ELSEVIER

Magnetic Resonance Imaging 21 (2003) 421–450

MAGNETIC RESONANCE IMAGING

Abstracts of Posters

Influence of stagnant zones on transient and asymptotic dispersion in macroscopically homogeneous porous media

D. Kandhai[1,2], D. Hlushkou[3,4], A. Hoekstra[1], P. M. A. Sloot[1], H. Van As[3], U. Tallarek[3,5] [1]Section of Computational Science, University of Amsterdam, Amsterdam, The Netherlands [2]Kramers Lab. of Physical Technology, Delft University of Technology, Delft, The Netherlands [3]Laboratory of Biophysics and Wageningen NMR Centre, Wageningen University, Dreijenlaan 3, 6703 HA Wageningen, The Netherlands [4]Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany [5]Lehrstuhl für Chemische Verfahrenstechnik, Otto-von-Guericke Universität Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany.

A detailed understanding of transport in porous media over the intrinsic temporal and spatial scales is important in many technological and environmental processes. Natural and industrial materials like soil, rock, filter cakes or catalyst pellets often contain low-permeability zones with respect to hydraulic flow of liquid through the medium or even stagnant regions which remain purely-diffusive. Despite numerous theorectical, experimental and numerical studies the transient and asymptotic behaviour of dispersion in porous media is not completely understood. In particular, the influence of stagnant zones with respect to the actual mesoscopic and macroscopic flow field heterogeneity of the medium has found little attention in theory and experiment.

We have studied diffusion-limited mass transfer (1), transient and asymptotic longitudinal dispersion in single-phase liquid flow through a fixed bed made of spherical, permeable (porous) particles, covering several orders of characteristic time and length scales associated with fluid transport. The observed behaviour was contrasted to the corresponding fluid dynamics in a random packing of equally sized impermeable (nonporous) spheres with interparticle void fraction of 0.37. Experimental data for Pe up to 100 were obtained by pulsed field gradient NMR and were complemented by numerical simulations employing a hierarchical transport model with a discrete (lattice-Boltzmann) interparticle flow field using computer generated models of the interparticle pore space (2). Finite-size effects in the simulation associated with the spatial discretization of support particles or the dimension and boundaries of the bed were minimized and the simulation results are in reasonable agreement with experimental results.

We conclude that the intraparticle liquid holdup clearly dominates over contributions caused by the intrinsic flow field heterogeneity and boundary-layer mass transfer.

References

[1] Tallarek U, Vergeldt FJ, Van As H. 1999. Stagnant mobile phase mass transfer in chromatographic media: Intraparticle diffusion and exchange kinetics. *J. Phys. Chem. B.* 103: 7654–7664.

[2] Kandhai D, Tallarek U, Hluskou D, Hoekstra A, Sloot PMA, Van As H. 2002. Numerical simulation and measurement of liquid hold-up in biporous media containing discrete stagnant zones. *Phil. Trans. R. Soc. Lond. Ser. A* 360: 521–534.

A new view of the spin echo diffusive diffraction on porous structures

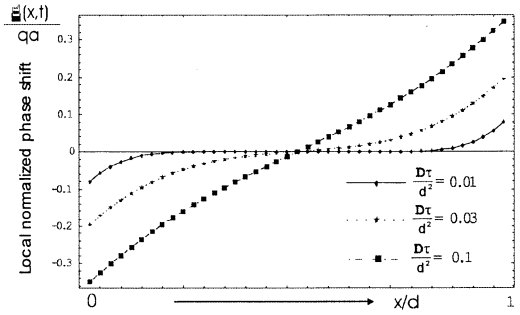

Figure 1.

Janez Stepišnik Physics Department, FMF, University of Ljubljana and J. Stefan Institute, Jadranska 19, 1000, Ljubljana, Slovenia

The diffraction-like effect of spin echo at the diffusion measurement in porous media1 conveys information about pore morphology. Phenomena was analysed with the use of characteristic functional for the stochastic motion. Its cumulant expansion in the Gaussian approximation gives the spin echo as $E(\tau) \approx \int V e^{i\phi(\tau,\mathbf{r})-\beta(\tau,\mathbf{r})} d\mathbf{r}$, where the phase shift depends on the local velocity $\phi(\tau,\mathbf{r})=\int_o^\tau \mathbf{F}(t).\langle \mathbf{v}(t,\mathbf{r})\rangle\, dt$ and the attenuation is related to the local velocity correlation function as $\beta(\tau,\mathbf{r}) = \int_0^\tau\int_0^t \mathbf{F}(t).\langle \mathbf{v}(t,\mathbf{r})\, \mathbf{v}(t',\mathbf{r})\rangle_c.\mathbf{F}(t')dt'\, dt$, where the dephasing $\mathbf{F}(t)$ is the integral of the gradient. As long as the number of molecular impacts at walls is small, the usual approximations with the mean velocity as $\langle \mathbf{v}(t,\mathbf{r})\rangle = 0$ and with the correlation $\langle \mathbf{v}(t,\mathbf{r})\, \mathbf{v}(t',\mathbf{r})\rangle_c$ as a delta function are reasonable. At longer times, we need better approximation. The average of cumulants with the probability distribution from Fick's diffusion equation2 provides distributions of phase shifts and attenuations in the volume of pore for any gradient sequence. Fig. 1 and Fig. 2 show the results for the diffusion between parallel planes, when PGSE sequence of sharp gradient pulses is applied. The integration over the space of pore gives the spin echo that exhibits diffraction-like patterns as shown in Fig. 3. The diffraction minima show dependence on gradient magnitude $q = F = \gamma\delta G$ as well as on time. At short times, they are shifted toward larger q, and depend on the spin displacement as $2q\sqrt{D/\pi} \simeq 2n\tau$. When the spin is starting to experience scattering on both opposite boundaries, the minima appear at value of $qa \simeq 2n\pi$\$, thus conveying information about pore dimension a. The method explains the dependence of diffraction on time and type of sequence. It introduces the diffusive diffraction as an interference of the

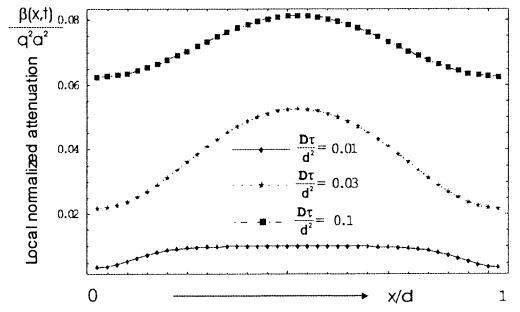

Figure 2.

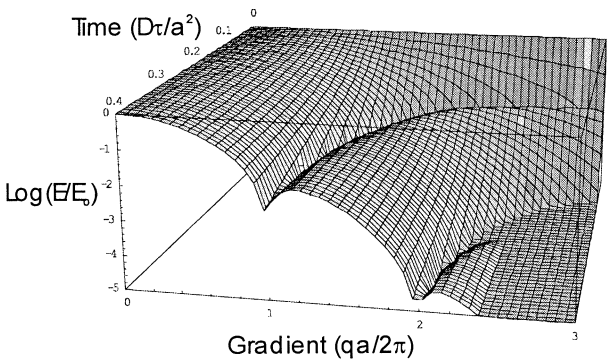

Figure 3.

phase shifts caused by the reflecting flow of spins scattered at the boundaries, when their displacements equal the phase grating created by applied gradients. This approach also enlightens the measurement of transport properties by the spin echo, particularly in the systems, where the molecular motion is constrained by structure or configuration.

References

[1] Callaghan PT, Coy A, MacGowan D, Packer KJ, Zelaya FO. Nature 1991;351:467–9
[2] Duh A, Mohorič A, Stepišnik J. Mag Res 2001;148:257–66
[3] Stepišnik J, Duh A, Mohorič A. To be published.

Spin relaxation enhancement in liquid gallium and indium confined within nanoporous matrices

E. V. Charnaya[a], D. Michel[b], C. Tien[c], Yu. A. Kumzerov[d] [a]Institute of Physics, St. Petersburg State University, St. Petersburg, Petrodvorets, 198504 Russia [b]Faculty of Physics and Geosciences, University of Leipzig, Leipzig, D-04103 Germany [c]Department of Physics, National Cheng Kung University, Tainan, 70101 Taiwan [d]A. F. Ioffe Physico-Technical Institute RAS, St. Petersburg, 194021 Russia

First studies of nuclear spin-lattice relaxation and lineshape in liquid gallium and indium confined within random and quasi-regular pore networks of porous glasses and artificial opals are presented. It is shown that drastic enhancement of the relaxation rate occurs for confined liquid gallium and indium which can be treated as a result of the rise in the quadrupolar contribution which follows the strong increase in the spectral densities at the Larmor frequency of the electric field gradient fluctuations and might evidence the remarkable slowing-down in atomic mobility.

The measurements were carried out using Avance400, MSL500 and MSL300 Bruker NMR spectrometers at room temperature for confined gallium and using an Avance400 spectrometer at 420 K for confined indium, the freezing transitions for metals within nanopores are lowered compared to that in bulk. The inversion recovery procedure was used to get data on spin-lattice relaxation.

The spin magnetization restoration curves obtained for both gallium isotopes, ^{69}Ga and ^{71}Ga, and for indium isotope ^{115}In showed remarkable enhancement in the relaxation rate compared to relevant bulk metals. The following main features can be noticed in data for gallium which contrast with those for bulk melt [1]: relaxation in the same field and in the same sample is noticeably faster for the ^{69}Ga isotope with greater quadrupole moment and smaller gyromagnetic ratio; the relaxation rate visibly depends on magnetic field for gallium within porous glasses. The fact that relaxation is faster for the isotope with larger quadrupole moment shows that the quadrupolar contribution dominates longitudinal relaxation in confined geometry contrary to the bulk case. This is also valid for transverse spin relaxation as can be seen from lineshapes. While NMR lines for both gallium isotopes are narrow and coincide for bulk, they are noticeably broadened for gallium within porous matrices and NMR linewidths are larger for ^{69}Ga than for ^{71}Ga. Moreover, the NMR linewidth against the ppm frequency scale increases with decreasing magnetic field, what corresponds to the quadrupolar nature of line broadening as in viscous liquids. NMR lines are also broadened for confined liquid indium. The remarkable enhancement of the quadrupolar relaxation rate as well as its dependence on the magnetic field show that the spectral densities of the electric field gradient correlation function which determine quadrupolar spin relaxation in confined gallium are strikingly increased and the extreme narrowing approximation is no longer valid. The results obtained for confined gallium as well as for confined indium are consistent with the assumption about strong increase in the correlation time of the electric field gradients fluctuations, which reflects remarkable slowing down atomic dynamics in nanopores. The estimates were made for the correlation time in pores, which depended on pore sizes.

References

[1] Charnaya EV, Loeser T, Michel D, Tien C, Yaskov D, Kumzerov Yu A. Phys Rev Lett 2002;88:097602

PFG NMR evidence for different apparent tortuosity factors in the Knudsen and bulk regimes of diffusion in a bed of NaX crystals

O. Geier, S. Vasenkov, J. Kärger Department of Interface Physics, University of Leipzig, Linnéstr 5, D-04103, Leipzig, Germany

Pulsed field gradient NMR was applied to study the ethane diffusion in beds of NaX zeolites for displacements, which are orders of magnitude larger than the size of the individual crystals. In order to probe the self-diffusion in the bulk and in the Knudsen regime the measurements were performed in a wide temperature range (193 K–413 K). The transition from the Knudsen to the bulk regime occurs with increasing temperature as a consequence of temperature dependence of the fractions of the molecules in the gaseous and adsorbed phases. All measurements were carried out using the home built PFG NMR spectrometer FEGRIS 400 operating at a ^{1}H resonance frequency of 400 MHz [1]. To rule out disturbing effects which are caused by internal field gradients together with the standard stimulated echo sequence also the 13-interval bipolar [2] PFG pulse sequence was employed.

Here, we report for the first time the direct experimental evidence that the apparent tortuosity factor in zeolite beds may be significantly larger in the Knudsen regime than in the bulk regime. The tortuosity factors were obtained by comparison of the measured diffusivities with those calculated using simple gas kinetic theory. The difference in the apparent tortuosity factors is not surprising in view of the different diffusion mechanisms in the Knudsen and in the bulk regimes. The reported results are in qualitative agreement with recent findings of dynamic MC simulations of gas diffusion in various porous systems [3,4]. The detailed explanation of the obtained results remains to be the subject of future research.

References

[1] Galvosas P, Stallmach F, Seiffert G, Kärger J, Kaess U, Majer G. Generation and application of ultra-high-intensity magnetic field gradient pulses for NMR spectroskopy. J Magn Reson 2001;151:260
[2] Cotts RM, Hoch MJR, Sun T, Markert JT. Pulsed field gradient stimulated echo methods for improved NMR diffusion measurements in heterogeneous systems. J Magn Reson 1989;83:25
[3] Burganos VN. Gas diffusion in random binary media. J Chem Phys 1998;109:6772
[4] Tomadakis MM, Sotirchos SV. Ordinary and transition regime diffusion in random fiber structures. AIChE J 1993;39:397