distributions. Regularisation methods [1] were employed throughout the investigation and are based on a second-order derivative penalty function with the optimal regularisation parameter chosen by a generalized cross-validation technique. The various parameter distributions permit relatively small changes in composition and structure in one of the phases to be studied. For example, separation of a LAS-rich phase was detected on the surface of the drying mixture which effectively acted as a barrier to further drying. The spatially resolved moisture distributions for both test geometries are being used to verify and improve various droplet-drying models.

A fast pulsed field gradient (PFG) technique, Difftrain [2], which features a stimulated echo, was also used to measure the variation in apparent diffusion coefficient with Δ. These data enabled the tortuosity and surface-to-volume ratio of the water phase to be measured, as it resided amongst the solid constituent material. These measurements were performed as a function of moisture content within the mixture and as a function of drying rate. This was performed in situ on the same sample, as permitted by the rapid acquisition time of the Difftrain pulse sequence. Consequently, the evolving 'pore structure' occupied by the water was quantified during drying. These data are extremely useful in the generation of accurate models of the drying process, in particular the assignment of appropriate diffusion coefficients.

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NMR of diffusion in porous media: branched or disordered structure?

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Measurement of the spin-echo attenuation due to restricted diffusion is a usual NMR technique to probe the geometry of porous media [1]. In particular, the surface-to-volume ratio of statistically isotropic confining domain could be found in the slow diffusion regime [2]. However, natural morphologies often exhibit a complex internal architecture (e.g., branching of the pulmonary acinus or pore network in rocks). One may thus wonder what is the role of such structures for NMR measurements?

To answer these questions, we have performed Monte Carlo simulations of restricted diffusion in three groups of three-dimensional structures with the same surface-to-volume ratio (Fig. 1). A basic domain was a cube of size L divided into 216 small cubic cells. The first group (A) was a set of random dichotomic labyrinths generated inside the cube by the Kitaoka algorithm [3]. The second group (B) consisted of two realizations of a long channel filling the same cube. In the third group (C), disordered porous media were generated by connecting a number of randomly chosen adjacent cells.

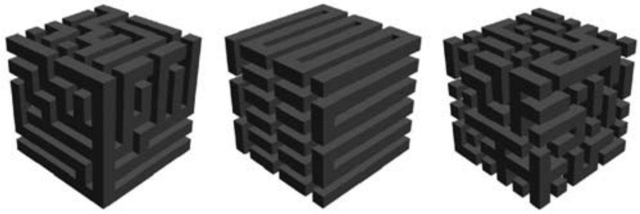

Fig. 1. Different porous media with an identical surface-to-volume ratio: a Kitaoka labyrinth (A), a long channel (B) and a disordered structure (C).

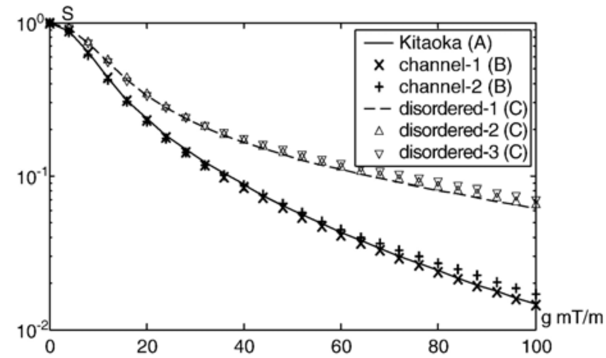

Fig. 2. Signal $S_{av}(g)$ for different porous structures shown in Fig. 1.

Stochastic trajectories of the diffusive motion $\mathbf{r}(t)$ with normal reflections on the boundary have been modeled as a sequence of n independent normally distributed random jumps with dispersion $(2D\tau)^{1/2}$, where D was the free diffusion coefficient, $\tau = T/n$ the smallest time scale and T the echo time. The total dephasing accumulated by a diffusing spin in a steady linear magnetic field gradient of intensity g in direction $\mathbf{e}$ was calculated as $(\mathbf{e}_x\varphi_x+\mathbf{e}_y\varphi_y+\mathbf{e}_z\varphi_z)$, where dephasing φ_i in direction i was

$$\varphi_i = \gamma g t \mathbf{e} \cdot \left(\sum_{k=1}^{n/2} \mathbf{r}(k\tau) - \sum_{k=n/2}^{n} \mathbf{r}(k\tau) \right)$$

γ being the nuclear gyromagnetic ratio (the minus sign accounts for gradient inversion, from the 180° RF pulse). The direction $\mathbf{e}$ of the applied gradient was uniformly averaged over all spatial orientations to reproduce isotropic behavior. The signal $S_{av}(g)$ was then obtained as the expectation:

$$S_{av}(g) = (4\pi)^{-1} \int_{|e|=1} \mathrm{d}\mathbf{e} \boldsymbol{E}\{exp[i(\mathbf{e}_x\varphi_x + \mathbf{e}_y\varphi_y + \mathbf{e}_z\varphi_z)]\} = \boldsymbol{E}\{sin(\varphi)/\varphi\}$$

where $\varphi = (\varphi_x^2+\varphi_y^2+\varphi_z^2)^{1/2}$. The probability distribution of the random variable $\ddot{u}$ was obtained by repeating Monte Carlo simulations N times. For water diffusion ($\gamma = 2.675 \cdot 10^8$ rad T^{-1} s^{-1}, $D = 2.3 \cdot 10^{-9}$ m^2/s) in a porous medium ($L = 60$ μm) with $T = 150$ ms, numerical results are summarized in Fig. 2 (here we used $N = 10^6$ and $n = 10^3$). One can see that the signal attenuation $S_{av}(g)$ for different *branched* structures (Groups A and B) are almost identical, while the signal for *disordered* media (Group C) is significantly higher. This is related to the fact that a disordered medium consists of a number of small disconnected patterns where the signal is less attenuated. We conclude that the internal structure of porous media may influence the restricted diffusion and NMR measurements and should be taken into account for practical applications.

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Probing a model pulmonary acinus by NMR gas diffusion

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Pathological changes in human lungs due to emphysema have been observed using MRI with hyperpolarised helium-3 (HP-^{3}He) [1,2]. The