

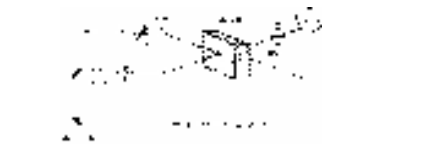


Dynamics of nanoconfined liquids

Introduction of OKE spectroscopy

Kerr Effect:

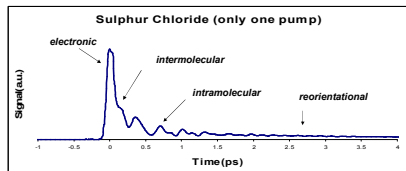
- Φ : Phase difference between the parallel & perpendicular components
- B: Kerr constant
- ℓ : The path length traveled in the sample
- λ : The light of wavelength



With the pump: $I = 0$

Without the pump: $I = 1$

Φ : Induced phase shift



Introduction of Nano-confinement

Effects:

- The structure of the liquids will be disrupted by the confinement at the scale of the structural correlation length of liquids;
- High surface-to-volume ratio induce strong liquid/surface interaction.

Technological applications: Separations, heterogeneous catalysis, lubrication, and microfluidics.

Nanoporous Sol-gel silicate

Glasses (excellent media):

- Pore size controllable;
- Surface modification;
- Different geometries;



Method

Preparation and Characterization of Sol-Gel Glasses

Preparation:

- Two-step acid/base-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS).
- Gellation: Pour the solution from step 1 into 1.5-cm-diameter polystyrene vials and cap tightly. The samples will gel within about 30 min.
- Aging: Control the final average pore size. One week or longer.
- Drying: A period of one month. By uncapping the sample vials and resealing them with Parafilm. The gel will harden and shrink during drying.
- Firing: Heating the dried monoliths in a muffle furnace to 800 ° C at a rate of 0.5 ° C per minute.

Characterization:

BET Sorptometer: the distribution of pore size.

Surface-Modification Procedure (*Hydrophilic* \rightarrow *Hydrophobic*)

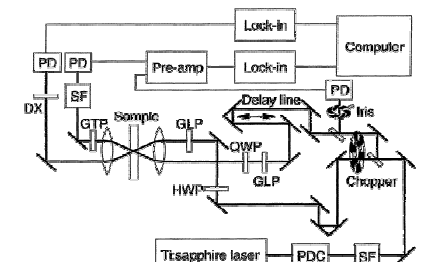
- Reflux sol-gel within an optical cell in a 50% solution of chlorotrimethylsilane in toluene (4 days);

- Washed successively in toluene, benzene, and methanol;

- In a 100° C vacuum oven for 24 hours to remove any volatile adsorbates.



Optical-Heterodyne-Detected OKE setup



- DX** = doubling crystal; **GLP** = Glan laser polarizer;
- GTP** = Glan-Thompson polarizer;
- HWP** = half-wave plate; **PD** = photodiode;
- PDC** = prism dispersion compensator;
- QWP** = quarter-wave plate; **SF** = spatial filter.

Results

Figure 1



Figure 2

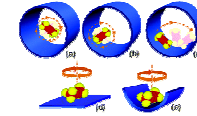


Figure 1, Collective orientational correlation functions for C6H6;
Figure 2, Collective orientational correlation functions for C6D6

The orientational time:

Hydrodynamic volume

Figure 3. Schematic depiction of the hydrodynamic volume required for a 2-butene molecule to reorient (a) far from a pore wall, (b) near a pore wall but pointing roughly along the surface normal, (c) off of a pore wall, (d) along a flat surface, and (e) along a curved surface.



Fit the OKE data: $S(\tau) \propto \sum_j A_j e^{-\tau/\tau_j}$

Sol-Gel cross-sectional schematic diagram

$$\frac{V_p}{V_{\text{Total}}} = \frac{\pi R_p^2 L}{\pi R^2 L} = \frac{A_p}{A} \rightarrow \frac{R_p}{R} = \sqrt{\frac{A_p}{A}}$$

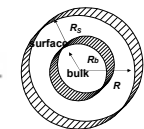


Table 1

Time (ps)	Signal
0	0
0.5	0.5
1.0	1.0
1.5	1.5
2.0	2.0
2.5	2.5
3.0	3.0
3.5	3.5
4.0	4.0

Table 2

Time (ps)	Signal
0	0
0.5	0.5
1.0	1.0
1.5	1.5
2.0	2.0
2.5	2.5
3.0	3.0
3.5	3.5
4.0	4.0

TABLE 1. Fit Parameters and Surface Layer Thickness for C6H6 in Unmodified Pores
TABLE 2. Fit Parameters and Surface Layer Thickness for C6D6 in Unmodified Pores

Figure 3



Figure 3, Collective orientational correlation functions for C6D6

Table 3, Fit Parameters and Surface Layer thickness for C6H6 in modified Pores

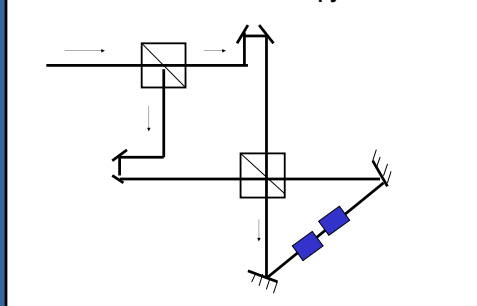
Table 4, Fit Parameters and Surface Layer thickness for C6D6 in modified Pores

Time (ps)	Signal
0	0
0.5	0.5
1.0	1.0
1.5	1.5
2.0	2.0
2.5	2.5
3.0	3.0
3.5	3.5
4.0	4.0

Conclusion

- In all cases the observed dynamics can be described well by the sum of two exponentials, (1) with a time constant that is somewhat longer than that for the bulk liquid and that depends on the pore size (2) with a much longer time constant that does not depend on pore size.
 - We assigned these two exponentials to bulk-like molecules in the pore centers and surface molecules, respectively. The slow surface relaxation is indicative of strong interactions between the liquid and the pore surfaces, which is consistent with the results of contact angle measurements.
 - In the unmodified pores, the surface layer has the thickness of about one benzene molecule, which suggests that the benzene molecules lie flat on the pore surfaces.
 - Comparison with Raman data supports this picture. Although benzene is not a networked liquid, in the centers of the pores its reorientational dynamics are still strongly influenced by confinement, which is reminiscent of what we have seen in confined water and suggests that benzene retains strong ordering in the nanopores.
- extend these studies to other confined aromatic systems and to make further comparisons with single-molecule orientational data.

Future Work: OKE microscopy



Acknowledgements



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