LETTERS TO NATURE

Commensurate 'freezing' of alkanes in the channels of a zeolite

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FLUIDS confined in narrow pores can have properties that are distinctly different from those of bulk fluids[1,2]. Most studies of fluids in pores have focused on simple fluids which can be modelled as near-spherical molecules. But molecular shape can also exert an influence on the fluid's behaviour, particularly for large and/or complex molecules. The adsorption isotherms of alkanes in the zeolite silicalite provide an apparent example of this: the short-chain (C_1 to C_5) and long-chain (C_{10}) alkanes have simple isotherms[3-5] whereas for hexane and heptane the isotherms are kinked[4,6], suggesting that some kind of phase transition takes place. Here we present computer simulations of the adsorption of straight-chain hydrocarbons in silicalite, which suggest that this phase transition is of a type not reported previously, arising as a consequence of the interplay between the length of the zig-zag pores and the length of the alkanes. When these two are comparable, the molecules can 'freeze' in a configuration that is commensurate with the pore structure, creating a kink in the isotherms. Such behaviour might be quite general for complex molecular fluids.

Zeolites are crystalline materials that have a well defined microporous structure. Next to their strong acidity, selective adsorption of molecules in the micropores forms the basis of the application of these materials as catalysts in refining and in the petrochemical industries[7]. Traditionally, research has focused on trying to understand catalytic conversion in the pores of the zeolite; less attention has been paid to the sorption properties *per se*. This lack of knowledge has long hampered the understanding of phenomena such as the 'compensation effect', which is the unexpectedly high conversion of long-chain alkanes seen in catalytic cracking[8]. The explanation of this effect has been the subject of many discussions and it is only recently that it has been attributed to differences in sorption behaviour of the alkanes[8]. This example shows that quantifying the sorption effects not only is a prerequisite for the design and optimization of catalysts, but can even lead to a better understanding of the fundamentals of zeolite catalysis.

Adsorption isotherms are also of fundamental interest as they may signal phase trasitions, such as capillary condensation or wetting, of the fluid inside the pores[2]. For example, if a system exhibits capillary condensation, one would measure a stepped adsorption isotherm with hysteresis. Steps or kinks without hysteresis are occasionally observed on flat substrates[1]. As the pores of most zeolites are of molecular dimensions, adsorbed alkane molecules behave like a one-dimensional fluid. In a one-dimensional system phase transitions do not generally occur[9] and therefore one would expect that for alkanes the adsorption isotherms are of type I[1], that is, they do not show kinks or steps. If steps occur, they are usually attributed to capillary condensation in the exterior secondary pore system formed by the space between different crystals[3]. For silicalite, adsorption isotherms have been determined for various *n*-alkanes: for the short-chain alkanes (methane–pentane) the isotherms are indeed of type I[3,4], as observed also for decane[3,5]. For hexane and heptane, however, a kink or step is observed[4,6]. To the best of our knowledge, no molecular explanation of this peculiar behaviour of hexane and heptane has been given.

At present, data on sorption properties are scarce because experiments are difficult and time-consuming, in particular at

reaction conditions[8]. Computer simulations seem to be an alternative to quantify the sorption behaviour. Molecular simulations of adsorption are conveniently performed in a grand-canonical ensemble, which corresponds closely to the experimental arrangement: a zeolite in open contact with a reservoir that fixes the temperature and chemical potential. The number of particles in the zeolite is allowed to fluctuate via Monte Carlo moves in which one attempts to add or remove a particle. Particularly
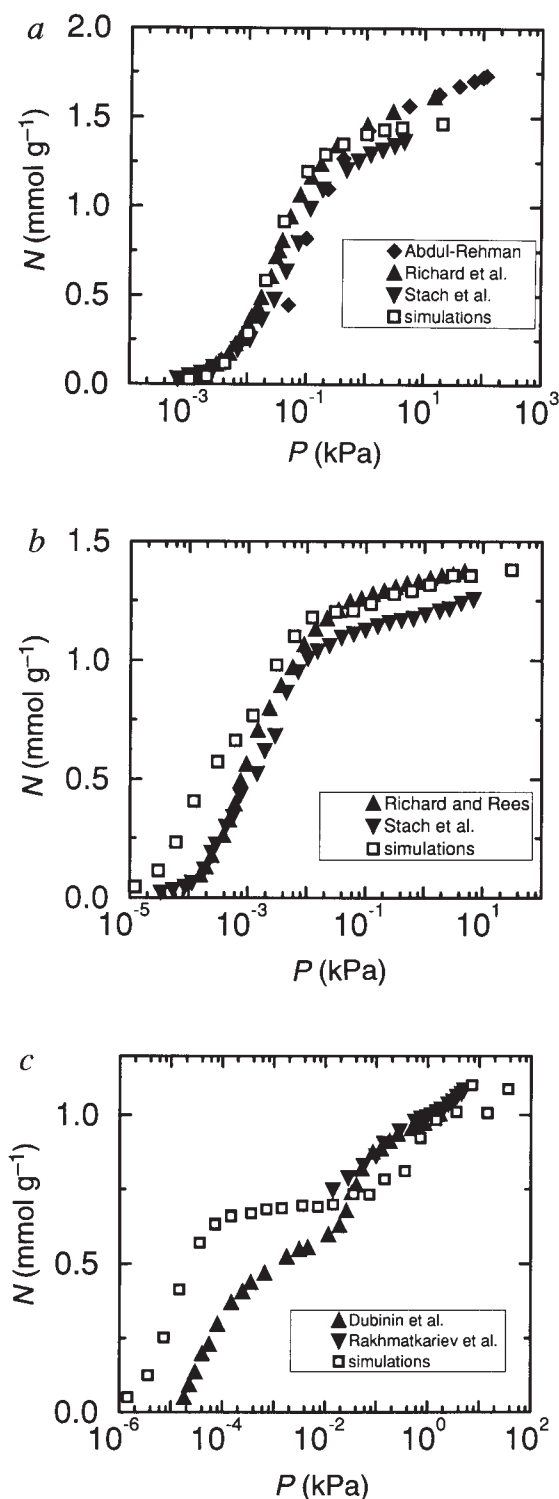

FIG. 1 Adsorption isotherms of butane (*a*), hexane (*b*) and heptane (*c*) in silicalite. Closed symbols, experimental data[3,4,6,18,19]; open symbols, results of simulations for temperature $T = 298$ K (this work). P, pressure of gas; N, mmol of gas absorbed per g silicalite.

for chain molecules, the insertion of molecules tends to be a disfavoured process in a conventional grand-canonical simulation[10]. To see this, consider a simulation of methane molecules adsorbed in a zeolite. Assume that a methane molecule can be inserted successfully if this molecule is placed at a randomly selected position where it does not overlap with one of the other atoms of the system. Depending on the loading, one needs of the order of 10^3 attempts to find such a position, for ethane this is of the order of 10^6, and for heptane even 10^{21}. The latter would result in a simulation of many years on a supercomputer, and allowing such simulations to equilibrate would be prohibitively time-consuming. For this reason, simulations of adsorption have focused on systems containing small molecules. To make grand-canonical simulations of long-chain alkanes possible, we have used the configurational-bias Monte Carlo technique[9-14] for the insertion step. In this technique a molecule is inserted atom by atom in such a way that overlaps are avoided. This 'growing' procedure introduces a bias that can be removed exactly by appropriate acceptance rules[15]. Depending on the chain length and conditions, this technique can be 10 to 50 orders of magnitude more efficient that a conventional grand-canonical simulation.

Here we model alkane molecules using a 'united-atom' model in which CH_3 and CH_2 groups are considered as single interaction centres[16]. The zeolite is modelled as a rigid crystal and the zeolite–alkane interactions are assumed to be dominated by dispersive interaction with the oxygen atoms, which are described
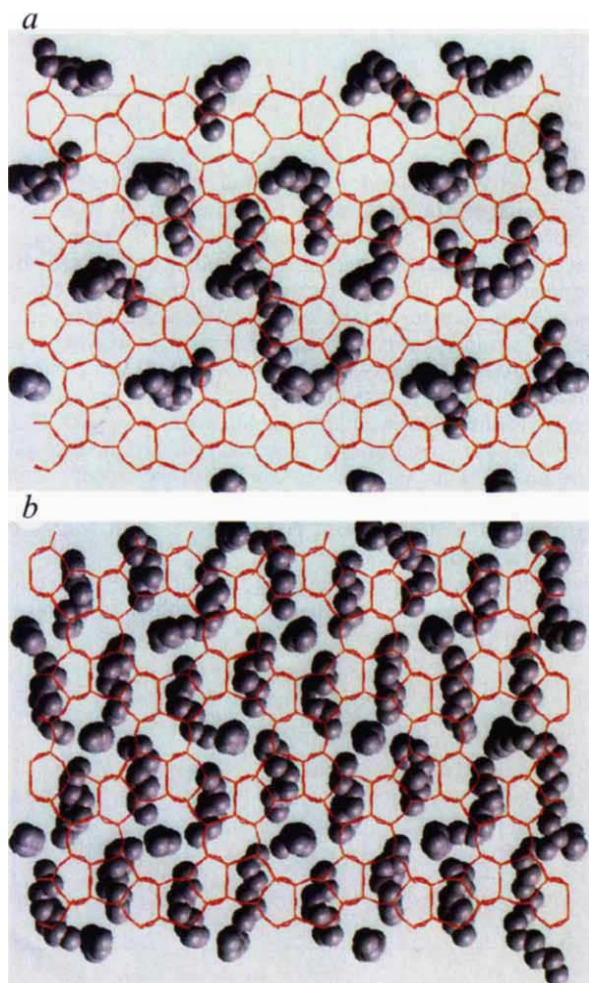
with a Lennard–Jones potential: $u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. The size ($\sigma$) and energy parameters (ε) have been fitted to the heats of adsorption and the Henry coefficients of the n-alkanes ranging from butane to decane in silicalite: $\varepsilon_{CH_3} = 87.5$ K, $\varepsilon_{CH_2} = 54.4$ K and $\sigma_{CH_3} = \sigma_{CH_2} = 3.64$ Å. The scatter in the experimental data for the Henry coefficients makes it difficult to arrive at a unique set of parameters. The values used in this work give a reasonable overall description of the Henry coefficients of these alkanes, but turned out to be less optimum for hexane and heptane (B.S., manuscript in preparation). In the simulations we used periodic boundary conditions and the simulation box contained 16 unit cells of silicalite with total size $40.14 \times 39.840 \times 53.680$ Å^3. The number of trial orientations in the configuration-bias Monte Carlo moves ranged from five for butane to eight for heptane[14].

In Fig. 1 the simulated adsorption isotherms of various alkanes in silicalite are compared with experimental data. For butane a type I isotherm is observed, and the agreement between experiments and simulation is good. For hexane and heptane there is some agreement at high pressures, but at low pressures deviations exist which indicate that the zeolite–alkane model may be further improved. It is interesting to note that for heptane both the experiments and the simulations show a step at approximately half the loading. Also for hexane detailed inspection of the calculated adsorption isotherm shows a kink at this loading. As the simulations are performed on a perfect single crystal, these deviations from the type I isotherm must be due to a transition of the fluid inside the pores and can not be attributed to the secondary pore system.

Silicalite has two types of channels, straight and zig-zag, which are connected via intersections. Figure 2 shows 'snapshots' of hexane molecules in the channels of silicalite at two different loadings: Fig. 2a is at approximately half the maximum loading and in Fig. 2b the zeolite is almost saturated. Note that the length of a hexane molecule is of the order of the length of the period of the zig-zag channel. At low chemical potential, the hexane molecules move 'freely' in these channels and the molecules will be in the intersections for some of the time. If part of the intersection is occupied, other molecules can not reside in the straight channels at the same time. At high pressures, almost all hexane molecules fit exactly into the zig-zag channel (Fig. 2b), and we find that they no longer move freely. In such a configuration the entire straight channel can be tightly packed with hexane molecules. This may explain the plateau in the adsorption isotherm: in order to fill the entire zeolite structure neatly, the hexane molecules located in zig-zag channels have first to be 'frozen' in these channels. This 'freezing' of the positions of the hexane molecules implies a loss of entropy, and will

FIG. 2 Hexane in silicalite: a, at approximately half the maximum loading; b, at almost maximum loading. The zig-zag channels are in the plane of the page, straight channels are perpendicular to the page. The hexane molecules are represented by grey spheres and red/orange lines represent the zeolite framework.
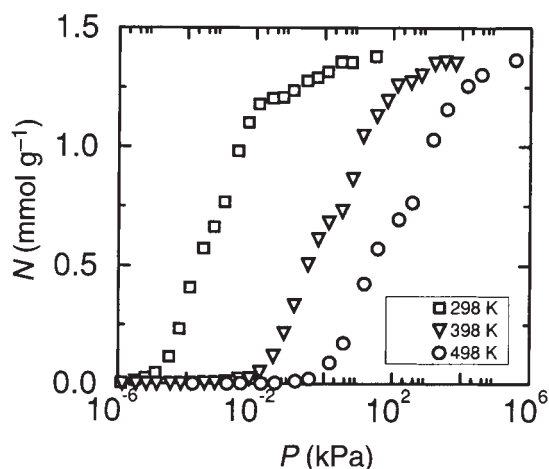

FIG. 3 Temperature dependence of the adsorption isotherms of hexane as obtained from simulations.

therefore only occur if the pressure (or chemical potential) is sufficiently high to compensate for this loss. This also makes clear why we do not observe a step for molecules that are shorter or longer than hexane or heptane. If the molecules are longer, they will always be partly in the intersection and nothing can be gained by a collective 'freezing' in the zig-zag channels. If the molecules are shorter than one period of the zig-zag channel, a single molecule will not occupy an entire period and a second molecule will enter which results in a different type of packing.

We can use these results to shed some light on the apparently conflicting data for hexane: the adsorption isotherms obtained by Lohse et al.[17] do not provide evidence for a kink at half loading whereas the one measured by Richard and Rees[4] does show such a kink. One difference between these sets of data is that the former were measured at temperature $T = 298$ K, whereas the latter were measured at $T = 308$ K. For higher temperatures, Richard and Rees observed that this kink becomes more pronounced. Figure 3 shows that the kink also becomes more pronounced in the simulations, and with increasing temperature even grow out to a small plateau. At high temperatures the entropy contribution is more important and a higher pressure must be imposed before the hexane molecules 'freeze' or get locked in the zig-zag channel; apparently the temperature in the experiments of Lohse et al.[17] was just too low to observe a kink. As far as we are aware, such a transition has never been observed experimentally. It is interesting to note that the observed 'freezing' is similar to the commensurate–incommensurate transitions observed for noble gases on graphite (ref. 20, and references therein). In both cases the geometrical aspects of the substrate play an essential role in 'locking' the fluid into a specific structure. □

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Controlled growth of microporous crystals nucleated in reverse micelles

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THE development of new methods for nucleating and growing microporous crystals has made available new framework structures and morphologies for these technologically important materials[1]. These approaches have included solution-based synthesis[2] and the use of simple organic structure-directing agents[3] and complex organic assemblies such as liquid-crystal phases[4,5]. Here we show that the growth of microporous zincophosphate[6–8] with the sodalite structure can be controlled by preparing the crystals from reactants included within the interior aqueous phase of reverse micelles dispersed in an organic solvent. The growth of inorganic phases in reverse micelles has been exploited previously for the preparation of monodisperse oxide[9], semiconductor[10] and metal particles[11]. In this study, we introduce the two inorganic components—zinc and phosphate ions—in separate micelles, so that crystallization is controlled by the collision and exchange kinetics of the surfactant structures. Moreover, the surfactant–water interface provides the site for crystal nucleation, favouring initial nucleation at the (111) and/or (110) crystal faces and subsequent growth of the zincophosphate crystals by deposition along the {100} faces. The growth process is ultimately interrupted by sedimentation when the crystals grow large enough, producing a precipitate of microcrystals several hundred nanometres in size. Our results indicate that this approach can provide a means of controlling the morphology as well as the size of growing crystals.

Mann and Williams reported that the crystallization of Ag_2O along specific crystal faces could be controlled by migration of OH^- through a Ag^+-containing vesicle interface[12]. Our goal was to develop a similar strategy for controlled crystal growth of microporous materials. Reverse micelles exist in certain compositions of oil–water–surfactant within a well defined temperature range[13]. The most commonly used surfactant in making reverse micelles is AOT (12 bis(2-ethyl hexyloxycarbonyl)-1-ethane sulphonate), with n-alkanes as the oil phase[13]. At temperatures used for conventional aluminosilicate zeolite synthesis (>90 °C), the reverse micellar structure is unstable and results in phase separation[14,15]. Thus we chose to work with the zincophosphate system, which Stucky and co-workers recently discovered can be synthesized under ambient conditions[6 8], with frameworks isostructural with zeolites.

The experimental strategy involved making a reverse micelle containing zinc ions and another with phosphate ions and then
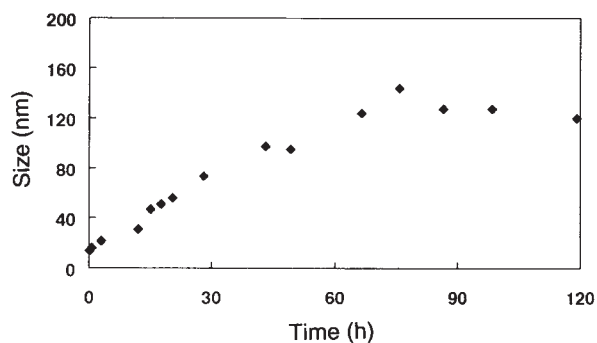

FIG. 1 Particle growth during synthesis of zincophosphate sodalite measured by dynamic light scattering. The initial size of the zinc-containing and phosphate-containing micelles were 8 and 15 nm, respectively.