

● *Short Communication***DIFFUSION AND RELAXATION IN INTERFACE LAYERS OF CRYSTALS IN NANOPOROUS GLASS**

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Water and tetradecane confined in porous glass of a mean pore diameter of 10 nm were investigated both above and below their freezing points with respect to their relaxation as well as diffusion behavior.

Below the freezing point, experimental data provide evidence for the existence of a non-frozen interface layer (NFL) between the crystal in the pore and the pore walls. The molecules in this layer are effectively confined in a quasi-two-dimensional space that forces them to reorient when moving along the curved pore surface. Through this relaxation mechanism, the translational mobility in the unfrozen phase reveals itself in a pronounced frequency dependence of the spin-lattice relaxation time. The experimentally observed drop of the self-diffusion coefficients by more than one order of magnitude below the phase transition can be interpreted in terms of geometric restrictions as well as interactions with the surface. © 1998 Elsevier Science Inc.

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INTRODUCTION

Previous relaxation studies of liquids confined in nanoporous glasses have revealed a strong frequency dependence of the spin-lattice relaxation time for polar liquids, in contrast to non-polar ones. These results were understood on the basis of bulk-mediated surface diffusion in the case of strong adsorption. In this case, reorientations mediated by translational displacements occur while molecules diffuse along the curved glass surface.¹ On the other hand, the reduction of the diffusivity with respect to the bulk is independent of molecular properties.² In addition, a pronounced frequency dependence was found in systems where the bulk-like phase is frozen and only a thin layer near the surface remains mobile for polar as well as for non-polar adsorbates.³ In this work, we compare the slow dynamics of water and tetradecane confined in porous glass above and below the phase transition. Furthermore, we investigate the self-diffusion properties of non-frozen layers (NFL) employing a constant field gradient of 60 T/m.

RESULTS AND DISCUSSION

Water and tetradecane were filled into porous glass with a mean pore diameter of 10 nm (Bioran B10, Schott Glaswerke, Mainz, Germany). Differential scanning calorimetry of freezing and melting inside the pores confirmed a narrow pore size distribution.⁴

For both adsorbates, the frequency dependence of the spin-lattice relaxation time below the melting point is characterized by a power law $T_1 \propto \nu^{0.65}$ for $2 \cdot 10^4 \text{ Hz} \leq \nu \leq 10^7 \text{ Hz}$ and a plateau value of T_1 of the order of 1 ms at lower frequencies (Fig. 1). Note the remarkable change of the relaxation dispersion of tetradecane in porous glass just above and just below the phase transition, while the slope of the curve for water remains about the same in both cases. The relaxation dispersion below the phase transition is governed primarily by reorientations mediated by translational displacements for water and tetradecane.

Free induction decays of both samples at temperatures down to the lowest accessible temperature show a slowly

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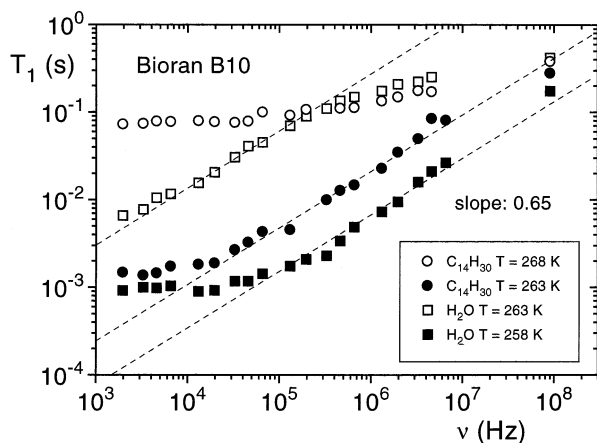


Fig. 1. Frequency dependence of the spin-lattice relaxation time of water and tetradecane in porous glass B10 (pore diameter, 10 nm) above and below the freezing or melting point, respectively. Below the phase transition, the data relate to the slowly decaying component, which corresponds to the NFL.

decaying component, which indicates the presence of a phase of high mobility. In the case of water, the T_2^* of this component approaches a plateau value below 220 K, whereas T_2 determined by the Hahn echo method is considerably longer in this temperature region (Fig. 2). Obviously, motional averaging is incomplete here and the Hahn echo decay is mainly determined by the exchange between the NFL and the crystal. A minimum in the temperature dependence of T_2 indicates an exchange process with an apparent activation energy of about 30 kJ mol⁻¹.

Water and tetradecane crystals may be considered as

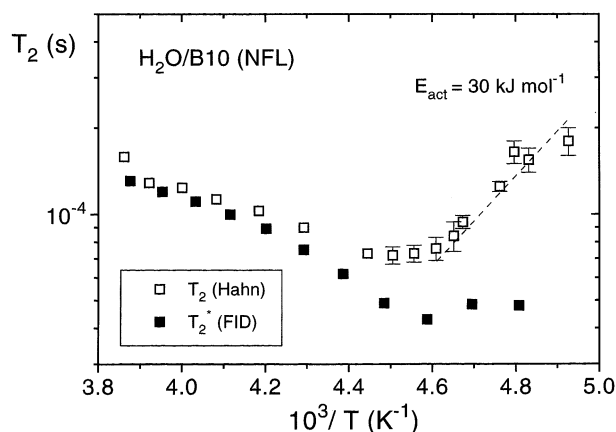


Fig. 2. Temperature dependence of T_2^* obtained from free induction decays and T_2 measured by the Hahn echo method for water in porous glass B10 (pore diameter, 10 nm). The data relate to the slowly decaying component corresponding to the NFL.

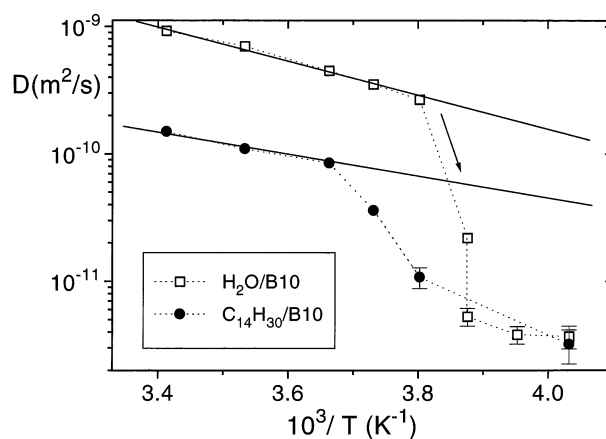


Fig. 3. Self-diffusion coefficients of water and tetradecane in porous glass (pore diameter, 10 nm), obtained with a diffusion time of 20 ms at a constant field gradient of 60 T/m. Straight lines represent Arrhenius fits to the experimental data above the freezing point.

rigid structures. The measured self-diffusion coefficients D therefore directly reflect the translational dynamics of the NFL. D is found to be time-dependent in the experimental range of diffusion times 5–50 ms. The values of the self-diffusion coefficient measured at 20 ms are shown in Fig. 3 for temperatures above and below the freezing point.

From the decrease of the nuclear magnetic resonance signal intensity it can be estimated that the presence of a solid phase reduces the space for the NFL down to 10–20% of the total pore space. The drop in D below the phase transition can be partly accounted for by this effect.

Although the absolute values of the diffusion coefficient for interface layers of water and tetradecane are similar, the reduction in D relative to the value above the freezing point is larger for water. In addition to a difference in the layer thickness, one can assume a further influence of molecule-surface interactions or an exchange process, as mentioned above, which immobilizes the molecules of water near the crystal surface for a certain time and therefore reduces their mobility.

CONCLUSIONS

The difference in the low-frequency relaxation behaviour of tetradecane confined in porous glass above and below the freezing point is shown to be a consequence of the phase transition. The self-diffusion coefficient of the unfrozen layers of water and tetradecane between the pore walls and the crystal inside the pore was directly determined for the first time. The reduction of the diffusion coefficient below the freezing point can at least in

part be attributed to the decrease in the effective porosity for the remaining liquid film. In the case of water, molecular interactions between the NFL and the solid surfaces probably are responsible for a further reduction of the molecular diffusivity.

REFERENCES

1. Stapf, S.; Kimmich, R.; Seitter, R.-O. Proton and deuteron field-cycling NMR relaxometry of liquids in porous glass-
es: evidence for Lévy-walk statistics. *Phys. Rev. Lett.* 75:2855–2858; 1995.
2. Kimmich, R.; Stapf, S.; Maklakov, A.I.; Skirda, V.D.; Khozina, E.V. Self-diffusion in fluids in porous glass: confinement by pores and liquid adsorption layers. *Magn. Reson. Imaging* 14:793–797; 1996.
3. Stapf, S.; Kimmich, R. Molecular dynamics in confined monomolecular layers: A field-cycling nuclear magnetic resonance relaxometry study of liquids in porous glass. *J. Chem. Phys.* 103:2247–2250; 1995.
4. Strange, J.H.; Rahman, M.; Smith, E.G. Characterization of porous solids by NMR. *Phys. Rev. Lett.* 71:3589–3591; 1993.