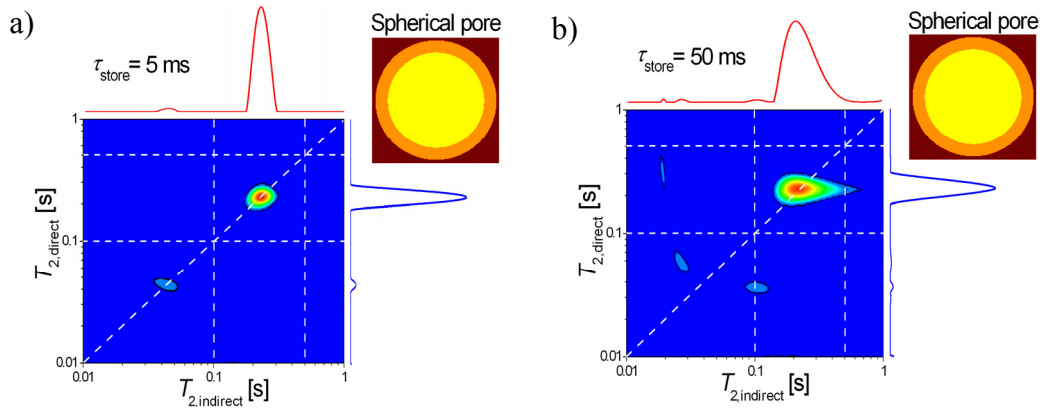

Fig. 1: Simulated 2D T_2–T_2 maps of exchange between bulk and a spherical shell of surface water for a) τ_{store} = 5 ms and b) τ_{store} = 50 ms. The vertical and horizontal dashed lines indicate the input T_2 values. For all simulations the diffusion coefficient was considered D = 2.299 × 10^{-9} m^2/s, the diameter of bulk water in spherical pore, d_{bulk} = 75 μm (yellow) and the pore diameter, d_{pore} = 95 μm (orange).

shifts on the diagonal peaks and strong asymmetry of the off-diagonal peaks. The interpretation of results in the presence of rapid exchange is not trivial, and Monte–Carlo simulations of molecular dynamics for systems composed of a relevant number of molecules, can be a useful approach. The 2D CPMG data were simulated assuming a fast exchange process and inverted using a fast Laplace inversion algorithm [3-4]. The results are T_2-T_2 exchange maps.

2. Monte-Carlo simulations of molecular exchange

The effect of molecular exchange on the 2D NMR T_2-T_2 distributions [1, 2] was studied by Monte–Carlo simulations. A homogeneous static magnetic field is assumed, and no disturbing effects like differences in the pore surface magnetic susceptibility are considered. The simulations consider a numerical map, were each voxel is defined by a particular value of the transverse relaxation time T_2. The transverse relaxation processes are considered for a relevant number of molecules, according to the molecular signature in the T_2 map. During the T_2–M_Z(store)–T_2 pulse sequence, a random-walk algorithm changes this position with a step dependent on the diffusion coefficient D. In all simulations, two relaxation times of 100 ms (represented in the T_2 maps by orange colour) and 500 ms (yellow colour) are considered. These values are represented in the 2D T_2–T_2 exchange maps by dashed lines. The line intersections represent the expected positions of the diagonal and off-diagonal peaks.

The main diagonal peaks areas are proportional to the population of components with a specific T_2 value. If the z-storage period, τ_{store} is large enough, the molecular exchange process is observed by the apparition of off-diagonal peaks (Fig. 1). Two additional effects can be observed: i) as a result of exchange processes, which depend on the ration of diffusion coefficient to pore size, the T_2 values are shifted to smaller values for all τ_{store} times (cf. Figs. 1a, b) and ii) the apparition of one or two non-symmetrical cross–diagonal peaks.

The molecular dynamics and the particular geometry of system can lead to a single off-diagonal peak (Fig. 2a). Such a single cross-peak it is often observed in the experimental data for fast exchange rates [2]. The simulation of 2D T_2–T_2 exchange maps of two spherical pores with the same diameter d_{pore} connected directly through a channel of length $d_{channel}$ presents this prevalent exchange. For a suitable distance between two pores, the classical pattern with two diagonal and two off-diagonal peaks is obtained (Fig. 2b). Geometrical factors of the system can be taken into account by changing the pore shape (Fig. 2c). In Fig. 2d the thickness of the pore shell, which is often described in terms of the surface–to–volume ratio, can have a great influence on the appearance of 2D T_2–T_2 exchange maps. A particular arrangement, observed experimentally in [1], is the occurrence of symmetrically positioned

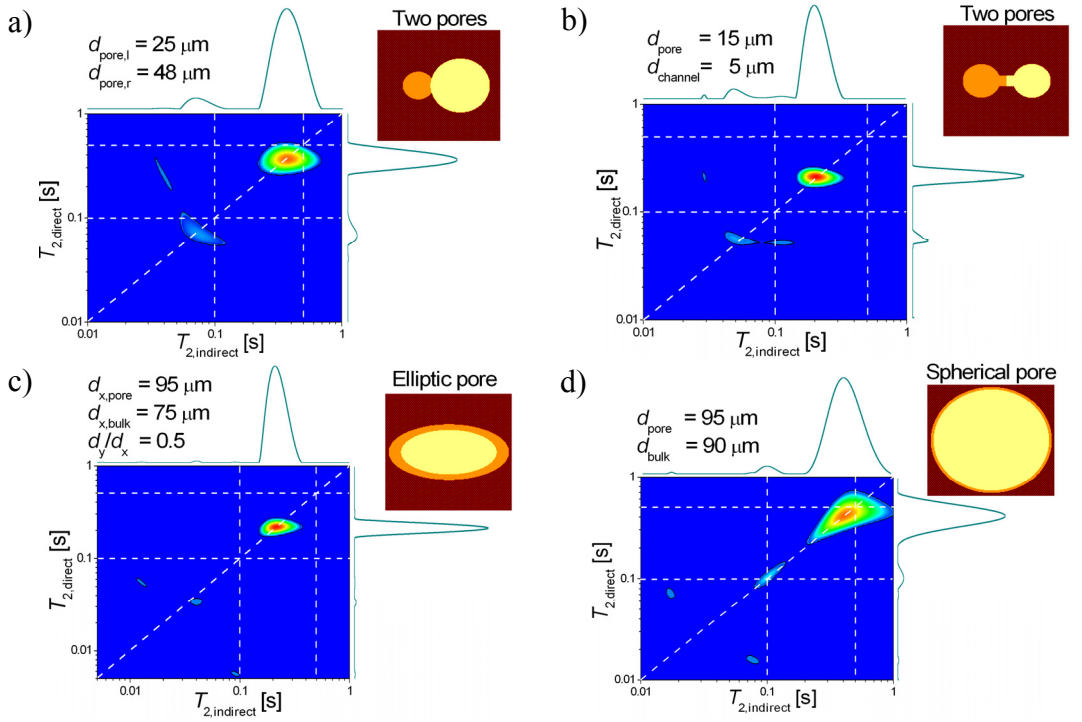

Fig. 2: Simulated 2D T_2–T_2 exchange maps at τ_{store} = 20 ms and D = 2.299 ×10^{-9} m^2/s for two pores connected a) directly; b) via a channel; c) elliptically pore and d) large pore with a small shell of surface water.

extra cross-peaks, which may wrongly be associated with an exchange process involving a rapidly relaxing component.

3. Conclusions

The Monte-Carlo technique was used to simulate the effects of molecular exchange on 2D NMR T_2–T_2 maps for idealized porous materials. Molecular exchange processes were considered during the CPMG encoding periods and storage time. These phenomena lead to particular features in 2D data, enriching in this way the structural and dynamic informations about porous materials. The matching of experimental data with simulated ones is considered to be an essential tool in understanding Laplace exchange NMR maps of complex materials. Compared to any analytical approach, the Monte-Carlo simulations can cover easily a broader range of relevant experimental situations. Moreover, relevant 2D or 3D maps of measured samples can be obtained, from NMR or other methods, and used in more realistic simulations.

Acknowledgements

This work was supported by Romanian Ministry of Research and Education under the project PN II 1102/2007.

References

[1]L. Monteilhet, J.-P. Korb, J. Mitchell, and P. J. McDonald, Phys. Rev. E **74**, 061404 (2006).
[2]R. Fechete, D. Moldovan, D. E. Demco, and B. Blümich, Diff. Fund. (MRPM9 Conf. Proc. accepted 2009).
[3]Y. Q. Song, L. Venkataramanan, M. D. Hürlimann, M. Flaum, P. Frulla, and C. Straley, J. Magn. Reson. **154**, 261-268, (2002).
[4]L. Venkataramanan, Y. Q. Song, M. D. Hürlimann, Solving Fredholm Integrals of the First Kind With Tensor Product Structure in 2 and 2.5 Dimensions, IEEE Trans. Sig. Process. 50, 1017-1026 (2002).