Hexane Self-Diffusion in Bed of Glass Spheres. Testing Applicability Range of the Pore-Hopping Model

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1. Introduction

PFG NMR experiment is in principle capable to provide important transport-structural parameters of system consisting of a liquid confined in a porous matrix such as surface-to-volume ratio and tortuosity. The apparent diffusion coefficient is easily obtained in the case of Gaussian shape of the diffusion propagator. Dependence of these values on the diffusion time in a short time limit is then used to derive the surface-to-volume ratio by means of the formula derived by Mitra [1]. Tortuosity is, on the other hand, derived from the long time limit of the apparent self-diffusion coefficient. The general description of the apparent diffusion coefficient dependence for all values of diffusion time has been facilitated by Padé approximant [2].

It has been shown previously several times that the assumption of Gaussian diffusion propagator may not be true for intermediate diffusion times. This effect is also called diffusion diffraction. Callaghan [3] reported interpretation of diffusion diffractions in beds of spheres by means of pore-hopping model.

2. Experiments and Methods

Glass spheres with diameters in the range 100 – 200 μm were placed into a standard NMR tube of 4.2 mm inner diameter. The tube was attached to a vacuum apparatus and evacuated for 2 hours at 200 C. Subsequently, distilled n-hexane was condensed into the cooled sample. Finally, the frozen sample was flame sealed.

The PFG NMR measurements were carried out on Bruker Avance 500 spectrometer operating at 500 MHz for ^{1}H. The pulse sequence based on stimulated echo and employing bipolar gradients of sine-bell shape (max. amplitude 0.56 T/m) was used.

3. Results and Discussion

The signal decays obtained in PFG NMR experiments for long diffusion times are reasonably Gaussian while the decays for short and intermediate times display significant deviations from Gaussian shape. This effect can be easily overlooked in the figure with

the scale linear in signal intensity because deviation from Gaussian shape occur at the values less than 10 % of maximum when they may also become hidden due to noise. Such simple minded fitting of a Gaussian results, however, in a significantly distorted dependence of apparent diffusion coefficient on the diffusion time.

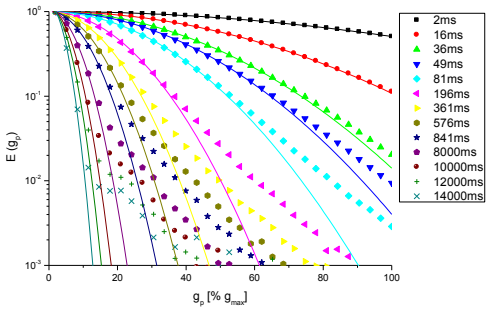

Fig. 1: Dependence of the obtained signal intensities E(g) (log scale) on the applied gradient (in relative units) for n-hexane in bed of glass spheres. Lines correspond to the Gaussian fit of the experimental datapoints.

We will test the applicability of the pore-hopping model [3] although some of its assumptions are not strictly fulfilled in this case. Firstly, the pore size *a* may not be truly negligible with respect to the diffusion time t (i.e. $\frac{D_0 t}{a^2} \gg 1$). Secondly, the size of pores varies over factor of 2 and, thirdly, distribution of distances between the cavities may not be sufficiently narrow.

3. Conclusion

Interpretation of the PFG NMR measurement in bed of spheres of ca. 100 μm diameter with a non-negligible distribution still presents a challenge to the available theoretical models.

References

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Acknowledgement The financial support by the Czech Science Foundation (P204/11/1206), by Charles University (SVV-2011- 263 305) and by the Ministry of Education of CR (research plan No. MSM 0021620835) is gratefully acknowledged.