Coherent dynamical recoupling of diffusion-driven decoherence in magnetic resonance

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During recent years, dynamical decoupling (DD) has gained relevance as a tool for manipulating quantum systems and extracting information from them. This is particularly relevant for spins involved in nuclear magnetic resonance (NMR), where DD sequences can be used to prolong quantum coherences, or for selectively couple/decouple the effects imposed by random environmental fluctuations. In this Letter, we show that one can exploit these concepts in order to selectively recouple diffusion processes in restricted spaces. The ensuing method provides a novel tool to measure restriction lengths in confined systems such as capillaries, pores or cells. The principles of this method for selectively recoupling diffusion-driven decoherence, its standing within the context of diffusion NMR, and corroborating experiments, are presented.

PACS numbers: 03.65.Yz, 76.60.Es, 76.60.Lz, 82.56.Lz.

Introduction.— Understanding and manipulating the lifetimes of quantum coherences, play central roles in contemporary physics. Quantum decoherence effects can be mitigated in several ways [1]; most often, this is achieved by rotation pulses that decouple the system from its environment. While such trains of refocusing pulses are known since the early days of nuclear magnetic resonance (NMR) [2–5], these concepts have been generalized within the quantum information community by “dynamical decoupling” (DD) ideas [6–8]. These efforts aim at modulating the dephasing effects that environmental fluctuations will have on a quantum spin system; e.g., on filtering out modes in the environment’s spectral density noise. One form to achieve this entails designing DD sequences so that the time modulations experienced by the spins will minimize their overlap with the the noise’s spectral density [7, 9, 10]. This is usually done by varying the number of inversion pulses or the interpulse delays; such DD process can also help to characterize an environment’s spectral density [11, 12]. Introducing such changes, however, may bring complications of their own: varying the number of pulses may become a source of apparent decoherence via pulse imperfections [13]; and even if pulses are kept constant, varying their interpulse delay may lead to different total experimental times that may hamper the measurement being sought -for instance, by imparting differing spin-spin relaxation ($T_2$) weightings. These complications can be avoided if DD sequences retain a constant overall duration and number of pulses [14, 15], but depart from the dogma of using constant inter-pulse delays [8, 16]. In NMR this has been suggested as a new imaging (MRI) source of contrast [14]. In spectroscopic characterizations, the power of this concept was recently demonstrated by Selective-Dynamical-Recoupling (SDR) sequences [15], where both the total evolution time and the number of pulses remain fixed, while the interpulse delay distribution is systematically varied. Unlike conventional CPMG sequences, the SDR approach is immune to decoherence effects driven by cumulative pulse imperfections and/or to intrinsic $T_2$ spin-spin relaxation. SDR leads to was a constant-time experi-
Figure 1. Selective dynamical recoupling (SDR) sequence proposed for probing the diffusion spectrum, and involving (a) a sequence of \( N \) \( \pi \) pulses applied to the spins during a total evolution time \( T_E \); and (b) a constant magnetic field gradient \( G \). A conventional CPMG sequence would arise if \( x = y = T_E / N \); we refer to the \( N = 1 \) case as a Hahn-echo sequence. (c) Modulating function \( f_N(t) \) imposed by the sequence of pulses.

Modeling diffusion under dynamical decoupling.— Whereas the method proposed herein is general for probing fluctuations in a quantum two-level system interacting with a bath via a second-order system-environment Hamiltonian [5, 7], we consider for conciseness an ensemble of \( S = 1/2 \) spins that do not interact with each other, but are coupled to a classical external magnetic field. This field involves a uniform component along the \( z \) axis defining a dominant Larmor frequency, and a perturbing linear field gradient \( G \). Due to this gradient, diffusion-induced displacements will subject the spins to fluctuating precession frequencies. In a usual rotating frame of reference [5], the resulting Hamiltonian will be a pure dephasing interaction \( \hat{H}_{SE}(t) = \omega_{SE}(t) \hat{S}_z \), where \( \omega_{SE}(t) = \gamma G \tau(t) \) is the frequency (noise) felt by the spin, with \( \tau \) denoting direction of the gradient: \( G = \partial B_z / \partial r \).

Consider the application of a sequence of strong \( \pi \) pulses as shown in Fig. 1a, that periodically refocuses the spin ensemble after it has been subject to excitation. The sequence assumes \( N \) instantaneous pulses at times \( t_i \), with an initial delay \( t_1 - t_0 = x / 2 \) (\( t_0 = 0 \)), uniform delays \( t_i - t_{i-1} = x \) between the pulses for \( i = 2, \ldots, N - 1 \), and a final pulse at \( t_N = T_E - y / 2 \). \( t_{N+1} = T_E \) is the total evolution time, and the \( x \) and \( y \) delays are such that \( T_E = y + (N - 1) x \). Given the equidistant train of \( \pi \) pulses involved in the first part of the sequence we refer to it as involving a “CPMG” modulation [3, 4], and to the final single-inversion part of the sequence as a Hahn modulation [2]. This conforms to the SDR sequence [15] shown in Fig. 1. A constant gradient \( G \) given by an external action or local fields, is assumed to be active throughout the pulse train.

Under pulse-free conditions, the spin evolution operator for a given realization of a spatial random walk will be \( \text{exp} \left\{ -i \phi(T_E) \hat{S}_z \right\} \), where \( \phi(T_E) \) is the accumulated phase gained by the diffracting spin during \( T_E \). The effects that the pulse train in Fig. 1 will impose on the evolving spin can be accounted for by instantaneous sign changes of the evolution frequencies \( \omega_{SE}(t) \). After applying the \( N \) pulses the accumulated phase will be \( \phi(T_E) = \int_0^{T_E} dt' f_N(t', T_E) \omega_{SE}(t') \), where the modulating function \( f_N(t', T_E) \) switching between \( \pm 1 \) is as shown in Fig. 1c. Given an initial state \( \hat{\rho}_0 = \hat{S}_x \), the normalized magnetization arising from an ensemble of non-interacting and equivalent spins under the effects of this sequence will be \( M(T_E) = \langle e^{-i \phi(T_E)} \rangle \), where the brackets account for an ensemble average over the random phases. Without pulses \( \langle \phi(T_E) \rangle \) would depend on the position of each spin in the sample; as with all DD sequences, however, the average for the SDR case will be \( \langle \phi(T_E) \rangle = 0 \). Thus, assuming that the random phase \( \phi(t) \) has a Gaussian distribution [30, 31], \( M(T_E) = \text{exp} \left\{ -1/2 \left( \phi^2(T_E) \right) \right\} \); the signal will evidence a decay depending on the random phase’s variance. Assuming that this is solely given by the spins’ diffusion within \( G \), the exponential’s argument can be written in a Fourier transform representation [7, 22, 25, 26, 32] as:

\[
\frac{1}{2} \phi^2(T_E) = \frac{\Delta \omega_{SE}^2}{2} \int_{-\infty}^{\infty} dw S(w) |F(w, T_E)|^2.
\] (1)

This expression entails a product of the spectral density \( \Delta \omega_{SE}^2 S(w) \) characterizing the diffusion-driven fluctuation, times the filter function \( F(w, T_E) \) given by the Fourier transform of the modulation function \( \sqrt{2\pi} f_N(t', T_E) \). The spectral density \( \Delta \omega_{SE}^2 S(w) \) is given in turn by the Fourier transform of the autocorrelation function \( g(\tau) = \langle \Delta \omega_{SE}(t) \Delta \omega_{SE}(t + \tau) \rangle \), where \( \Delta \omega_{SE}(t) = \gamma G \left[ r(t) - \tau(t) \right] \) is the spin’s instantaneous frequency deviation from its average value, and \( \Delta \omega_{SE}^2 = \langle \Delta \omega_{SE}^2(0) \rangle \). Assuming \( g(\tau) \) follows an exponential decay, the spectral density of this fluctuation will be given by the Lorentzian function [30] [33]

\[
\frac{\mathcal{F} \mathcal{T} \{ g(\tau) \}}{\sqrt{2\pi}} = \Delta \omega_{SE}^2 S(w) = \frac{\Delta \omega_{SE}^2 \tau_c}{(1 + \omega^2 \tau^2_c)},
\] (2)

Here the correlation time \( \tau_c \) will be associated to a characteristic length \( l_c \), given by the diffusion process according to the Einstein’s expression \( l_c^2 = 2D_0 \tau_c \), where \( D_0 \) is the free diffusion coefficient. It also follows that \( \Delta \omega_{SE}^2 = \gamma^2 G^2 D_0 \tau_c \). If considering now diffusion in a pore or restricted cavity, the specific relation between \( l_c \) and the restriction length \( d \) of the pore will depend on its geometry; e.g. for cylinders a good approximation is \( \tau_c \approx 0.26^2 d^2 / D_0 \) [26, 34] and then \( l_c \approx 0.37 d \), where
$d$ is the cylinder’s diameter. Figure 2 compares the different behavior that, in units of the correlation time $\tau_c$, will be evidenced by the spin’s mean displacement $\langle |r(t)|^2 \rangle = \left\langle \left( r(t) - r(0) \right)^2 \right\rangle$ depending on whether diffusion is free or restricted.

Restricted and free diffusion: Effects on the SDR modulations.— With this scenario as background, we consider next the effects of the sequence in Fig. 1 for probing the kind of behaviors illustrated in Fig. 2. The “gist” of SDR is that it manages to distinguish these cases without varying $TE$ or the total number of intervening pulses, but rather using the flexibility that the delays $x$ and $y$ in Fig. 1, afford for shaping the $F(\omega, TE)$ filter function. To see this more clearly, consider the two segments in the SDR sequence - the Hahn and the CPMG modulations—separately. The diffusion-driven signal decay for a Hahn-echo sequence ($N = 1$, $x = 0$ in Fig. 1) [2] can be obtained analytically [35–37]; its decay is shown in Fig. 3 by the red dashes and circles. Also the analytical expression for the signal decay of a CPMG sequence, characterized by $N$ equispaced pulses ($x = y = TE/N$ in Fig. 1) can be calculated [37]; the ensuing magnetization decay is plotted in Fig. 3 (green crosses and triangles). The free diffusion regime exhibits the simplest behavior: since the delays between pulses $x, y \ll \tau_c$, the filter function $F$ peaks at frequencies $\omega \gg 1/\tau_c$ [10, 12, 25] and decoherence effects are dominated by the tail of the spectral density $D(\omega) \propto 1/\omega^2 \tau_c$ [38] (dashed red line in Fig. 4, top). The signal decay therefore follows a decay rate proportional to $\omega^{-2} = (TE/N)^2$ (dashes and crosses in Fig. 3). This result is well known and is derived in the original CPMG paper for freely diffusing spins [3]. By contrast, in the restricted diffusion regime, $\tau_c$ is short due to the confinement. The delays between pulses $x, y \gg \tau_c$, and the dominant peaks of the filter functions $F$ are at frequencies $\omega \ll 1/\tau_c$. In these cases the signal decay follows an exponential argument

$$\frac{1}{2} \langle \phi^2(TE) \rangle \approx \Delta \omega^2_{SE} \tau_c (TE - (1 + 2N) \tau_c). \quad (3)$$

The exponential magnetization decay at a rate $\Delta \omega^2_{SE} \tau_c$, is evidenced by the slopes in the solid black lines in Fig. 3. The second term in Eq. (3) [39] gives a shift depending on $N$, and is responsible for the $\Delta M_{SDR}$ gap separating the Hahn and the CPMG decays in Fig. 3. While normally the usual expression used for the restricted diffusion decay rate is just the first term of (3) [36, 40], the second term derived here is unique to the SDR sequence and provides a new degree of freedom for probing restrictions according to the choice of $x$. In particular if $x \ll \tau_c \ll y$, the decay of the signal during the SDR is dominated by the Hahn portion of the sequence and approaches $M_{SDR}(y) = \exp \{ 3(\Delta \omega^2_{SE} \tau_c^2 \} \exp \{ -\Delta \omega^2_{SE} \tau_c \}$; but if $x = y = 2TE/N \gg \tau_c$ the SDR decay will be $M_{restricted}(TE, N) = \exp \{ (1 + 2N) \Delta \omega^2_{SE} \tau_c \}$ exp $\{ -\Delta \omega^2_{SE} \tau_c \}$. Thus, the SDR approach allows one to probe $\tau_c$, and hence a confinement length $l_c$, from the difference between the Hahn and the CPMG decays $\Delta M_{SDR}$ that is built into the sequence. Notice that if $TE, y \gg \tau_c$, $\Delta M_{SDR} \propto \exp \{ 2(N - 1) \Delta \omega^2_{SE} \tau_c^2 \}$ independently from $TE, x$ or $y$. Moreover, while the exponential rate typically used for determining $l_c \propto \Delta \omega^2_{SE} \tau_c \times l_c^2$, the shift term $\ln \{ \Delta M_{SDR} \} \propto (N - 1) \Delta \omega^2_{SE} \tau_c^2 \propto (N - 1) l_c^2$ amplifies this new source of contrast with $N$, and makes it a more sensitive reporter on the value of $l_c$.

It follows that the sequence in Fig. 1 can interrogate restricted diffusion while fixing $TE$ as well as the number of inversion pulses, by dividing an echo train into periods.
representing an interference between these two filters: the sum of a CPMG portion, a Hahn portion, plus a cross term \( | | Hahn \text{ modulating functions.} \) The filter function \( f \) dominated regimes. The total sequence’s time modulation and determine the transition between Hahn- and CPMG-

involving different interpulse delays \( x \) and \( y \). By controlling the ratio \( x/y \) one can probe the spectral density \( S(\omega) \) and determine the transition between Hahn- and CPMG-dominated regimes. The total sequence’s time modulation \( f_{SDR} \) will then be given by

\[
f_{SDR}(t, TE) = f_{CPMG}^{N-1}(t, (N-1)x) + (-1)^{N-1} f_{Hahn}^{1}(t, (N-1)x, y), \tag{4}
\]

where \( f_{CPMG}^{N-1} \) and \( f_{Hahn}^{1} \) are the CPMG and the Hahn modulating functions. The filter function \( [F_{SDR}(\omega, TE)]^2 \) associated to SDR will thus be the sum of a CPMG portion, a Hahn portion, plus a cross term representing an interference between these two filters:

\[
[F_{SDR}(\omega, TE)]^2 = |F_{CPMG}^{N-1}(\omega, (N-1)x)|^2 + |F_{Hahn}^{1}(\omega, y)|^2 + 2 \text{Re} \{ e^{i\omega TE} [ -1 ]^{(N-1)x} y/2 \}
\]

This filter-function formalism allows one to derive a solution for the resulting signal decay

\[
M_{SDR}(TE, x, y, N) = M_{CPMG}^{N-1}(N-1)x, N-1) \times M_{Hahn}(y) \times M_{Cross-SDR}(TE, x, y, N), \tag{6}
\]

whose analytical expression is given in the supplementary information [37].

If \( x, y \gg \tau_c \), the restricted effects dominate both portions of the sequence; in such case \( M_{Cross-SDR} \approx 0.5 \exp \{-\Delta \omega^2_{SDR} \tau_c^2 \} \), and the SDR decay is independent of \( x \) and \( y \). This is just as the decay incurred by a CPMG sequence with \( N \) pulses (triangles in Fig. 3). If \( x < \tau_c \ll y \), the CPMG filter is far from \( S(\omega) \)’s maximum (Fig. 4); the SDR filter is mainly given by the Hahn portion, and the ensuing signal decay is dominated by \( M_{Hahn}^{restricted}(y) \). The interferences between the filters plays an important role when both the Hahn and the CPMG filter overlap strongly, close to \( S(\omega) \)’s origin (Fig. 4). The transition between these two decays happens around \( x \sim \tau_c \) (see Sup. Inf. for further details [37]).

It is worth concluding this paragraph by noting that the correlation time \( \tau_c \) can also be extracted by comparing the exponential decay curves of independent Hahn and CPMG sequences, or by changing the \( N/TE \) ratio of a CPMG set. Such variations, however, would require comparing signal decays arising from measurements involving different number of pulses or different overall \( TE \)’s. Only SDR manages to keep those parameters -whose variation could eclipse the diffusion effects being sought- constant throughout the measurements. As an example, the empty circles in Fig. 4(top) show the modification imparted on the noise spectrum by an intrinsic \( T_2 \) relaxation source, assumed given by a constant contribution within the plotted \( \omega \) range. If probed solely by CPMG, these changes would look similar to the effects brought about by changes in diffusion.

SDR measurements of restricted lengths.— As proof of SDR’s capabilities to accurately measure restricted diffusion, the sequence was applied to examine the diameter of water-filled microcapillaries with a nominal value of \( 5 \pm 1 \mu m \) (Polynrco Technologies, Phoenix, Az, USA). A free diffusion coefficient \( D_0 \sim 2.3 \times 10^{-5} \text{cm}^2/\text{s} \) was measured by a conventional NMR sequence [28] in which the orientation of an applied gradient vector coincided with the principal axis of the microcapillaries. \(^1\)H SDR curves of water diffusing within the capillaries were recorded in the presence of a transverse magnetic field gradient using a 9.4T Bruker microimaging NMR scanner, where the effects of background gradients \((G=0)\) were found negligible. Figure 5 shows the SDR modulations observed as a function of \( x \) with \( TE = 80 \text{ms} \), for values of \( G = 14.4 \) and \( 21.6 \text{G/cm} \). A transition from the diffusion-driven Hahn decay \((x \sim 0)\) to the CPMG decay \((x = TE/N)\) can be clearly appreciated in each data set; the difference between the \( x = 0 \) and \( x = TE/N \) conditions, \( \Delta M_{SDR} \), together with the dependence on \( x \) in general, provide a robust determination of the diffusion’s correlation time -and from there of \( l_c \). The fit between the analytical expression derived for the SDR decay (Eqs. (1.4)-(1.21) in the Sup. Inf. [37]) corresponding to particles diffusing in a cylinder [26, 34] and the experimental data is excellent, and so is the
agreement with the nominal inner diameter provided by the capillaries’ supplier. Note the resemblance in the behavior of the SDR curves in Fig. 5 and the $\langle \Delta r^2 \rangle$ in Fig. 2; in both cases curves plateau for times $x > \tau_c$, evidence a full sampling of the restricting space.

Discussion.— The fact that the different $\Delta M_{SDR}$ measured by SDR at constant $TE$ and $N$ are solely defined by $\tau_c$ and hence by $l_c$, provides a novel and simpler approach for determining restriction lengths by NMR. Alternative noninvasive methodologies for probing the compartment dimensions, foremost among them diffusion-diffraction phenomena [17, 28, 29], require very strong magnetic field gradients - stronger by $\sim 2$ orders of magnitude than the gradients demanded by SDR, when small pores are considered. For example, measuring diffraction patterns in cylindrical pores characterized by a restricting length scale of $\sim 5\mu m$ such as the ones used in this study, would require gradient amplitudes exceeding 1000 G/cm. Furthermore, methodologies that focus on probing a transition from free to restricted diffusion, will usually do so focusing on the deviations observed for the spectral density from power-law tails [21, 24–27, 40]. Instead, in the SDR case, the decay is dominated by the restricted diffusion regime: this makes $\Delta M_{SDR}$ a much more robust and sensitive means for determining length constraints.

This study demonstrated another instance where -as was the case with chemical exchange and $J$-coupling effects [15]- suitable DD schemes can extract coherent modulations from restricted NMR spectral fluctuations. As in previous spectroscopic demonstrations, a key ingredient to achieve these modulations is to have spins exchanging within a discrete/bound frequency spectrum, which DD can then probe by adjusting its filtering characteristics. The ensuing SDR method is particularly simple and undemanding; extensions of these studies to MRI measurements will be shown in upcoming publications. Additionally, we expect that this method can be useful for imaging other kinds of spectra at the nanoscale; for example by sensing the noise fluctuations generated by a host system on single spins in diamonds [11, 41].

We are grateful to Pieter Smith, Guy Bensky and Gershon Kurizki (Weizmann Institute) for fruitful discussions and to Prof. Yoram Cohen (School of Chemistry, Tel Aviv University) for providing the micro-capillaries used in this study. This research was supported by the Kamin-Yeda Project 711237 (Israel Ministry of Trade and Industry), a Helen and Martin Kimmel Award for Innovative Investigation, and the generosity of the Perlman Family Foundation. GAA acknowledges the support of the European Commission under the Marie Curie Intra-European Fellowship for career Development.

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Supplementary information for “Coherent dynamical recoupling of diffusion-driven decoherence in magnetic resonance”

Full analytical expressions of the SDR signal evolution under diffusion

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As mentioned in the section “Modeling diffusion under dynamical decoupling” section of the main text, the normalized magnetization arising from an ensemble of non-interacting and equivalent spins under the effects of a sequence of pulses will be \( M(t) = \langle e^{-i\phi(t)} \rangle \), where the brackets account for an ensemble average over the random phases \( \phi(t) \). For the dynamical decoupling sequences being considered the average phase \( \langle \phi(t) \rangle \) will be equal to zero. Then, assuming that the random phase \( \phi(t) \) has a Gaussian distribution \([1, 2]\), \( M(t) = \exp \left\{ -\frac{1}{2} \langle \phi^2(t) \rangle \right\} \): the signal will evidence a decay depending on the random phase’s variance. It is convenient to describe this variance in terms of the modulating functions.

\[
\frac{1}{2} \langle \phi^2(TE) \rangle = \frac{1}{2} \int_0^{TE} dt' \int_0^{TE} dt'' f_N(t', TE) f_N(t'', TE) \langle \omega^{SE}(t') \omega^{SE}(t'') \rangle
\]

\[
= \frac{1}{2} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt'' f_N(t', TE) f_N(t'', TE) g(t'' - t'),
\]

where \( f_N(t', TE) = 0 \) if \( t' < 0 \) or \( t' > TE \) (i.e., outside the evolution time range), and the evolution is given in terms of the frequency fluctuation correlation function \( g(\tau) = \langle \omega^{SE}(t') \omega^{SE}(t' + \tau) \rangle \). This correlation function is related to the fluctuation’s spectral density \( S(\omega) \) by a Fourier transform: \( \mathcal{F} \{ g(\tau) \} / \sqrt{2\pi} = \Delta \omega^{SE}_\omega S(\omega) \), where \( \Delta \omega^{SE}_\omega = \langle \Delta \omega^{SE}_\omega(0) \rangle \) is the mean square frequency fluctuation. Equation (S.1) can thus be recast in its Fourier representation \([3–8]\) as:

\[
\frac{1}{2} \langle \phi^2(TE) \rangle = \frac{\Delta \omega^{SE}_\omega}{2} \int_{-\infty}^{\infty} d\omega S(\omega) |F(\omega, TE)|^2,
\]

where \( F(\omega, TE) \) is the filter function introduced in Eq. 1 of the main text. Under the usual assumption of an exponential correlation function \( g(\tau) = \Delta \omega^{SE}_\omega \exp(-\tau/\tau_c) \), the ensuing spectral density will be

\[
\Delta \omega^{SE}_\omega S(\omega) = \frac{\Delta \omega^{SE}_\omega \tau_c}{(1 + \omega^2 \tau_c^2)} \pi
\]

where \( \tau_c \) is the correlation time of the fluctuations.

To calculate now the filter function \( F(\omega, TE) \) for the SDR sequence, it is convenient to consider the three time-modulating functions \( f(t, TE) \) in Fig. S.1. \( f^{free} \) is a Boxcar function, null if \( t < 0 \) or \( t > TE \) and constant otherwise (Fig. S.1a). Its filter function is therefore

\[
F^{free}(\omega, TE) = \sqrt{2\pi} \mathcal{F} \{ f^{free}(t, TE) \} = e^{-\frac{\omega \tau_c}{2}} \frac{\sin(\omega TE/2)}{\omega/2}.
\]

Following the recipe in Eqs. (S.1) and (S.3), this filter leads to a magnetization \([10, 11]\)

\[
M^{free}(TE) = \exp \left\{ -\Delta \omega^{SE}_\omega \tau_c TE \left[ 1 - \frac{\tau_c}{TE} \left( 1 - \exp \left( -\frac{TE}{\tau_c} \right) \right) \right] \right\}.
\]

Similarly one can obtain the Hahn echo filter by FT of the step function in Fig. S.1b:

\[
F^{Hahn}_1(\omega, TE) = i e^{-i \omega TE/4} \frac{\sin^2(\omega TE/4)}{\omega},
\]

and the corresponding signal becomes

\[
M^{Hahn}(TE) = \exp \left\{ -\Delta \omega^{SE}_\omega \tau_c TE \left[ 1 - \frac{\tau_c}{TE} \left( 3 + \exp \left( -\frac{TE}{\tau_c} \right) - 4 \exp \left( -\frac{TE}{2 \tau_c} \right) \right) \right] \right\},
\]

For a constant \( G \) and well defined pore geometries, the spectral density is a weighted sum of Lorentzian functions with different correlation times \([7, 9]\). However, usually one of these functions is more significant than the others and, particularly in our method dealing with confined planar, spherical or cylindrical geometries, a single term of the kind given in (S.4) dominates the SDR evolution. If the remaining terms also need to be accounted for, a weighted sum of decay terms in \( \frac{1}{2} \langle \phi^2(TE) \rangle \) with suitable, multiple values for \( \Delta \omega^{SE}_{i,\epsilon} \) and \( \tau_{c,i} \) in a series of Lorentzian terms need to be considered.
as is known from Refs. [10, 11]. Finally, for the CPMG square-wave modulation function in Fig. S.1c, the corresponding filter can be written as

$$F_N^{CPMG}(\omega, TE) = \frac{i 2 e^{-i^\omega TE} \sin \left( \frac{1}{4} \omega \frac{TE}{N} \right) \left( e^{i^\omega TE} + (-1)^{N+1} e^{-\frac{1}{2} i^\omega TE} \right)}{\cos \left( \frac{1}{2} \omega \frac{TE}{N} \right) \omega},$$

and we have calculated the corresponding magnetization as

$$M_{CPMG}(TE, N) = \exp \left\{ -\Delta \omega_{SE}^2 \tau_c \left[ TE - \tau_c (A + B) \right] \right\},$$

$$A = (2N + 1) - (-1)^N e^{-\frac{TE}{\tau_c}},$$

$$B = 4 (-1)^{N+1} \frac{e^{-\frac{\omega TE}{2\tau_c}} (e^{-\frac{\omega TE}{2\tau_c}} + e^{-\frac{\omega TE}{N\tau_c}} + e^{-\frac{\omega TE}{(N-1)\tau_c}} + e^{-\frac{\omega TE}{(N-2)\tau_c}} + e^{-\frac{\omega TE}{(N-3)\tau_c}} N + e^{-\frac{\omega TE}{(N-4)\tau_c}} (N-1))}{\left( e^{-\frac{\omega TE}{\tau_c}} + 1 \right)^2}. \quad (S.9)$$

One can use a similar approach to derive analytical expressions for the magnetization’s decay incurred by the SDR sequence considered in our study. The modulating function for the sequence \((x/2 - \pi - x - \pi - x/2)^{N-1} - (y/2 - \pi - y/2)\), entails a sum of the two cases just analyzed

$$f_{N,x,y}^{SDR}(t, TE) = f_{N-1}^{CPMG}(t, (N-1)x) + (-1)^{N-1} f_1^{Hahn}(t - (N-1) x, y). \quad (S.10)$$
Therefore, its corresponding filter function is
\[
|F^{SDR}_{N,x,y}(\omega, TE)|^2 = |F^{CPMG}_{N-1}(\omega, (N-1)x)|^2 + |F^{Hahn}_{1}(\omega, y)|^2
+ (-1)^{N-1}2\Re\left\{e^{i(TE-y)}F^{CPMG}_{N-1}(\omega, (N-1)x)F^{Hahn}_{1}(\omega, y)\right\}.
\] (S.11)

Hahn/CPMG cross-term

The analytical solution for the signal is then given by
\[
M_{SDR}(TE, x, y, N) = M_{CPMG}((N-1)x, N-1) \times M_{Hahn}(y) \times M_{Cross}(TE, x, y, N).
\] (S.12)

The first two terms on the right-hand side of Eq. (S.12) are as in Eqs. (S.8) and (S.9), while the cross term \(M_{Cross}(TE, x, y, N)\) has an argument

\[
- \ln \{M_{Cross}\} = \Delta \omega_{SE}^2 \tau_c^2 \left[1 + e^{-2/\tau_c} - 2e^{-\tau_c/\tau_c'} - 2e^{-2/\tau_c} + e^{-\tau_c/\tau_c'} + 4e^{-2/\tau_c} - 2e^{-2/\tau_c} + e^{-\tau_c/\tau_c'} + 4\right] + \left(-1\right)^{N} \times \left(e^{-\frac{N-1}{\tau_c'}} - 2e^{-\frac{3x}{\tau_c'}} + e^{-\frac{2(3x-2N)}{\tau_c'}} - 2e^{-\frac{3x}{\tau_c'}} + \frac{x(N-2)}{\tau_c'} + e^{-\frac{x(N-2)}{\tau_c'}}\right) / \left(\tau_c + 1\right).
\] (S.13)

With these general expressions at hand, one can consider the effects of a specific dynamics on DD; for example, the effects of free or a restricted diffusion. These will differ by their corresponding parameters \(\Delta \omega_{SE}^2\) and \(\tau_c\) and their respective spectral densities. In the restricted diffusion regime that concerns us we expect \(x, y \gg \tau_c\); the main contribution to the overlap (S.3) causing the signal’s decay, will then be dominated by the low frequencies at the center of the spectral density [12, 13]. In this case the signal decays of the sequences discussed in the previous paragraph become

\[
M^{restricted}_{free}(TE) \approx \exp \left\{-\Delta \omega_{SE}^2 \tau_c (TE - \tau_c)\right\},
\] (S.14)

\[
M^{restricted}_{Hahn}(TE) \approx \exp \left\{-\Delta \omega_{SE}^2 \tau_c (TE - 3\tau_c)\right\},
\] (S.15)

\[
M^{restricted}_{CPMG}(TE, N) \approx \exp \left\{-\Delta \omega_{SE}^2 \tau_c (TE - (1 + 2N)\tau_c)\right\},
\] (S.16)

\[
M^{restricted}_{Cross}(TE, x, y, N) \approx \exp \left\{-\Delta \omega_{SE}^2 \tau_c^2\right\}.
\] (S.17)

and the overall SDR decay is given by

\[
M^{restricted}_{SDR}(TE, x, y, N) \approx \exp \left\{-\Delta \omega_{SE}^2 \tau_c (TE - (2N + 2)\tau_c) - \Delta \omega_{SE}^2 \tau_c^2\right\},
\] (S.18)

\[
= \exp \left\{-\Delta \omega_{SE}^2 \tau_c (TE - (1 + 2N)\tau_c)\right\},
\] (S.19)

\[
= M^{restricted}_{CPMG}(TE, N).
\] (S.20)

Notice that in this restricted \(x, y \gg \tau_c\) regime all SDR decays are equal, and are actually independent of the \(x\) and \(y\) values: for all cases particles have experienced a maximum displacement between pulses. By contrast, if \(y \gg \tau_c\) but \(x\) is much smaller than \(\tau_c\), only the Hahn-echo portion of SDR will experience the restricted regime. In this limit \(M^{SDR}_{y,\tau_c}(TE, x \sim 0, y, N) = M^{Hahn}_{y,\tau_c}\). Important to highlight within the context of Fig. 2 that \(M^{y,\tau_c}_{SDR}\) grows with an exponential-like behaviour as \(x/\tau_c\) increases until achieving the value \(M^{y,\tau_c}_{SDR}(TE, x = y, y, N) = M^{restricted}_{CPMG}(TE, N) \approx \exp \left\{-\Delta \omega_{SE}^2 \tau_c (TE - (1 + 2N)\tau_c)\right\}\). Within this regime

\[
M^{y,\tau_c}_{Cross-SDR}(TE, x, y, N) \approx \exp \left\{-\Delta \omega_{SE}^2 \tau_c^2 \left(1 - \frac{2e^{-\frac{x}{\tau_c'}}}{1 + e^{-\frac{x}{\tau_c'}}}\right) \left(1 + (-1)^{N} e^{-\frac{x(N-1)}{\tau_c'}}\right)\right\},
\] (S.21)

and the overall signal becomes

\[
M^{y,\tau_c}_{SDR}(TE, x, y, N) \approx M^{restricted}_{Hahn}(y) \times M^{CPMG}_{y,\tau_c}((N-1)x, (N-1)) \times M^{y,\tau_c}_{Cross-SDR}(x, N).
\] (S.22)

Equation (S.12) was used for fitting the experimental data of Fig. 5 of the main text; however, the approximate expression (S.22) is indistinguishable from Eq. (S.12) for our experimental parameters.

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