

# Anomalous behaviour of pentane adsorbed at the graphite/liquid interface

Miguel A. Castro,<sup>a</sup> Stuart M. Clarke,<sup>\*b</sup> Akira Inaba,<sup>c</sup> Thomas Arnold<sup>d</sup> and Robert K. Thomas<sup>d</sup>

<sup>a</sup> Instituto de Ciencia de Materiales de Sevilla, Avda. Americo Vespucio, Sevilla, Spain

<sup>b</sup> Cavendish Laboratory, Madingley Road, Cambridge, UK CB3 0HE

<sup>c</sup> Department of Chemistry and Research Centre for Molecular Thermodynamics, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

<sup>d</sup> Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3OZ

Received 12th July 1999, Accepted 1st October 1999

Calorimetry and neutron diffraction have been used to identify and characterise the formation of a solid monolayer of pentane adsorbed on graphite and coexisting with liquid pentane. The observed behaviour is quite different from other alkanes in that the monolayer does not melt above the melting temperature of the pure pentane but at a temperature very similar to that of the bulk material. The lower melting point of the bulk pentane in the pentane/graphite system, when it is present in a relatively small amount, allows the melting point of the solid monolayer to be clearly resolved.

## Introduction

The adsorption of simple molecules such as alkanes, carboxylic acids and alcohols on to solid surfaces from their liquids has been extensively studied by calorimetry and isotherm measurements.<sup>1–3</sup> These are model systems for a variety of interesting problems such as lubrication, detergency and colloidal stabilisation. Identification and characterisation of adsorbed layers in this type of system is difficult largely because the presence of the liquid creates a buried interface, which is difficult to access with structural probes. Some structural information from buried interfaces is available using techniques such as specular neutron reflectivity<sup>4</sup> and scanning tunnelling microscopy (STM).<sup>5</sup> However, reflectivity measurements only provide structural information normal to the plane of the interface and there is still often significant uncertainty over the interpretation of the results from STM techniques. Additionally, STM images of the monolayer cannot be obtained if the material above the monolayer is solid. We have recently shown that the combination of calorimetry, incoherent elastic neutron scattering and neutron diffraction is effective for the investigation of monolayers adsorbed from their liquids and solutions.<sup>6,7</sup>

Recently, we presented data for a number of materials from the homologous series of alkanes in liquid contact with graphite. In all cases, except pentane, it was demonstrated that solid monolayers are adsorbed from the liquid on to the solid substrate, the melting points of these layers being approximately 110% of that of the bulk alkane in the absence of graphite.<sup>8</sup> This behaviour has also been observed for alcohols and carboxylic acids.<sup>7,9</sup> Pentane appears to be a notable exception to this behaviour. Thus, as the previous investigation of the pentane/graphite system,<sup>8</sup> using incoherent elastic neutron scattering, no evidence for the melting of a solid monolayer could be found above the bulk melting point. Here we present adiabatic calorimetry and neutron diffraction results that show that pentane does form a solid, crystalline monolayer but has a very similar melting point to that of the bulk such that the bulk melting would have obscured the monolayer transitions in the earlier study.

## Experimental

### Adiabatic calorimetry

The method and experimental details of adiabatic calorimetry have been presented in detail elsewhere.<sup>10</sup> Essentially, the heat capacity of a sample of substrate (graphite) dosed with a known amount of adsorbate (pentane) is directly determined as a function of temperature by adding tiny amounts of electrical heating energy to the sample and measuring the temperature rise. Transitions are indicated as peaks in the heat capacity and the transition enthalpy can be obtained from the peak area.

### Neutron diffraction

Details of the neutron diffraction technique and apparatus are presented elsewhere.<sup>11,12</sup> The instrument used in this work was the multidetector powder diffractometer D20 at the Institut Laue–Langevin, Grenoble<sup>13</sup> with an incident wavelength of 0.241 nm. Scattering from crystalline two-dimensional adsorbed layers gives rise to diffraction peaks,<sup>14,15</sup> which can be used to determine the structure of the layer in a manner analogous to diffraction from three dimensional crystals. Diffraction from two-dimensional crystalline structures gives rise to peaks with a characteristic saw-tooth line shape,<sup>14,15</sup> while fluid phases give rise to very broad, symmetrical diffraction peaks. The diffraction pattern from the adsorbed material is obtained by subtraction of the scattering from the substrate alone from that of the substrate and adsorbed material together.

### Samples

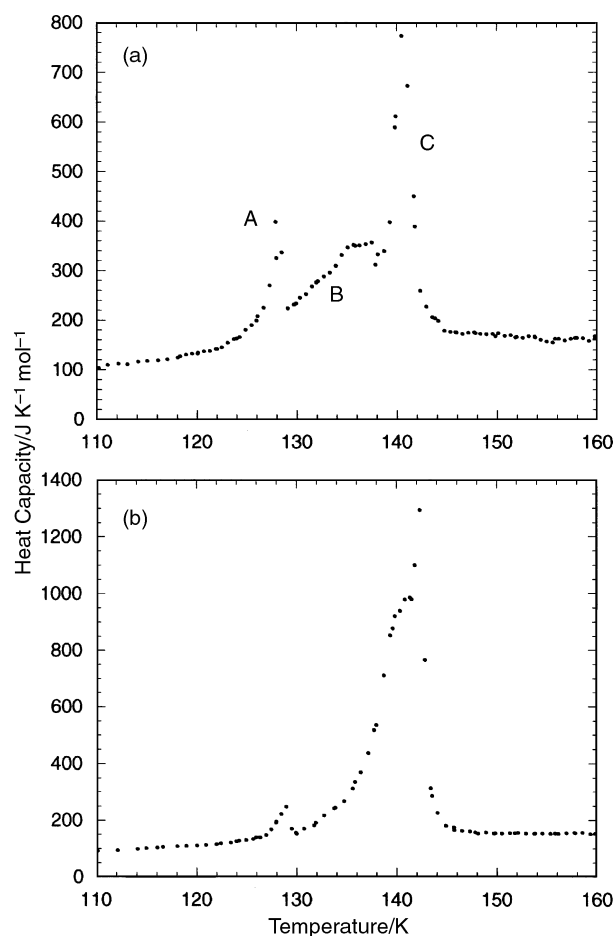
The adsorbent used for the neutron diffraction was recompressed exfoliated recompressed graphite Papyex (Le Carbone Lorraine) with a specific area of 14 m<sup>2</sup> g<sup>-1</sup> determined by adsorption of nitrogen. Approximately 16 g of graphite was used in these experiments. The Papyex used for the adiabatic

calorimetry had a specific surface area of  $16.6 \text{ m}^2 \text{ g}^{-1}$  with approximately 9 g used for each measurement. The graphite substrates were outgassed under vacuum in an oven at  $350^\circ\text{C}$  before known quantities of alkane were added as liquid by micro-syringe under an inert atmosphere of helium. Protonated n-pentane was used for the calorimetry measurements. Fully deuterated n-pentane was used for the neutron diffraction measurements to reduce the incoherent scattering that would have arisen with the protonated alkanes and was obtained from Cambridge Isotope Laboratories with quoted deuteration levels of  $>99\%$ . When dosing the graphite it is convenient to know the approximate number of equivalent monolayers adsorbed. This can be estimated from the area per molecule, based on the approach of Groszek,<sup>3</sup> and the specific surface area of the graphite.

## Results

### Adiabatic calorimetry

Fig. 1(a) and (b) presents the adiabatic calorimetry measurements from 3 and 7 equivalent monolayers of pentane adsorbed on graphite. There are no transitions in the heat capacity of pure graphite in this temperature region. The heat capacity is normalised by the total quantity of adsorbate in the cell. Although only two coverages were investigated here it is clear that the behaviour of the transitions with coverage can be used to assign the observed transitions. Bulk transitions are expected to scale approximately as the total amount of



**Fig. 1** Adiabatic calorimetry measurements from (a) 3 and (b) 7 equivalent monolayers of pentane on graphite. The heat capacity is normalised to the total amount of adsorbate in the cell.

adsorbate while, in contrast, any monolayer transition will keep the same absolute magnitude once the nominal coverage is greater than a monolayer. With this scaling bulk peaks therefore remain essentially unchanged in size with increasing coverage while monolayer peaks will appear smaller.

At a coverage of 3 monolayers, Fig. 1(a), there are several transitions evident: a sharp peak at 128 K (designated A), a much broader peak at 136.5 K (B) and another sharp peak at 140.6 K (C). In Fig. 1(b) there are again three peaks but peak B has increased in magnitude and shifted to a significantly higher temperature of 140.4 K. Peaks A and C, in contrast, have only shifted slightly to 128.5 and 142.4 K respectively with the increase in coverage.

Given that the data have been normalised as already described, the change in relative magnitude of the peaks with increasing coverage can be used to identify and distinguish monolayer and bulk transitions. Peak A decreases with increase in coverage indicating a transition in an adsorbed layer. Peaks B and C overlap somewhat at higher coverage and a simple curve fitting procedure was used to estimate the relative contributions. On the basis of this simple curve fitting, peak B increases slightly in magnitude, consistent with a bulk transition, while peak C decreases indicating that it is associated with a transition in an adsorbed layer. The width of peak B is also reduced on increasing the coverage.

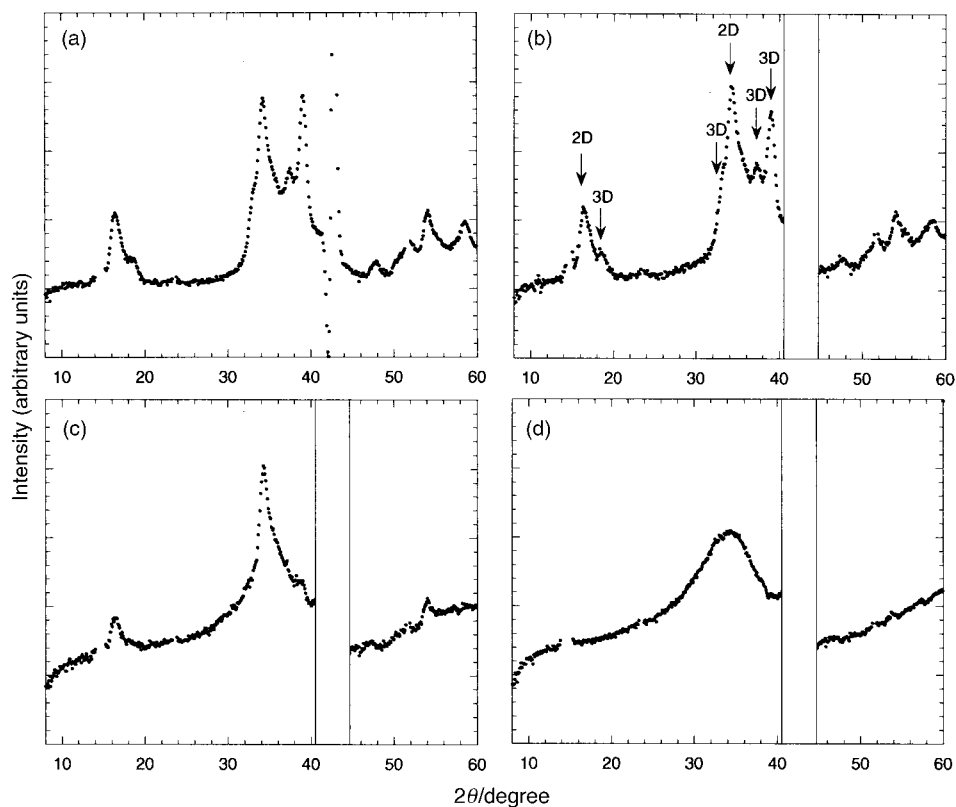
The behaviour of the peak assigned to bulk pentane at first sight is somewhat surprising. However, shifts from low temperature towards the normal bulk value ( $143.48 \text{ K}^{16}$ ) with increasing coverage have been observed for inert gases in contact with graphite<sup>17</sup> and for other linear alkanes with graphite.<sup>8</sup> The reason is not completely clear but is probably associated with the presence of small crystallites of bulk material trapped in small pores of the graphite. In previous studies the normal bulk temperature is obtained after 5–10 equivalent monolayers have been deposited on the surface.<sup>8</sup>

### Neutron diffraction

The neutron diffraction patterns from deuterated pentane,  $\text{C}_5\text{D}_{12}$ , adsorbed on graphite at a coverage of 3 equivalent monolayers at temperatures of (a) 70, (b) 120, (c) 140 and (d) 150 K are shown in Fig. 2. The scattering from the graphite background has been subtracted and the residual feature at  $2\theta = 41\text{--}44^\circ$  arises from imperfect subtraction of the intense (002) reflection from the graphite basal planes. Sharp peaks due to detector instability at  $2\theta \approx 15, 23$  and  $52^\circ$  have also been removed. The remaining peaks in the figure are diffraction peaks from the pentane.

Very little change occurs in these patterns with increasing temperature up to a temperature of 120–130 K where a broad peak characteristic of a fluid begins to appear in the region  $2\theta = 30\text{--}45^\circ$ . This fluid scattering continues to grow up to 140 K, at which point a number of the sharp peaks evident at 70 K have disappeared. The intensities of the sharp peaks that still remain at 140 K have decreased at 145 K and have vanished completely by 150 K.

It is reasonable to assume that after 2 equivalent monolayers have been added, any further pentane added will form bulk material and therefore those peaks that change in magnitude can be identified as arising from bulk pentane. This is supported by other workers considering the adsorption of alkanes on graphite who have also identified bulk nucleation at coverages above 2 equivalent monolayers.<sup>18</sup> Here we assume that any bulk pentane present when 2 equivalent monolayers have been added has a structure (and extent of preferred orientation on the surface) similar to material added subsequently. Fig. 3 shows the subtraction of the pattern at 2 equivalent monolayers from that at 5 equivalent monolayers at 70 K and should therefore represent the scattering from bulk pentane. Indeed, the positions of the peaks in this pattern



**Fig. 2** Experimental neutron diffraction pattern from 3 equivalent monolayers of deuterated pentane,  $C_5D_{12}$ , adsorbed on graphite at temperatures of (a) 70, (b) 120, (c) 140 and (d) 150 K. The scattering from the graphite substrate in the absence of any adsorbate has been subtracted in preparing this figure. The feature at  $2\theta = 41\text{--}44^\circ$  in (a) is a region of imperfect subtraction of the intense graphite (002) reflection. The arrows in (b) indicate some of the peaks arising from the solid monolayer (2D) and those from the bulk (3D), as described in the text.

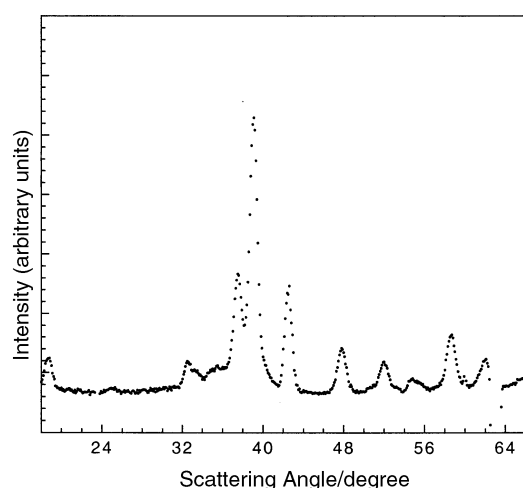
agree well with those of the published structure of bulk pentane<sup>19</sup> as shown by the results in Table 1. On the basis of this argument we identify the peaks corresponding to bulk pentane in the diffraction pattern in Fig. 2 (marked 3D) and assign the remaining peaks to scattering from the monolayer (marked 2D).

The peaks that we have assigned to bulk pentane are those that disappear at 120–140 K and therefore it is the bulk pentane that melts first, well below the normal melting point of bulk pentane at 143.48 K, but in excellent agreement with the calorimetry data (at 3 monolayers the melting peak is at

136.5 K). The peaks that remain above 130 K must be those associated with the adsorbed monolayer, which coexists with bulk liquid pentane. It is the bulk liquid pentane that is responsible for the broad peak underneath the peak from the monolayer at  $34^\circ$  seen in Fig. 2(c). The adsorbed monolayer melts at about 145 K, approximately the same as the normal bulk melting point.

To extract a diffraction pattern from the adsorbed monolayer alone requires an estimate of the scattering from the liquid pentane at 140 K in Fig. 2(c) to be made. Above 150 K all the pentane has melted and the corresponding pattern can be used to estimate the level of scattering from the liquid. Fig. 4 presents the resulting diffraction pattern, *i.e.* the diffraction pattern of the solid adsorbed monolayer of pentane that coexists with liquid pentane at 140 K. The pattern contains peaks with the asymmetric line shape characteristic of diffraction from two-dimensional layers,<sup>14,15</sup> confirming that this is indeed scattering from an adsorbed monolayer.

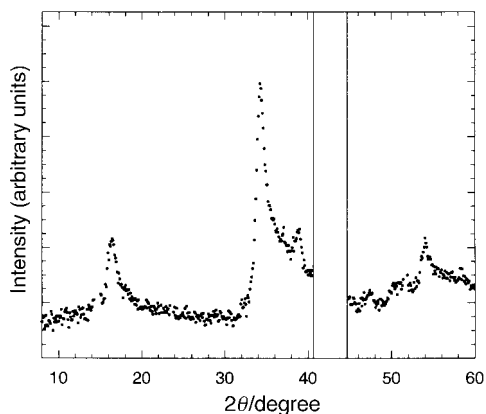
Fig. 5 presents neutron diffraction data from deuterated pentane,  $C_5D_{12}$ , adsorbed on graphite at the higher coverage of 5 equivalent monolayers at temperatures of (a) 70, (b) 140,



**Fig. 3** Neutron diffraction pattern from 'bulk' pentane calculated from the subtraction of the scattering patterns at 2 equivalent monolayers from that at 5 monolayers at 70 K. The intensity scale of this figure is twice that of Fig. 2.

**Table 1** Comparison of the experimentally observed position of peaks from 'bulk' pentane from Fig. 3 with those expected from the orthorhombic bulk structure of pentane<sup>19</sup> ( $a = 0.410$ ,  $b = 0.9076$ ,  $c = 1.4859$  nm)

Peak	$2\theta_{\text{obs}}/\text{degree}$	$2\theta_{\text{calc}}/\text{degree}$	Index
1	18.7	18.1, 18.9	(110), (020)
2	24.8	24.5	(120)
3	32.5	32.6	(130)
4	35.8	35.7	(011)
5	37.5	37.8, 38.4	(101), (040)
6	39.1	39.1, 39.5	(111), (021)
7	42.5	41.6, 42.6, 42.7	(140), (121), (230)



**Fig. 4** The neutron diffraction pattern from the solid monolayer of pentane after removal of the scattering from liquid pentane. The intensity scale of this figure is half that of Fig. 2.

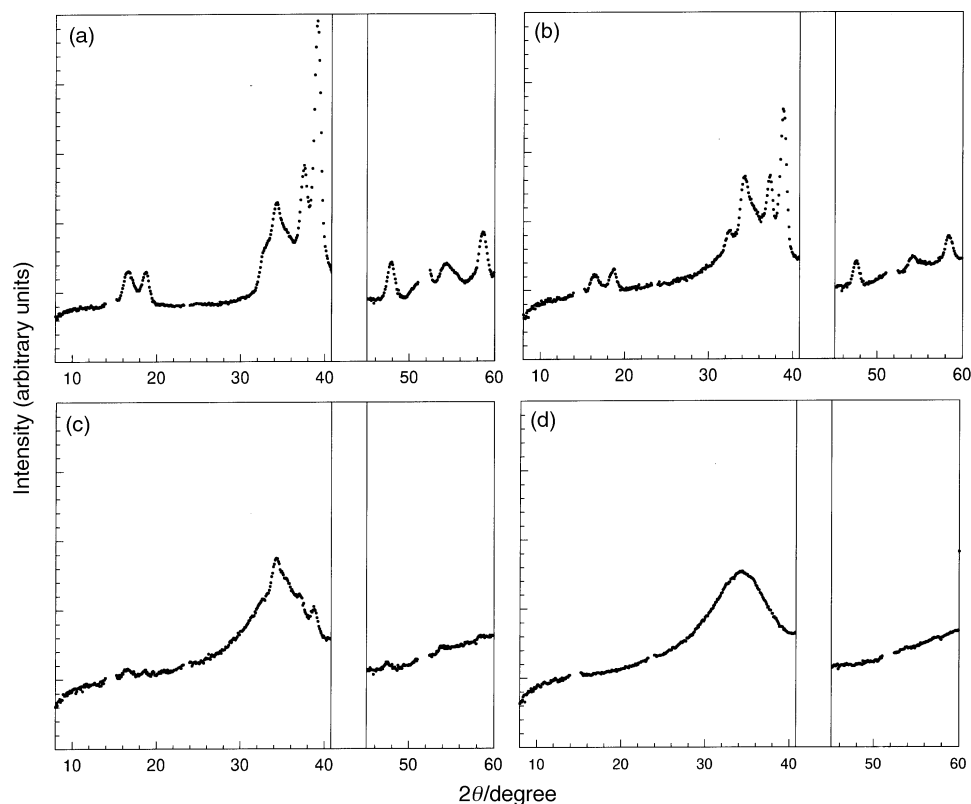
(c) 145 and (d) 150 K. The behaviour observed at 5 monolayers is qualitatively similar to that obtained at 3 monolayers given in Fig. 2. At low temperatures the patterns are dominated by the intense scattering from 3D pentane which falls as the bulk material begins to melt. The bulk peaks are significantly reduced in intensity but are still clearly evident at 140 K, and have almost gone at 145 K. This behaviour is in good agreement with the calorimetry data where the melting point at 5 monolayers coverage is found to be 140.4 K and significantly higher than that observed at 3 monolayers coverage. The peaks characteristic of the 2D monolayer, given in Fig. 2(a) and 4, are also evident at in Fig. 5(a). These have also reduced in intensity by 145 K coexisting with remnants of the bulk peaks. By a temperature of 150 K only a broad peak characteristic of a fluid remains indicating that by this temperature both 2D and 3D solids have melted, again in good agreement with the calorimetry data. At this higher coverage

of 5 equivalent monolayers the melting points of the monolayer and the bulk are clearly much closer than at 3 equivalent monolayers coverage.

It is clear that the behaviour observed with the diffraction measurements are entirely consistent with the results from calorimetry presented above. Thus, the bulk pentane in the system melts significantly below the normal bulk melting temperature at low coverages with the melting point shifting towards the normal bulk melting point with increasing coverage. The presence of an adsorbed monolayer with a melting point close to that of normal bulk pentane is also clearly indicated by both the diffraction and the calorimetry.

## Discussion and conclusions

The presence of a solid adsorbed monolayer of pentane coexisting with bulk liquid is clearly demonstrated by the combination of sensitive calorimetry and neutron diffraction. The existence of such an adsorbed monolayer is the same as for the other linear alkanes adsorbed on graphite from liquid or solution (in other alkanes). However, pentane is quite different from the other alkanes in that the adsorbed monolayer melts at approximately the same temperature as the melting point of bulk pentane. Comparable adsorbed layers of the other alkanes all typically melt at temperatures about 10% higher than their normal bulk melting points. It is interesting that the only reason that the melting of the adsorbed monolayer of pentane can be observed is that bulk pentane in this situation itself has a significantly lower melting point than the normal bulk material. Previous measurements on the pentane/graphite system were performed at a much higher coverage than the work here.<sup>8</sup> At higher coverages the melting of the bulk material and that of the adsorbed monolayer increasingly tend to coincide. This effect is already evident in Fig. 1(b) and Fig. 5. At the coverage used for our earlier incoherent neutron scattering experiments, we would now expect not to



**Fig. 5** Experimental neutron diffraction patterns from 5 equivalent monolayers of deuterated pentane,  $C_5D_{12}$ , adsorbed on graphite at temperatures of (a) 70, (b) 140, (c) 145 and (d) 150 K. The scattering from the graphite substrate in the absence of any adsorbate has been subtracted in preparing this figure. The intensity scale of this figure is twice that of Fig. 2.

be able to distinguish the melting of the adsorbed monolayer from that of the bulk, as indeed was observed.

Pentane is clearly anomalous in its adsorption behaviour relative to the other linear alkanes. It is noteworthy that pentane also has a quite different bulk crystallographic structure from the other alkanes. In most of the alkanes with orthorhombic crystals the molecules lie parallel to one another and the basal plane, but in pentane they lie at an angle to each other and the basal plane.<sup>19</sup> Understanding the overall pattern of behaviour of the adsorbed alkanes will require crystallographic detail of the adsorbed monolayer structures, which we are currently attempting to gather.

The calorimetry revealed a second transition in the adsorbed monolayer at temperatures below the depressed melting point of the bulk pentane. We are currently unable to identify this transition. It is possible that it is a transition to a rotator or hexatic phase before the adsorbed monolayer melts. If the transition corresponds to the onset of a rotational motion on the surface where the molecules reorient between  $n$  sites then the expected configurational entropy change,<sup>20,21</sup>  $\Delta S$ , would be  $R \ln(n)$  or 5.8, 9.13, 11.53 ...  $\text{J K}^{-1} \text{mol}^{-1}$  for  $n = 2, 3, 4 \dots$ . The entropy may be estimated from the experimental data using  $\Delta S = \Delta H/T$ , where the enthalpy,  $\Delta H$ , is estimated from the area of the peak in the calorimetry data ( $811 \text{ J mol}^{-1}$ ) and  $T$  the transition temperature (128 K). The experimentally determined value of  $\Delta S$  is therefore  $6.34 \text{ J K}^{-1} \text{mol}^{-1}$ . This value is consistent with the onset of a two fold reorientation corresponding to the molecules 'flipping over' on the surface. Several other linear alkanes both at multilayer and sub-monolayer coverages on graphite show evidence for an additional monolayer transition where incoherent neutron scattering data indicate there is only a single layer.<sup>8,10</sup> In these cases the transitions are well above the bulk melting point and can only arise from the adsorbed monolayer. Further diffraction and quasi-elastic neutron scattering measurements will be needed to resolve this issue.

### Acknowledgements

The authors thank the instrument scientists and staff at ILL, Grenoble, France. We also thank the UK EPSRC, the

Spanish DGICYT, the British Council and the Grant-in-aid for Scientific Research from Monbusho (AI) for financial support. Contribution No. 5 from the Research Centre for Molecular Thermodynamics.

### References

- 1 G. H. Findenegg, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 1799.
- 2 G. H. Findenegg, *J. Chem. Soc., Faraday Trans. 1*, 1973, **69**, 1969.
- 3 A. J. Groszek, *Proc. R. Soc. London, Ser. A*, 1970, **314**, 473.
- 4 G. Fragneto, R. K. Thomas, A. R. Rennie and J. Penfold, *Langmuir*, 1996, **12**, 6036.
- 5 J. P. Rabe and S. Buchholz, *Science*, 1991, **253**, 424.
- 6 M. A. Castro, S. M. Clarke, A. Inaba and R. K. Thomas, *Physica B*, 1998, **241–243**, 1086.
- 7 M. A. Castro, S. M. Clarke, A. Inaba, C. C. Dong and R. K. Thomas, *J. Phys. Chem. B*, 1998, **102**, 777.
- 8 M. A. Castro, S. M. Clarke, A. Inaba, T. Arnold and R. K. Thomas, *J. Phys. Chem. B*, 1998, **102**, 10528.
- 9 M. A. Castro, S. M. Clarke, A. Inaba and R. K. Thomas, *J. Phys. Chem. B*, 1997, **101**, 8878.
- 10 S. M. Clarke, A. Inaba, T. Arnold and R. K. Thomas, *J. Therm. Anal. Calorim.*, 1999, **57**, in press.
- 11 S. M. Clarke, DPhil thesis, University of Oxford, 1986.
- 12 R. A. Bucknall, S. M. Clarke, R. A. Shapton and R. K. Thomas, *Mol. Phys.*, 1989, **67**, 439.
- 13 Neutron Research Facilities at the ILL High Flux Reactor, Institut Laue-Langevin, Grenoble, France.
- 14 J. K. Kjerns, L. Passell, H. Taub, J. G. Dash and A. D. Novaco, *Phys. Rev. B*, 1976, **13**, 1446.
- 15 B. E. Warren, *Phys. Rev.*, 1941, **59**, 693.
- 16 K. N. Marsh, *Thermodynamic Properties of Organic Compounds and their Mixtures*, Springer-Verlag, Berlin, 1995.
- 17 G. B. Hess, in *Phase Transitions in Surface Films 2*, ed. H. Taub, G. Torzo, H. J. Lauter and S. C. Fain, Jr., New York, 1991, p. 267.
- 18 K. W. Herwig, J. C. Newton and H. Taub, *Phys. Rev. B*, 1994, **50**, 15287.
- 19 H. Mathisen, N. Norman and B. F. Pedersen, *Acta. Chim. Scand.*, 1967, **21**, 127.
- 20 G. Ungar, *J. Phys. Chem.*, 1983, **87**, 689.
- 21 G. Ungar and N. Masic, *J. Phys. Chem.*, 1985, **89**, 1036.

Paper 9/05597E