Time-Dependent Molecular Diffusion in Partially Filled Porous Glasses with Heterogeneous Structure

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Abstract. Nuclear magnetic resonance (NMR) microscopy of silica glasses with micrometer pores (Vitrapori5) partially filled with water or cyclohexane reveals a heterogeneous distribution of liquid on a length scale much longer than the pore dimension. This heterogeneity, which is not observed in MR imaging of saturated samples, is attributed to the spatial variation of the granular microstructure visible in scanning electron micrographs. As a consequence of an inhomogeneous filling degree, the effective transverse relaxation time varies, which in turn leads to NMR imaging contrasts. Since the spatial distribution of the transverse relaxation time prevents reliable measurements with a standard pulsed gradient stimulated echo technique, a combination of the fringe field stimulated echo method, on the one hand, and the magnetization grid rotating-frame imaging technique, on the other, was employed. Four decades of the diffusion time from 100 ms to 1 s can be covered on this basis. The data were compared with Monte Carlo simulations of a model structure showing a qualitatively equivalent behavior in the common time window. The self-diffusion in partially filled porous systems is known to be strongly affected by a vapor phase. Here we have shown that the vapor phase contribution to the effective diffusivity is particularly efficient on a diffusion time scale corresponding to mean-squares displacements of the order of the pore dimension.

1 Introduction

Porous silica glasses are random objects intrinsically implying spatially fluctuating heterogeneities of the local pore size, the local magnetic susceptibility, the local transverse relaxation time of fluid, the local diffusion coefficient and other properties. These heterogeneities can be characterized by introducing spatial correlation functions defined as \( \langle f(\vec{r}_0) f(\vec{r}_0 + \vec{r}) \rangle \), where \( f(\vec{r}) \) is a property of the porous medium at the position \( \vec{r} \). The function \( f(\vec{r}) \) can be the fluctuating part of any of the quantities mentioned above. Assuming a vanishing ensemble average for spatial fluctuations, that is, \( \langle f(\vec{r}) \rangle = 0 \), and the coarse grain isotropy, we can restrict ourselves to an arbitrary direction, for example, \( x \). The correlation length \( l_c \) of any of those quantities is then defined by
\[ l_c = \int_0^\infty \frac{f(x_0)f(x_0 + x)}{f^2(x_0)} \, dx. \]

If the spatial correlation function is monexponential, this definition is consistent with \( \langle f(x_0)f(x_0 + x) \rangle / \langle f^2(x_0) \rangle = \exp(-x/l_c) \).

The correlation length may vary in an extremely wide range depending on the material. It will be shown that the porous glass mainly studied in the present paper, Vitrapor#5, with a nominal pore size of about 1 \( \mu \)m is subjected to heterogeneities almost approaching the sample size. One may speculate that the correlation length characterizing the extension of spatial fluctuations scales with the nominal pore size. That is, porous glasses such as the well-known and frequently studied Vycor with a nominal pore size of 4 nm may be subjected to the same sort of heterogeneities, which, however, are scaled down to a correlation length below the spatial resolution of magnetic resonance (MR) microscopy.

The use of a porous glass with pores in the micrometer regime thus permits to explore the nature of heterogeneities and their influence on measuring quantities such as the diffusion coefficient. The spatial variation of the fluid properties thus can readily be studied in the frame of the spatial resolution of MR microscopy \cite{1, 2}. It is the objective of the present study to demonstrate the material heterogeneities relevant for nuclear magnetic resonance (NMR) parameters and to compare them with scanning electron microscopy (SEM) images as far as available for systems with different nominal pore size and preparation history.

Unsaturated porous media are systems of coexisting liquid and vapor phases subjected to geometrical restrictions by the pore network, molecular exchange, and adsorption–desorption processes. The consequence is that the effective diffusion coefficient tends to be a function of the diffusion time \( t \). A time-dependent diffusion coefficient is defined by

\[ D(t) = \langle r^2(t) \rangle / 6t, \]  

where \( \langle r^2(t) \rangle \) is the mean-squares displacement of molecules. The time dependence is of particular interest since it globally reflects the spatial distribution of liquid in the pore space, the molecular exchange rates, the polarity of liquid and pore walls, and the geometrical character of the confining pore space.

Apart from treatment of the model unspecific limits of time-dependent diffusion coefficients \cite{3–5} and scaling arguments for certain percolation and fractal models \cite{6}, first-principles theoretical descriptions of the diffusion in partially filled pore spaces are rare. The reason is the complex nature of the microstructure that cannot be expressed in simple terms. Monte Carlo simulations are, therefore, a good way to relate and compare the experimental data with the model treatments.

There are a number of models for the spatial fluid distribution in partially filled porous media \cite{7, 8}. These morphology models often refer to the structure units such as plugs, puddles, surface layers of constant thickness, etc., which seem to be of a somewhat artificial character. In the present study, we therefore try to