

SUPPLEMENTARY INFORMATION

Simulations of the MRI experiments, results of which are seen in the theoretical curve fits to the data of Figs. 4a (direct spectral imaging) and 4b (indirect diffusional exchange based imaging), were derived from full first-principles Monte Carlo simulations purposely coded for analyzing the double-disc structure experiments. To ensure accurate results, the Monte Carlo simulations tracked the position, orientation and phase of upwards of several million simulated spins simultaneously randomly diffusing (with discrete time-steps down to a microsecond) through a three-dimensional water volume (that matched the dimensions of the chip sample holder) surrounding a two-dimensional grid of double-disc structures that corresponded to the test chip layouts. Cyclic boundary conditions were used to reduce the number of double-disc structures that needed to be simulated. Larmor frequencies at each spatial location in this volume (used to compute the total accumulated phase of each spin over its random walk) were calculated based on numerically integrated calculations of the fields from the array of magnetized double-disc structures. 90-degree off- and on-resonance pulses (and for the direct detection, also 180-degree spin-echo pulses) were simulated via re-orientation of only those spins that fell within the simulated resonant bandwidth of the applied pulses, as determined by the local Larmor frequency shifts at the location of each spin. Because self-diffusion distances over periods of order 100 microseconds (the typical pulse durations) can be appreciable at the micrometre scale, care was taken to simulate diffusion not just between applied RF pulses, but also during each RF pulse. Continual T_1 -longitudinal relaxation was accounted for by re-orientation of a set percentage of randomly chosen spins back into alignment with B_0 during each integration time-step. Signal acquisition was simulated based on the (time-varying) integrated field of all those spins within the readout bandwidth over the duration of the final simulated FID or spin-echo acquisition; since this integrated field included all magnetic field vector information (from orientation and phase of each spin), coherence / dephasing information was retained. Such coherence information impacts the direct imaging spin-echo spectra, but, apart from loss of transverse coherence between RF 90-pulses, it does not impact the indirect diffusional exchange experiments. For the direct spectral imaging, the simulated acquired spin-echo signals were then numerically Fourier-transformed to give the final spectra (such as that shown in Fig. 4a); for the indirect diffusion-based imaging, the total percentage of spins saturated out, or essentially the integrated area under the simulated FID, gives the value of any point in the z-spectra shown in Fig 4b (that is, the simulation is rerun for each point in the z-spectra instead of the single simulation run required for each direct imaging spectrum