. G. Nagy, IR Tools: a MATLAB package of iterative regularization methods and large-scale test problems, *Numer. Algorithms* **81**, 773 (2019).
- [48] A. Chaudhari and J. Kulkarni, Noise estimation in single coil MR images, *Biomed. Eng. Adv.* **2**, 100017 (2021).

- [49] C. L. Lawson and R. J. Hanson, *Solving Least-Squares Problems* (Prentice Hall, Upper Saddle River, NJ, 1974).
- [50] N. A. B. Riis, *Characterizing and Reducing the Influence of Model Errors in Inverse Problems* (Technical University of Denmark, Kongens Lyngby, Denmark, 2021).
- [51] A. Afrough, M. Pérez-Mendigorri, and T. Vosegaard, automated data processing workflows for non-expert users of NMR facilities, *Magn. Reson. Chem.* **63**, 604 (2025).
- [52] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/v4pb-vvd2> for evaluation of the present method for different signal-to-noise ratios.
- [53] X. Qí, K. G. Malmos, F. W. J. van den Berg, F. B. Grumsen, and S. Bakalis, Crystal size, a key character of lactose crystallization affecting microstructure, surface chemistry and reconstitution of milk powder, *Food Res. Int.* **177**, 113872 (2024).
- [54] A. Afrough, P. Andersen, T. N. A. Weihrauch, D. W. Juhl, S. Bakalis, K. G. Malmos, and T. Vosegaard, Mobility of lactose in milk powders, *Food Res. Int.* (2025).
- [55] K. D. Foster, J. E. Bronlund, and A. H. J. (Tony) Paterson, The prediction of moisture sorption isotherms for dairy powders, *Int. Dairy J.* **15**, 411 (2005).
- [56] M. Müller-Petke, J. O. Walbrecker, and R. Knight, The inversion of surface-NMR T_1 data for improved aquifer characterization, *Geophysics* **78**, EN83 (2013).
- [57] J. O. Walbrecker and A. A. Behroozmand, Surface-NMR measurements of the longitudinal relaxation time T_1 in a homogeneous sand aquifer in Skive, Denmark, *J. Appl. Geophys.* **87**, 46 (2012).
- [58] M. Hansen and B. Pjetursson, Free, online Danish shallow geological data, *Geol. Surv. Den. Green. Bull.* **23**, 53 (2011).
- [59] C. L. Bray, R. G. Bryant, M. J. Cox, G. Ferrante, Y. A. Goddard, S. K. Sur, and J. P. Hornak, The ^1H nuclear magnetic resonance spin-lattice relaxation rate of some hydrated synthetic and natural sands, *J. Environ. Eng. Geophys.* **14**, 49 (2009).
- [60] A. J. Rossini, A. Zagdoun, M. Lelli, A. Lesage, C. Copéret, and L. Emsley, Dynamic nuclear polarization surface enhanced NMR spectroscopy, *Acc. Chem. Res.* **46**, 1942 (2013).
- [61] M. A. Hope, D. M. Halat, P. C. M. M. Magusin, S. Paul, L. Peng, and C. P. Grey, Surface-selective direct ^{17}O DNP NMR of CeO_2 nanoparticles, *Chem. Commun.* **53**, 2142 (2017).
- [62] A. Karabanov, D. Wiśniewski, I. Lesanovsky, and W. Köckenberger, Dynamic nuclear polarization as kinetically constrained diffusion, *Phys. Rev. Lett.* **115**, 020404 (2015).
- [63] J. Lehmann, A. Cowie, C. A. Masiello, C. Kammann, D. Woolf, J. E. Amonette, M. L. Cayuela, M. Camps-Arbestain, and T. Whitman, Biochar in climate change mitigation, *Nat. Geosci.* **14**, 883 (2021).
- [64] Y. Yuan, Q. Liu, H. Zheng, M. Li, Y. Liu, X. Wang, Y. Peng, X. Luo, F. Li, X. Li, and B. Xing, Biochar as a sustainable tool for improving the health of salt-affected soils, *Soil Environ. Health* **1**, 100033 (2023).
- [65] E. L. Belmont and D. L. Sanchez, Biochar's Long Game: Unraveling the Science of Carbon Permanence, 2025.
- [66] H. Sanei, A. Rudra, Z. M. M. Przyswitt, S. Kousted, M. B. Sindlev, X. Zheng, S. B. Nielsen, and H. I. Petersen, Assessing biochar's permanence: An inertinite benchmark, *Int. J. Coal Geol.* **281**, 104409 (2024).
- [67] H. Sanei, H. I. Petersen, D. Chiaramonti, and O. Masek, Evaluating the two-pool decay model for biochar carbon permanence, *Biochar* **7**, 9 (2025).
- [68] Y. Kuz'yakov, I. Bogomolova, and B. Glaser, Biochar stability in soil: Decomposition during eight years and transformation as assessed by compound-specific ^{14}C analysis, *Soil Biol. Biochem.* **70**, 229 (2014).
- [69] A. Afrough and T. Vosegaard. Zenodo. Lifetime distribution of multi-exponential recovery processes—data, <https://doi.org/10.5281/zenodo.15804940> (2025).
- [70] D. W. Juhl, Z. Tošner, and T. Vosegaard, *Versatile NMR Simulations Using SIMPSON* (2020), pp. 1–59.
- [71] J. Koppe, A. V. Yakimov, D. Giofrè, M.-E. Usteri, T. Vosegaard, G. Pintacuda, A. Lesage, A. J. Pell, S. Mitchell, J. Pérez-Ramírez, and C. Copéret, Coordination environments of Pt single-atom catalysts from NMR signatures, *Nature* **642**, 613 (2025).
- [72] M. W. Maciejewski, A. D. Schuyler, M. R. Gryk, I. I. Moraru, P. R. Romero, E. L. Ulrich, H. R. Eghbalian, M. Livny, F. Delaglio, and J. C. Hoch, NMRbox: A resource for biomolecular NMR computation, *Biophys. J.* **112**, 1529 (2017).