Ultraslow Molecular Dynamics of Organized Fluids: NMR Experiments and Monte-Carlo Simulations[1]

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1. Introduction

Recent successes in molecular engineering and nano-sciences have resulted in ever expanding production of new materials with complex structures and tailored properties. A complex functionality of these materials is in many cases achieved due to specific molecular ordering on meso- and macroscopic length scales. Such an ordering is in turn accompanied by multiple molecular (individual or collective) dynamical processes tending to range over many time decades. The challenging problems of modern NMR methods are concerned with addressing hierarchic structures, multi-scale molecular dynamics and ever increasing role of interfacial phenomena.

2. Methods

This work demonstrates the experimental results obtained for various fluids constrained in nano-structured materials by a few NMR techniques: stimulated echo relaxation studies [1], Field-Cycling Relaxometry [2], 2D-exchange spectroscopy [3], Pulsed Field Gradient diffusion measurements. The choice of the experimental techniques is determined by a necessity of decomposing numerous overlapping stochastic processes contributing to dipolar fluctuations in the same frequency or time scales.

3. Results and Discussion

All experimental data including transverse and longitudinal relaxation and diffusion demonstrate dramatic influence of cavity constraints on molecular collective and non-collective dynamical properties of confined liquids. This in particular refers to liquid crystals both above and below the bulk isotropization temperature. A strong pore size effect is reported for confined cyanobiphenyls.

For the interpretation, Monte Carlo computer simulations [3] were carried out. A reduced dipolar correlation function, $G_0^{red}(t)$, was evaluated for a random walker diffusing in a closed spherical or cylindrical cavity with ordering and/or adsorbing surface properties. Figure 1 shows typical results for a walker diffusing in a spherical cavity with ordered surface layer of thickness δr. The correlation function is characterized by fast and slowly decaying parts. Fast attenuation is due to dipolar correlation losses as the molecule diffuses from the ordered layer to the isotropic "bulk". The slowly decaying part is due to repeated returns of molecules to the ordered surface layer where the correlation to the initial orientation can partially be restored (the so-called process of Reorientations Mediated by Translational Diffusion [2]). The correlation time

of this process was examined as a function of δr, pore radius and surface adsorbing strength. Simulation results are discussed in comparison to experimental data.

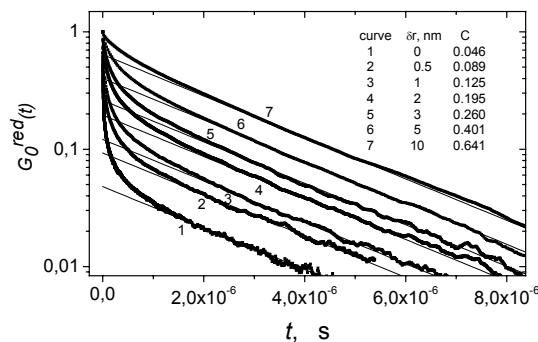| curve	δr, nm	C
1	0	0.046
2	0.5	0.089
3	1	0.125
4	2	0.195
5	3	0.260
6	5	0.401
7	10	0.641

Fig.1. Monte Carlo simulations of the reduced dipolar correlation function. The values of the thickness of the surface-ordered layer, δr, are indicated in the plot. The solid lines are fits of the function $C \exp(-t / \tau_c)$ to the long tails of the simulated functions.

3. Conclusion

NMR techniques supported by Monte Carlo simulations provide new insights to ultra-slow dynamics in organised liquids and permit one to determine important quantitative parameters like the correlation times of collective molecular motions or the correlation length of the surface-induced order in confined liquid crystals.

References

[1] F. Grinberg, M. Vilfan, E. Anoardo, in: E. E. Burnell, C. A. de Lange (Eds.), NMR of ordered liquids, Kluver Academic Publishers, Boston, Dordrecht, London, 2003.
[2] R. Kimmich, NMR: Tomography, Diffusometry, Relaxometry, Springer-Verlag, Heidelberg, 1997.
[3] F. Grinberg, in: J. Fraissard and O. Lapina (Eds.), NATO SCIENCE SERIES "Magnetic Resonance in Colloid and Interface Science", Kluver Academic Publishers, Dordrecht, 2002.

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[1] Most of the experiments were performed in the Sektion Kernresonanzspektroskopie (Universität Ulm, 89069 Ulm, Germany). Pulsed Field Gradient diffusion experiments were performed at Max-Planck Institute for Metals Research (Heisenbergstr. 3, 70569 Stuttgart, Germany)