How do rod-like molecules freeze and arrange in mesopores?

Patrick Huber, Dirk Wallacher, Tommy Hofmann and Klaus Knorr

Technische Physik, Universität des Saarlandes, 66123 Saarbrücken, Germany

E-mail: p.huber@mx.uni-saarland.de.

Abstract
We present an x-ray diffraction study on rod-like molecules, i.e. the normal
alkanes $C_{19}H_{40}$ and C_9H_{20} condensed in nanoporous Vycor glass. Temperature-
dependent diffraction patterns elucidate how the structure and phase behaviour
of these molecules are affected by the random substrate disorder and the
geometric confinement. For the medium-length alkane $C_{19}H_{40}$ a quenching
of the lamellar ordering is observed, whereas this geometric ordering principle
survives in the case of the short-length C_9H_{20}, although in a modified fashion.

1. Introduction

Studies of the influence of geometric confinement and random substrate disorder on physical
properties are topics of current interest which are under close scrutiny. There has already
been a tremendous deepening of the understanding of such phenomena resulting from studies
of condensates in nanoporous glasses (Christenson 2001, Radhakrishnan *et al* 2002). It has
been established for many types of pore filling, including van der Waals cryo-systems (Molz
et al 1993), many organic liquids (Jackson and McKenna 1990), and also water (Antoniou
1964) and metals (Unruh *et al* 1993), that the melting point T_m is lowered with respect to the
bulk triple point T_3, $\Delta T = T_3 - T_m$ being roughly proportional to the inverse pore radius R.
Despite the drastic geometric restrictions, diffraction studies on globular systems embedded in
nanopores have shown that the confined solids are closely related to the bulk state. Prominent
examples are krypton, argon, nitrogen, oxygen, and H_2O (Morishige *et al* 2000, Huber and
Knorr 1999a, Huber *et al* 1999b, Wallacher *et al* 2001).

Here, we focus on the structure and phase transitions of more complex molecular crystals,
built out of rod-like molecules, where the length L of the molecules is comparable to the pore
diameter D. It will be demonstrated that the alkane series allows one to probe in a systematic
way confinement effects, not by varying the confining host, but rather by changing the length
of the molecules.

For our study we have chosen the normal alkanes C_nH_{2n+2}, $n = 19$ and 9, embedded in Vycor glass. Vycor glass is a standard mesoporous substrate. Judging from a transmission electron microscope photograph, it can be described as a network of three-dimensional (3D) randomly connected tubular pores with relatively uniform diameter $d \sim 7$ Å (Levitz *et al* 1991). The normal alkanes constitute one of the most basic organic series. They are building blocks for surfactants, liquid crystals, and lipids. The C atoms of the zigzag backbone are all in the *trans*-configuration, so all of them are located in a plane. Since the alkane molecule length L_n is proportional to the number of C atoms n, whereas their diameter is independent of n, the alkane series allows one to easily vary the aspect ratio L_n/D of the molecule.

In the bulk state the medium-length alkanes form layered crystals. For $C_{19}H_{40}$ the molecules are aligned perpendicular to the layers. Within the layers the molecules are close packed, side by side, in a quasi-hexagonal two-dimensional (2D) array, described by in-plane lattice parameters a and b. The azimuth of the rotation of the –C–C– plane around the long z-axis of the molecule defines an orientation. In the low-temperature phase of the bulk alkane, termed 'crystalline' C, there are two different orientations which alternate in a herringbone fashion (figure 1(a), inset). On heating, this phase undergoes a phase transition at 294.8 K into a state of partial orientational disorder, the so-called 'rotator' phase R_I (Doucet *et al* 1981, Sirota *et al* 1993). Here the molecules flip between two equivalent positions. This phase melts at 304.5 K. Somewhat longer alkanes C_nH_{2n+2}, $21 < n < 26$, display another mesophase with complete orientational disorder (Sirota *et al* 1993), the phase R_{II}, in which the molecules perform hindered rotations or flips around the z-direction between three equivalent orientations. This phase has a strictly hexagonal metric, that is $a/b = \sqrt{3}$. See figure 1(a) for the orientational pattern of the three phases C, R_I, R_{II}. In figure 1(a) the x-ray powder pattern of the R_I phase of the bulk solid is depicted. The dominant peaks are a series of (00l) reflections at lower Bragg angles 2θ, which are related to the layered arrangement of the molecules, and the two principal in-plane reflections around 22°. In the hexagonal lattice of phase R_{II}, these two peaks would merge.

The short-length C_9H_{20} forms a triclinic phase upon freezing, with lattice parameters $a = 4.16$ Å, $b = 4.85$ Å, $c = 25.75$ Å, $\alpha = 83.4°$, $\beta = 77.4°$, $\gamma = 74.9°$. Due to the aspect ratio of L_9/D of 2.5, there is still a tendency towards formation of layers; however, the molecules are tilted by about 15° with respect to the c-direction; cf figure 2. In figure 2(a) the resulting bulk diffraction pattern is depicted. The quasi-layering gives rise to the two reflections at low angles ((002) and (004)), similar to the layering peaks of $C_{19}H_{40}$. Note, however, the plethora of reflections in the angular range from 20° to 30° due to the triclinic rather than orthorhombic cell in the case of $C_{19}H_{40}$.

2. Experiment

For the study of the pore condensed molecules, the Vycor glass matrix has been soaked with the liquid alkanes in an evacuated glass chamber at $T = 310$ K. Weight measurements of the glass monolith before and after filling, the known mass density of the bulk liquids, and the specific pore volume allowed us to calculate a filling fraction of $98 \pm 2\%$ of the pores for both samples. For an inspection of the structure of the different alkanes in the pores, x-ray diffraction patterns have been recorded between 200 and 310 and between 100 and 200 K for $C_{19}H_{40}$ and C_9H_{40} respectively, using a Bragg–Brentano para-focusing geometry (Cullity 1978). The radiation comes from a rotating Cu anode operating at 10 kW and is monochromatized by reflection from a graphite (002) crystal ($\lambda = 1.542$ Å). The diffraction patterns cover scattering angles 2Θ from 4° to 50°. The scattering background due to the amorphous SiO_2 matrix has been subtracted, properly accounting for the different x-ray absorption lengths.
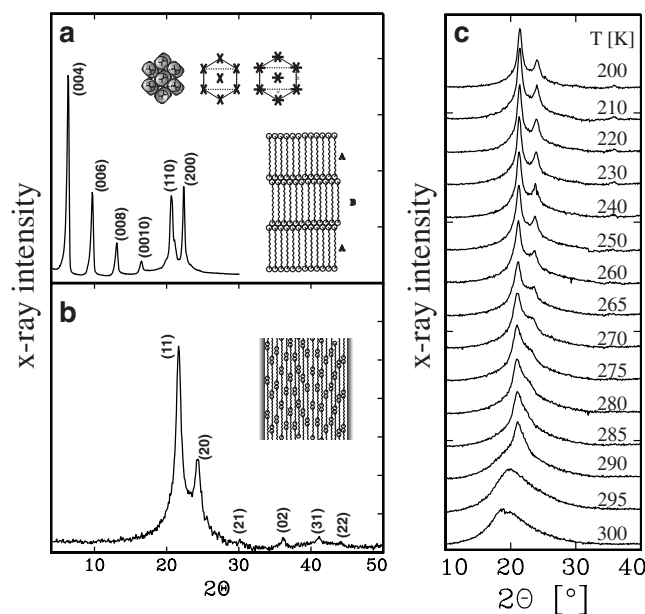
Figure 1. (a) The powder diffraction pattern of the R_I phase of bulk $C_{19}H_{40}$; indicated are the orthorhombic (*hkl*) reflections. The insets represent illustrations of the two building principles of the bulk crystals: the layering as well as a view along the chain axis of the bulk phases C, R_I, R_{II} (from left to right) showing the various degrees of order and disorder of the orientation of the plane of the –C–C– plane. (b) The powder diffraction pattern of pore condensed $C_{19}H_{40}$. The reflections are indexed on the basis of a 2D rectangular mesh. The schematic diagram depicts a schematic side view of *n*-alkane $C_{19}H_{40}$ in a mesopore. (c) Diffraction patterns of confined $C_{19}H_{40}$ in Vycor while cooling.

3. Results

3.1. Confined nonadecane—$C_{19}H_{40}$

The diffraction pattern of $C_{19}H_{40}$ embedded in Vycor at $T = 200$ K is shown in figure 1(b). The overall appearance is totally different from the bulk reference pattern: stronger diffracted intensity is confined to scattering angles of about 22°. In particular, the (00l) series of the bulk state has disappeared. In fact, the pattern of the pore solid can be derived from the bulk pattern by projecting the (*hkl*) Bragg peaks onto the basal plane, allowing for a slight adjustment of the in-plane lattice parameters *a* and *b*. The resulting indices based on this rectangular mesh can be found in figure 1(b). This means that the pore solid is an effectively 2D crystalline arrangement of molecules with random *z*-coordinates, while its in-plane arrangement has changed little. Hence one basic geometric ordering principle of the bulk crystalline alkane, i.e. the layering, is suppressed. An analysis of the coherence length ξ based on the widths of the diffraction peaks fitted with Lorentzians yields a continuous increase of ξ from about 30 Å just after freezing ($T = 292$ K) to about $\xi_{max} = 80$ Å at $T = 200$ K (Huber *et al* 2002). The saturated value ξ_{max} is close to the mean pore diameter of 70 Å in Vycor. This result can be explained only by an arrangement of the molecules' long axis parallel to the pore axis. A schematic view of the resulting structure of the pore solid with respect to the pore geometry is depicted in figure 1(b). Despite the obvious disorder of the *z*-positions, one should note that the confined alkane achieves by means of this adaptation to the pore geometry a close-packed lateral arrangement.

To further elucidate the phase sequence, particularly the freezing process, diffraction patterns were taken upon cooling. Figure 1(c) depicts selected patterns focusing on the angular range 20°–30°. At 305 K as well as 300 K, the diffraction pattern is governed by a broad peak centred around 19°. It is representative of the confined liquid alkane. Both temperatures are well below the melting temperature $T_m = 317$ K of bulk $C_{19}H_{40}$; thus the diffraction experiment indicates a reduced melting temperature for the confined alkane. At 290 K, the diffraction pattern shows additionally a peak at about 21°. This is the principal peak of a 2D triangular arrangement of the molecules and will be denoted as (11) in our nomenclature based on the aforementioned 2D rectangular mesh. During further cooling, the broad peak at 19° vanishes and a (20) satellite peak starts to develop. This behaviour witnesses the gradual loss of the hexagonal metric and an increase of the orientational order of the –C–C– backbones. A closer examination of the temperature dependence of the ratio a/b based on the splitting of the reflections reveals that for T lower 250 K a herringbone ordering is reached, very similar to the ordering known from the bulk state (Huber *et al* 2002).

3.2. Confined nonane—C_9H_{20}

Upon cooling of C_9H_{20}, diffraction peaks appear at 202 K, 17 K below the freezing point of the bulk liquid. In figure 2(b), we show the diffraction pattern of confined C_9H_{20} at 180 K. It is very similar to the one recorded for confined $C_{19}H_{40}$. In particular, the two reflections at 22° and 24° are at the same positions as the (11) and (20) reflections observed for confined $C_{19}H_{40}$. Note, however, that additional peaks are observable at about 6.5° and 13.4°. This is close to the quasi-layering reflections known from the bulk crystals, but both are shifted by about 1° to lower angles. The layer distance extracted from those reflections corresponds to 13.39 Å, a value which is in excellent agreement with 13.32 Å assuming an alignment of the molecules perpendicular to the c-direction. Along with the similarities with the confined $C_{19}H_{40}$, this suggests that for C_9H_{20} the confinement imposes an alignment of these molecules perpendicular to the layers, accompanied by an increased layering distance compared to that in the bulk C_9H_{20} with its tilted molecules. Furthermore, it should be noted that the reflections around 23° and above can be indexed as $(hk0)$ in terms of an orthorhombic unit cell. This means that any correlations of the lateral positions of the layers are lost in the pores. If such correlations existed, peaks of the type $(hkl), l \neq 0$, should show up. In summary, pore-confined C_9H_{20} still forms layers, but the correlations between the layers are lost and the molecules are aligned perpendicular with respect to the layers.

4. Discussion and summary

For both rod-like molecules, we observed a reduced freezing temperature of the confined liquid, in agreement with the results for many other liquids confined within nanopores. Additionally, the experiments on $C_{19}H_{40}$ revealed a quenching of one basic building principle of the confined solid, i.e. the lamellar ordering. Despite this disorder along the z-direction, the solid is able to mimic the orientational transitions known from the bulk.

On changing from a medium-length alkane to a short-length alkane, while keeping the pore diameter unchanged, the aforementioned disorder mechanism breaks down: for C_9H_{20} confined in Vycor glass, the lamellar ordering principle survives, which indicates that the interlayer interaction can overcome the disorder imposed by the glass matrix. Considering the stronger interlayer interaction in the short-length molecules, witnessed by the absence of true rotator phases in the bulk (Dirand *et al* 2002) as well as the reduced molecule length compared to the pore diameter and the accompanying reduced geometric constraints, this is perhaps not too surprising.
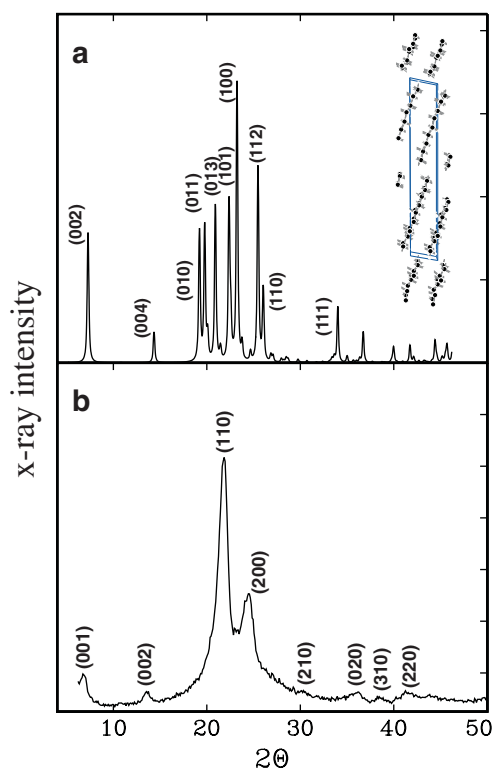
Figure 2. The powder diffraction pattern of bulk C_9H_{20} at $T = 216$ K. The reflections are indexed based on a triclinic cell (Espeau *et al* 1996). The schematic diagram illustrates the arrangement of the molecules in the triclinic unit cell. (b) The diffraction pattern of C_9H_{20} confined in porous glass at $T = 180$ K. The reflections (*hkl*) are indexed based on an orthorhombic unit cell.

In summary, this study provides a good example showing how the *n*-alkane series is well suited for use in studies focused on a systematic variation of the conditions of geometric confinement. Of course, further studies varying the pore diameter while keeping the chain length fixed would be interesting. Such studies may allow one to extract quantitative parameters for the interplay of interlayer and intralayer interactions in alkanes as well as parameters for the disorder imposed by the confining glass matrix. Therefore, they could go beyond the merely qualitative picture presented here.

References

Antoniou A A 1964 *J. Phys. Chem.* **68** 2754
Christenson H K 2001 *J. Phys.: Condens. Matter* **13** R95
Crawford G P and Zumer S (ed) 1996 *Liquid Crystals in Complex Geometries* (London: Taylor and Francis)
Cullity B D 1978 *Elements of X-ray Diffraction* (Reading, MA: Addison-Wesley)
Dirand M, Bouroukba M, Chevallier V and Petitjean D 2002 *J. Chem. Eng. Ref. Data* **47** 115

Doucet J, Denicolo I and Craievich A 1981 *J. Chem. Phys.* **75** 1523

Jackson C L and McKenna G B 1990 *J. Chem. Phys.* **68** 9002

Espeau P, Robles L, Mondieig D, Haget Y, Cuevas-Diarte M A and Oonk H A J 1996 *J. Chim. Phys. Phys.-Chim. Biol.* **93** 1217

Huber P and Knorr K 1999a *Phys. Rev.* B **60** 12657

Huber P, Wallacher D and Knorr K 1999b *Phys. Rev.* B **60** 12666

Huber P, Wallacher D, Albers J and Knorr K 2002 to be published

Levitz P, Ehret G, Sinha S K and Drake J M 1991 *J. Chem. Phys.* **95** 8

Molz E, Wong A P Y, Chan M H W and Beamish J R 1993 *Phys. Rev.* **48** 5741

Morishige K, Kawano K and Hayashigi T 2000 *J. Phys. Chem.* B **104** 10298

Radhakrishnan R, Gubbins K E and Sliwinska-Bartkowiak M 2002 *J. Chem. Phys.* **116** 1147

Sirota E B, King H E, Singer D M and Shao H H 1993 *J. Chem. Phys.* **98** 5809

Unruh K M, Huber T E and Huber C A 1993 *Phys. Rev.* B **48** 9021

Wallacher D, Ackermann R, Huber R, Enderle M and Knorr K 2001 *Phys. Rev.* B **64** 4203