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Orientational ordering of linear *n*-alkanes in silicon nanotubes

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Orientational ordering of short and intermediate *n*-alkanes confined to silicon nanotubes has been studied using ^{1}H NMR. The measured residual nuclear dipolar couplings characterizing the degree of molecular ordering were found to depend on the pore size and the molecular length in a complex way. It is inferred from the experimental results that the observed behavior is governed by concomitance of surface and intermolecular interactions as well as the effect of confinement.

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Liquids under mesoscalic confinement exhibit different physical properties as compared to bulk state [1,2]. This is primarily determined both by increasing impact of surface interactions as scale goes down to nanometers and by effects of the confined space itself, leading to complex molecular organization. Prediction of a structure of confined liquids subjected to various interactions is therefore of general interest. In nanoscopically small objects, distinguishing between contributions of different interaction terms is often far from trivial and the possibility of their fine tuning may help to resolve their role on molecular properties. Today, controlled mesoporous materials with an option of surface modification are available that give a nice chance of fine tuning the steric and surface interactions. Simultaneously, choosing molecules as members of chemical family, e.g., *n*-alkane homologies, allows a systematic variation of the intermolecular term.

There is plenty of experimental evidence that *n*-alkane molecules (C_nH_{2n+2}) tend to orient at liquid-vapor as well as at liquid-solid interfaces [3,4]. One of the prominent examples is the surface freezing of long-chain *n*-alkanes ($n > 16$) near interfaces occurring at temperatures T_s higher than the bulk freezing point [4]. At higher temperatures, $T > T_s$, preferential orientation of *n*-alkanes is also observed, with the alignment director either perpendicular or parallel to the surface [5]. The effect of nanoscalic confinement upon molecular orientations achieved using two parallel surfaces has also been addressed in the literature (see, e.g., Ref. [6] and references therein), but rarely presented for mesoporous materials, where it is expected to be even more pronounced. Indeed, computer simulation studies of alkane-like molecules confined to cylindrical nanopores indicated their complex orientational behavior as a function of the position within the pore [7–9]. To explore these effects experimentally, application of noninvasive methods such as NMR may be advantageous [10–12].

The nuclear dipolar interaction is widely used to study the structure of molecules, relying on its dependency on the orientation of the internuclear vector and on the internuclear distance. In isotropic liquids it averages to zero due to fast molecular reorientations and fast molecular motion. In order to evade such averaging in the liquid state, there should be a molecular mechanism leading to an incomplete sampling of all orientations. This can be achieved if some source of anisotropy is present. Use of anisotropically arranged compartments, such as liquid crystals or lamellar structures, is one of the efficient methods to introduce a partial alignment of solute molecules leading to an observable residual dipolar coupling [13]. The latter is directly related to the molecular order parameter S and can be used to get insight into details of the molecular arrangement under confinement. In this paper, we exploit NMR spectroscopy to experimentally address the problem of orientational ordering of *n*-alkane molecules subject to anisotropic confinement at temperatures above the freezing point. Essentially, by the use of macroscopically extended one-dimensional pores instead of random pore networks, the averaging of the dipolar interaction on the NMR time scale of the order of milliseconds could be avoided [14,15].

As a porous material, porous silicon (PS) with one-dimensional channels oriented perpendicular to the substrate has been used [16]. It was prepared by electrochemical etching of single-crystalline (100)-oriented *p*-type Si wafers with resistivity of $(2-5)\times 10^{-3}$ Ωcm. The electrolyte contained HF (48%) and C_2H_5OH in a ratio of 1:1. PS with different pore sizes were produced using different anodization current densities j from 20 to 100 mA cm^{-2}. For removing the porous silicon film from the substrate, an electropolishing step with $j=700$ mA cm^{-2} was applied for 2–3 s. The thickness of the obtained PS wafers was about 60 μm. It is reported in the literature that this procedure, if at all, yields only a small density of intersections between the channels [17]. Two types of PS have been used, freshly made (the pore surface is SiH_x terminated, $x=1,2,3$) and thermally oxidized at 573 K in ambient air atmosphere for 3 h (SiO_2 terminated). For NMR experiments, well-powdered PS was used. NMR cryoporometry [18] exhibited a sufficiently narrow distribution of the pore sizes, yielding mean pore diameters from 6 to 10.2 nm and half-widths on half-height from 0.4 to 1.2 nm, respectively. These values were further found to be in a good agreement with the SEM data. The above described oxidation procedure resulted in a decrease of the pore diameters by about 0.4 nm due to the formation of a SiO_2 monolayer on the pore surface.

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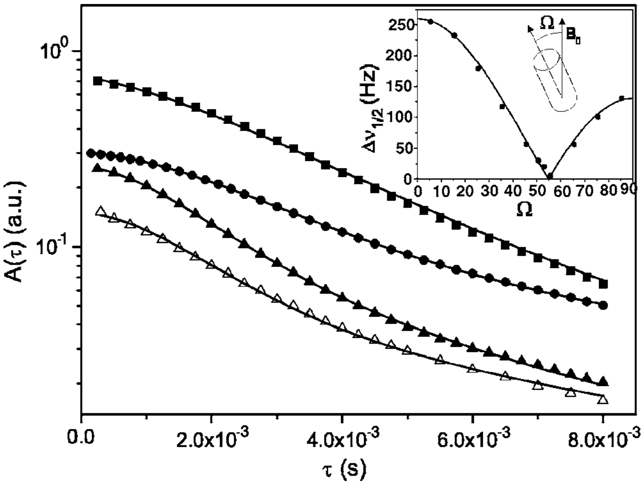

FIG. 1. Hahn spin-echo attenuation curves for heptane (squares), decane (circles), and pentadecane (triangles) in powdered PS with 6 nm pore diameter at 294 K. The filled and open symbols refer to measurements performed at different magnetic fields corresponding to proton resonance frequencies 400 and 125 MHz, respectively. The solid lines show the best fits using Eq. (2). Inset: The experimentally measured apparent dipolar broadening $\Delta\nu_{1/2}$ for pentadecane in oriented PS wafer. The solid line is a function 260 Hz $\times|(3\cos^2\Omega-1)/2|$.

^{1}H NMR transverse relaxation studies have been performed using the Hahn spin-echo pulse sequence $90°$-τ-$180°$-τ-echo. The spectrometer operated on a proton resonance frequency of 400 MHz. Typical experimental relaxation curves are shown in Fig. 1. They clearly do not follow the simple exponential form $A(\tau)=A_0\exp(-2\tau/T_2)$, typical of bulk liquids. Transverse nuclear magnetic relaxation of spin-1/2 nuclei in the homogeneous external magnetic field is caused by the interaction of nuclear spins with the fluctuating microscopic magnetic field. In porous materials, additional fluctuations arise from diffusion of spin bearing molecules in the inhomogeneous magnetic field due to magnetic susceptibility difference $\Delta\chi$ between the solid phase and the fluid filling the pore space. Depending on the ratio $D_s\tau/\xi^2$, where D_s is the self-diffusion coefficient and ξ is the characteristic length scale of the induced field inhomogeneities, one may distinguish two limiting cases [19]: (*i*) In the motional averaging regime $(D_s\tau/\xi^2\gg 1)$ the extra relaxation term in the spin-echo intensity is $2K(\omega_0\Delta\chi)^2\xi^2\tau/D_s$, where K is a geometry-dependent constant. (*ii*) In the limit of long correlation length $(D_s\tau/\xi^2\ll 1)$ the relaxation term is calculated to $2K(\omega_0\Delta\chi)^2D_s\tau^3/\xi^2$. With ξ of the order of the pore size and $D_s\approx 3\times 10^{-11}$ m^2 s^{-1} for the slowest diffusing molecule (eicosane; see Fig. 4), $D_s\tau/\xi^2\approx 8\times 10^2\gg 1$. This estimate yields that our experimental conditions well correspond to the regime (*i*) characterized by an exponential spin-echo decay with an effective relaxation time T_2^e. Thus, magnetic susceptibility effects cannot account for the nonexponential relaxation in our case.

The secular part of the homonuclear dipolar interaction of a two-spin system is given by

$$D_{ij}=-\frac{\mu_0\gamma^2}{4\pi r_{ij}^3}\frac{3\cos^2\theta_{ij}-1}{2}, \qquad (1)$$

where r_{ij} is the internuclear distance and θ_{ij} is the angle between the internuclear vector and the external magnetic field $\mathbf{B}_0$. This interaction may be of both intra- and intermolecular origin. In confined liquids, the orientations θ_{ij} may be not equally probable. Thus, the average over all molecular orientations, weighted by their probability, may result in a nonzero intramolecular residual dipolar coupling. Confined liquid crystals in isotropic phase [12] or partially oriented solute molecules between aligned liquid crystal molecules [13] exemplify such situations. It should be noted that intermolecular dipolar interaction of molecules confined to nanoscale volumes may also be subject to noncomplete averaging [20]. In our case, this mechanism may be ruled out because it should lead to equal dipolar couplings for liquids of the same density which is the case for *n*-alkanes.

In the presence of nonaveraged dipolar interactions the spin-echo intensity is modified to $A(\tau)=A_0\exp(-2\tau/T_2^e-2M_2\tau^2)$, where M_2 is a residual second moment which is related to the full-width at half-height dipolar line broadening $\Delta\nu_{1/2}$ measured in Hz by $\Delta\nu_{1/2}=2.36\sqrt{M_2}/2\pi$ [20]. Because of the tubular morphology of the pores in PS, the apparent second moment M_2 will depend on the orientation Ω of the pore axis with respect to the magnetic field $\mathbf{B}_0$, yielding the functional dependence $M_2(\Omega)=\bar{M}_2(3\cos^2\Omega-1)^2/4$ with $\bar{M}_2$ determined by the details of molecular alignment within the pore [12]. For isotropic arrangement of the PS wafers the spin-echo decay is therefore

$$A(\tau)=A_0\int_\Omega \exp[-2\tau/T_2^e-2M_2(\Omega)\tau^2]\sin\Omega d\Omega. \qquad (2)$$

Notably, the experimental data for $A(\tau)$ in Fig. 1 are well fitted by Eq. (2). The magnitudes of $\bar{M}_2$ obtained at different magnetic fields coincide with the estimate by Eq. (2) within the experimental precision, confirming the dipolar origin of nonexponential relaxation rather than magnetic susceptibility effects. Experiments performed with noncrashed PS wafers oriented at well-defined angles Ω with respect to the magnetic field (inset in Fig. 1) also show the $(3\cos^2\Omega-1)$ dependence, relevant for dipolar interaction.

The residual dipolar couplings (in the following referred to as D), as resulting from the measured second moments $D=2.36\sqrt{\bar{M}_2}/2\pi$ for *n*-alkanes of different chain lengths in PS with 6 nm pore diameter, are presented in Fig. 2. Remarkably, up to $n=15$, D increases with increasing chain length and thereafter decreases after some transient. Because D is related to the order parameter S (the estimated value of S is of the order of 1%), we may conclude that the molecules exhibit partial alignment. A similar increase of the order parameter has been reported for the short *n*-alkanes $(6<n<10)$ dissolved in a nematic liquid crystal serving as an aligning medium [21]. In our case, the observed decrease of D for $n>15$ may have two origins: (*i*) an increase of the molecular flexibility with the preserved orientation director leading to an additional averaging of the internuclear orien-

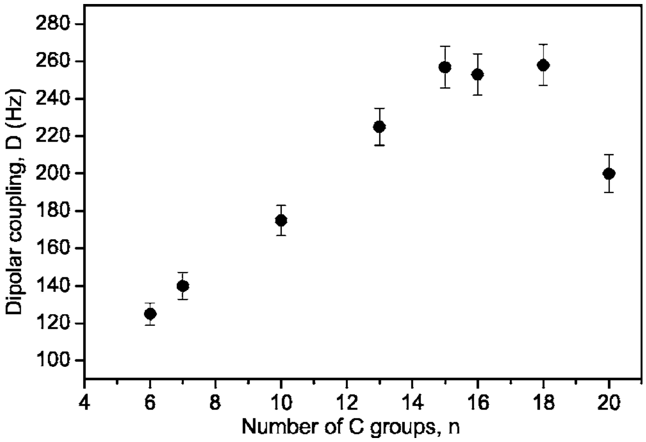

FIG. 2. Residual dipolar coupling D for linear alkanes C_nH_{2n+2} in SiH_x terminated porous silicon with 6 nm pore diameter as a function of the chain length.

tations and (*ii*) change of the orientation director to a state with a lower D. In what follows, we address this question using PS samples with different pore dimensions and surface chemistry.

In Fig. 3, typical dependencies of D on the pore size are shown. For $n \leqslant 16$ [Fig. 3(b)], D increases with pore size decreasing from 10.2 to 6 nm. However, for PS with $d=5.6$ nm a sudden decrease of D is observed. It is worth noting that PS with $d=5.6$ nm was obtained by thermal oxidation of freshly made, and hence SiH_x terminated, PS with $d=6$ nm, just like the samples with $d=9.8$ nm and $d=7.6$ nm have been prepared from SiH_x terminated PS with $d=10.2$ nm and $d=8$ nm, respectively. Since in these cases thermal oxidation gives rise to a slight increase of D, the drop of D observed for the PS with $d=5.6$ nm cannot be explained by possible changes of the surface interaction strength or the pore morphology. For longer n-alkanes, viz. eicosane with $n=20$ [Fig. 3(a)], some specific features become crucial. (*i*) In the SiH_x terminated pores eicosane exhibits the same tendency as observed for the shorter molecules. However, the drop of D with decreasing pore size is shifted to $d=6$ nm. This also supports the previous surmise that the decrease of the order parameter for the smaller pores does not ultimately result from the surface modification. (*ii*) Upon surface oxidation, D decreases by a factor of about 1.5 as compared to the freshly made samples.

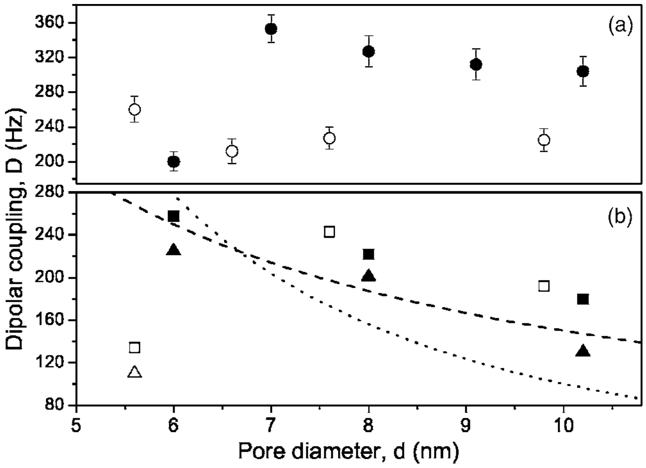

FIG. 3. Residual dipolar coupling D of n-alkanes as a function of the pore diameter d: (a) Eicosane $C_{20}H_{42}$ (circles) and (b) hexadecane $C_{16}H_{34}$ (squares) and tridecane $C_{13}H_{28}$ (triangles). The filled and open symbols refer to the freshly made (SiH_x terminated) and the thermally oxidized (SiO_2 terminated) porous silicon, respectively. Measurements have been performed at $T=297$ K except with eicosane which was measured at $T=300.5$ K. The dashed and dotted lines are the functions $1500/d$ and Eq. (3) with $r_c=1$ nm, respectively.

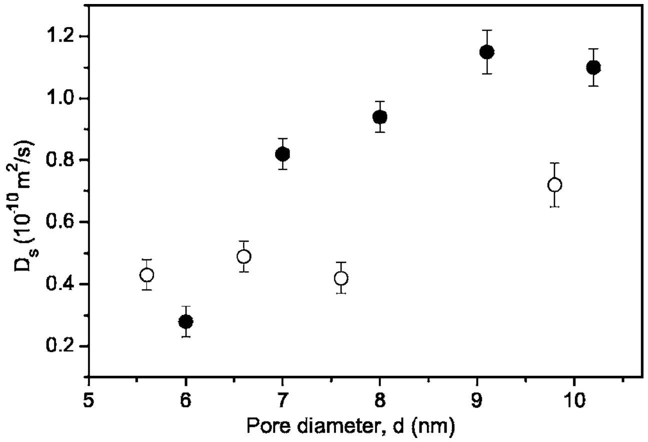

FIG. 4. Self-diffusion coefficients D_s for eicosane measured along the pore axes in freshly made (filled circles) and thermally oxidized (open circles) porous silicon as a function of the pore diameter d.

If the observed molecular alignment is mainly brought about by the short-range surface interaction, one may expect that only the molecules adjacent to the surface contribute to the overall measured D, which, in this case, has to scale with the specific surface area $S_v \propto d^{-1}$. The corresponding function shown in Fig. 3 by the dashed line fails to reproduce the experimental data. On the other hand, according to the Landau-de Gennes formalism developed for liquid crystals, the surface-induced molecular order in the isotropic phase may extend to ranges far from the surface. At distance r from the surface of a cylindrical pore of radius R, the molecular order parameter S is $S(r)=S_0\cosh(r/r_c)/\cosh(R/r_c)$ [12], where S_0 is the order parameter at the surface, and r_c is the correlation length. The average order parameter $\bar{S}(R)=\int_0^R rS(r)dr/\int_0^R rdr$ is then given by

$$\bar{S}(R) \approx \frac{2S_0 r_c}{R}\frac{\sinh(R/r_c)}{\cosh(R/r_c)}. \tag{3}$$

As an example, this function is shown in Fig. 3 by the dotted line. Noting that D is directly proportional to the order parameter $\bar{S}$, we may conclude that also this approach does not accurately enough describe the details of orientational ordering of n-alkanes in the system under study and that, hence, more sophisticated theories are required. Indeed, molecular simulation studies of flexible decane-like molecules in carbon nanotubes with radii of about 0.7 and 1.2 nm show that the order parameter is a complex function of the position within a cylindrical pore [7,8]. Particulary, it was found that near the surface molecules preferentially aligned along the pore axis, while at some position within the tube perpendicular orientation was preferred.

Our experimental results reveal that molecular orientational ordering is governed by an interplay of the surface and the intermolecular interactions as well as the effect of confinement. Consequently, with changing pore dimension, the distribution function of molecular orientation will correspondingly be modified to yield a lower free energy. The sudden drop of the dipolar coupling constant observed in small pores is, presumably, a manifestation of a change of the orientation director. Likewise, the passing of D through a maximum with increasing molecular length in the pores of a certain dimension may be considered as such an indication. Basing on the molecular geometry of n-alkanes, viz. the distances between the different protons and their orientation with respect to the molecular axis, it can be shown that alignment of the latter along the pore axis yields higher values of D. Thus, our experimental findings may be discussed in the framework of a partial orientation of the molecules along the pore axis in bigger pores and perpendicular to the surface in smaller pores. The same is relevant for eicosane in freshly made and oxidized PS samples. This picture is further supported by the data on molecular self-diffusivities shown in Fig. 4 as obtained using the pulsed field gradient NMR method [22]. Eicosane in the SiH_x terminated pores with $d > 6$ nm exhibits higher diffusivities as compared to that in PS with $d=6$ nm as well in the SiO_2 terminated pores. As expected, stretching of the molecules along the pore axis yields higher diffusivities [7].

In summary, the NMR method has been employed to study the details of molecular arrangement of n-alkanes in silicon nanotubes. Molecular length, pore size, and surface chemistry are identified as crucial properties to direct molecular orientation in either of the two limiting cases of preferential alignment along the pore axis and perpendicular to the surface.

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