SURFACE CRYSTALLIZATION IN NORMAL-ALKANES AND ALCOHOLS

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Abstract

A new, rare surface freezing phenomenon is observed in molten normal-alkanes and their derivatives (alcohols, thiols, *etc.*). X-ray and surface tension measurements show the formation of a crystalline monolayer on the surface of the liquid alkane at temperatures up to 3°C above the bulk solidification temperature, T_f. For alcohols, a single *bilayer* is formed. In both cases, the molecules in the layer are hexagonally packed and oriented normal to the surface for short chain lengths, and tilted for long ones. In both cases the isngle layer persists down to T_f. In terms of wetting theory, this constitutes a very limited partial wetting of the liquid surface by the crystalline layer. The new surface phase is obtained only for chain lengths $14 < n \leq 50$ in alkanes, and $16 < n < 30$ in alcohols. The measurements are satisfactorily accounted for within a simple theory based on surface energy considerations.

1   Introduction

Molecules residing at the free surface of a liquid or solid are less confined than those in the bulk. Their higher entropy renders the melting temperature of the surface *lower* than that of the bulk. This effect, called surface melting, is a general result of statistical mechanics and was observed in numerous materials ranging from molecular crystals[1], through water[2], to semiconductors[3] and metals[4]. The opposite phenomenon, that of surface melting, i.e. the ordering of the surface at temperatures *higher* than that of the bulk is a very rare phenomenon, detected until recently only in liquid crystals[5, 6]. Even there the order is not crystalline but smectic. We review here our recent work, which revealed true surface freezing in normal-alkanes and their derivatives. The simplicity of these molecules and their interactions, as compared to liquid crystals, indicates that surface freezing is a fundamental consequence of the inherently anisotropic interactions in chain molecules.

Liquid n-alkanes and alcohols, which are linear hydrocarbon chains, $[CH_3\text{-}(CH_2)_{n-2}\text{-}CH_3$, or, in short, Cn for alkanes and $CH_3\text{-}(CH_2)_{n-2}\text{-}CH_2OH$, denote CnO for alcohols], are basic structural units of many organic and biological molecules including lipids, surfactants, and

liquid crystals, and determine their properties to a large extent[7, 8]. As they are the major constituents of oils, fuels, polymers, and lubricants they also have an immense industrial importance. Their surface properties, which remain largely unexplored, are important to applied as well as basic science. Recent x-ray scattering[9, 10], surface tension[9, 10, 11], optical[12], and simulation studies[13] have shown that these chain molecules exhibit remarkable behavior at the free surface.

In our x-ray scattering and surface tension measurements the abrupt formation of a crystalline monolayer on the surface of n-alkanes is observed at temperatures of up to 3°C above their bulk melting temperatures, for a range of chain lengths $14 < n \leq 50$. For alcohols, the same phenomena are observed. Here, however, a bilayer is formed over a smaller temperature range of up to 1°C and a chain length range of $16 < n < 30$. These appear to be the simplest systems in which surface-induced 2D crystalline ordering has been observed. The vanishing of the surface layer for the short chain end of the range can possibly be interpreted as the first observation of a transition from surface freezing to surface melting behaviour. The vanishing of the layering at the long chain end of the range is likely due to the proliferation of conformational distortions in the individual chains.

The next sections describe the experiments, the main body of results and our conclusions.

2   Experimental.

The samples, purchased from either Sigma, Aldrich or Fluka, were of purity $> 99\%$ and used as received. A small amount was placed on a 3 inch silicon wafer, forming a $\sim$0.5mm thick film after melting. The wafer was placed inside a sealed cell whose temperature was regulated and uniform to within a few mK. The free surface of the samples was studied as a function of temperature by X-ray reflectivity (XR), X-ray grazing incidence diffraction (GID), and Bragg-rod (BR) measurements using the Harvard/BNL Liquid Surface Diffractometer at beamline X22B, NSLS, Brookhaven National Laboratory, with a typical wavelength $\lambda = 1.54$Å. XR yields information on the electron density profile *normal* to the surface, such as the thickness and density of a surface film. Here, the formation at the surface of a layer of electron density different from that of the bulk results in an oscillatory modulation on the otherwise monotonically varying reflectivity curve. The GID measurements provide information on the structure of a film within the surface plane. A surface crystalline layer yields sharp Bragg peaks in the diffraction curve. The orientation of the molecular chains is obtained from the Bragg-rods (BR), i.e. the surface-normal dependence of the scattered intensity at the position of each in-plane GID peak. These techniques are able to resolve the surface structure on an Å level both in-plane and perpendicular to the surface. For a full review we refer the reader to Ref. [14].

We have also carried out surface tension (ST) measurements, using the Wilhelmy plate method, in a cell similar to that used for the x-ray measurements. These provide information on the excess free energy of the molecules at the surface over those in the bulk. The formation of the layer at T_s is seen here as sharp change from a negative to a positive slope in the surface tension $\gamma(T)$ curve. The temperature was scanned at a rate ≤ 0.3 mK/sec to ensure ample thermal equilibration. For further details see Refs. [10, 15].

3   Results and Discussion.

Reflectivity curves above and below the solid monolayer formation temperature T_s for C18 and C18O are shown in Fig. 1 . Note the smooth monotonic decrease of both curves for $T > T_s$ which is typical of liquid surfaces broadened by capillary wave roughness[16]. These surfaces

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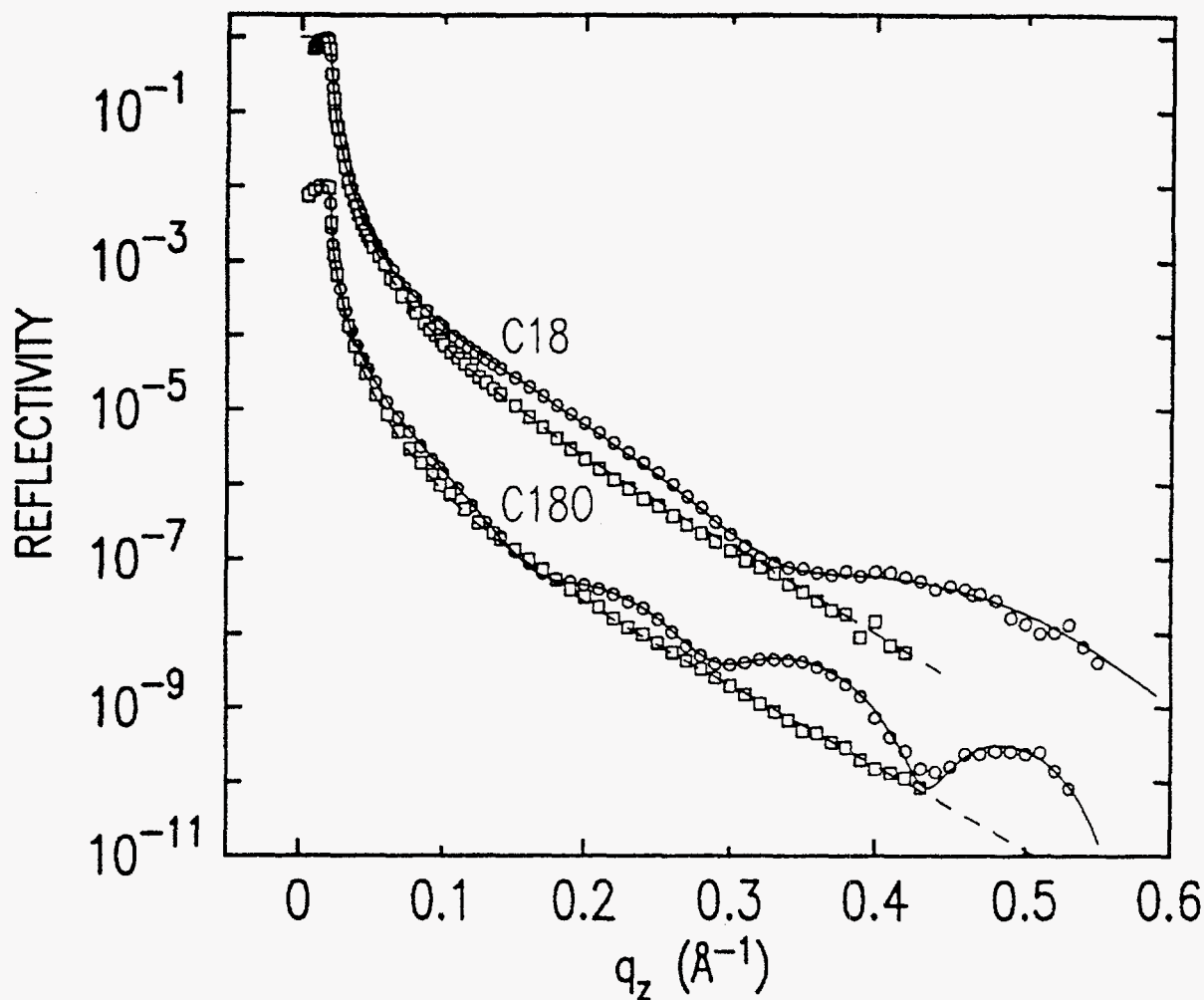
Figure 1: X-ray reflectivities for C18 and C18O in the liquid surface phase (circles) and the surface monolayer phase (squares). The solid and dashed lines are fits to the data, corresponding to the density profiles shown in Fig. 2.

are modeled well by an Error-function-like density profile with a Gaussian width parameter of $\sigma \approx 4.3\text{Å}$. Since for capillary wave dominated surface roughness σ scales as the square root of the surface tension ratio, this value is in good agreement with the $\sigma_{H_2O} = 2.8\text{Å}$ measured for water[17]. The reflectivity at $T < T_s$ shows an oscillatory modulation indicative of a surface layer, as discussed above. Note, however, that the periods of the oscillations differ by a factor of two for the alkane and the alcohol, indicating a twofold thicker surface layer for the alcohols.

To obtain quantitative information on the density profile a simple multiple slab model is used in which the interfacial broadening between neighboring slabs is accounted for by a Gaussian roughness factor. The densities, thicknesses and the Gaussian roughness factors are determined by fitting the Fourier transform of the model to the normalized reflectivity curve, R/R_F, where R_F is the universal Fresnel reflectivity curve of Optics[14, 18]. Such a fit for the C18 alkane, shown as a solid line in Fig. 1, requires only two slabs, and provides an excellent representation of the data. The corresponding density profile is shown in Fig. 2. For all chain lengths below $n \leq 30$, the layer thickness obtained is very close to the extended length of the molecule and the density is ~15% higher than that of the underlying liquid. We consider, therefore, the layer to be a densely packed (solid) mono-molecular layer of vertically aligned molecules. The GID measurements[9] show a single resolution-limited peak for $T < T_s$, indicating that the
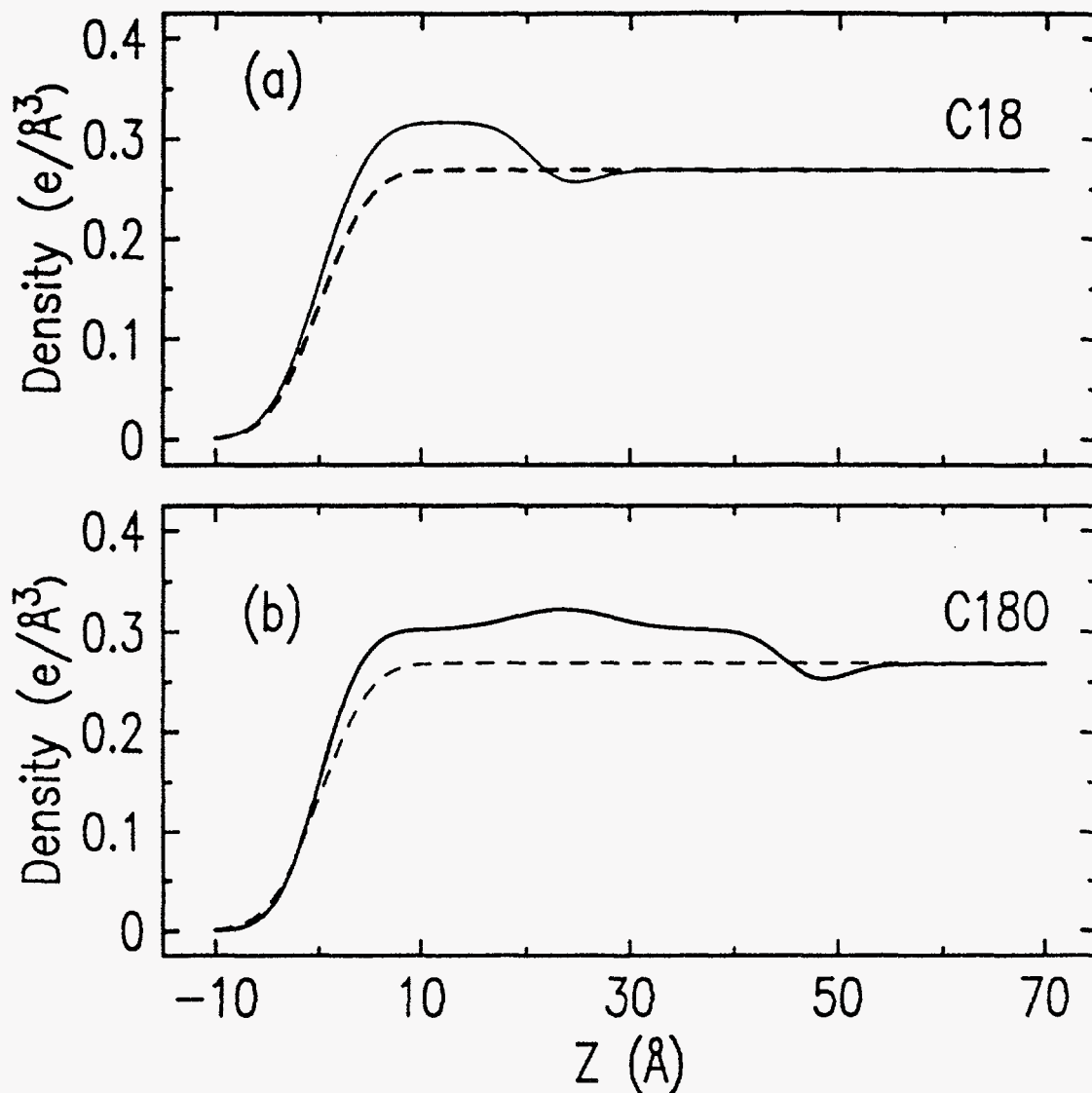
Figure 2: Electron density profiles for C18 and C18O corresponding to the solid and dashed lines in Fig. 1. Note the dense solid monolayer in C18 and bilayer in C18O on top of the less dense liquid. The higher and lower density regions in C18O are discussed in the text.

monolayer is an hexagonally packed crystal, with a nearest neighbour distance of 4.76Å and an in-plane crystalline coherence length exceeding a few thousand Å. This structure is very similar to the bulk rotator R_{II} phase[7]. For chains longer than $n \approx 30$ the molecules start tilting, with the tilt angle increasing with chain length and reaching 16° for C36. The BR measurements show the tilt to be in the nearest neighbour direction. The crystalline coherence length for the monolayers of the tilted molecules is considerably smaller than that of the vertical ones: a few hundred Å, in agreement with the increased disordering tendency of the longer chains. The structure of the alcohol surface layer is significantly different from that of the alkane. Here the twofold shorter modulation period of R/R_F indicates a twofold thicker layer: a bi-, rather than a mono-, layer. A slab model now requires a thin, high-density slab to be added at the center of the wide slab representing the bilayer, as well as a small depression near the bilayer-liquid interface, as shown in Fig. 2. As the density of the OH group is higher, and that of the CH_3 is lower, than that of the CH_2 group comprising the main body of the chain, the central slab is interpreted as a layer of the OH head groups, while the low density depression is due to a layer of terminal CH_3 groups. We thus find that the molecules in the upper layer are oriented with their
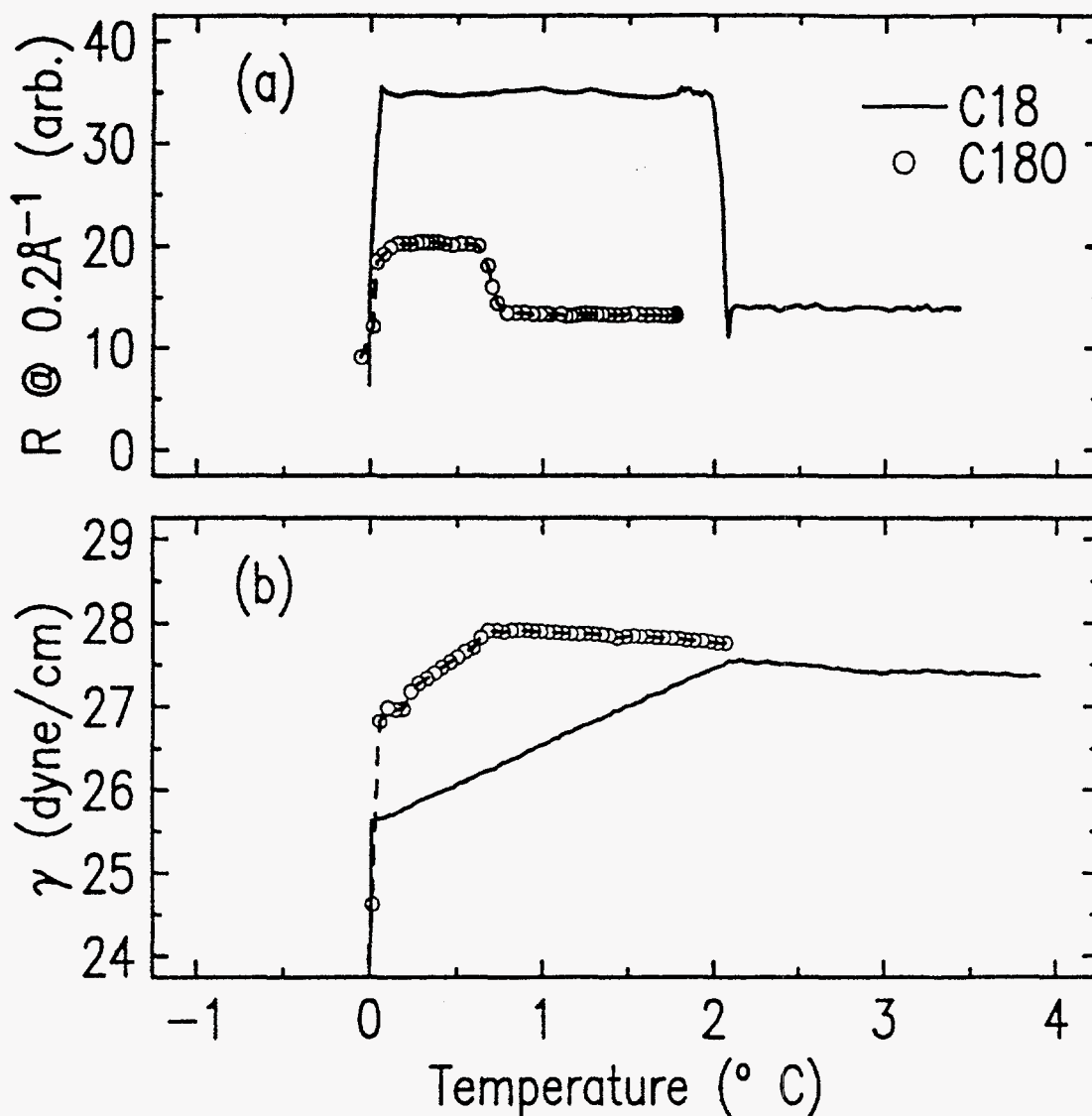
Figure 3: (a) Temperature scan of the reflectivity of C18 and C18O at a fixed q_z=0.20 Å^{-1}. Note the abrupt changes on solidification at T_f and the surface layer formation, at T_s. (b) Surface tension of C18 and C18O in cooling. Note the slope changes discussed in the text.

head groups at the bottom, while those in the lower layer have theirs at the top. The GID and BR measurements show an in-plane crystalline structure, where the molecules are hexagonally packed in each layer with vertical molecules for $n \leq 22$ and tilted ones for $n \geq 24$. The tilt angle increases with n and reaches 22° for $n = 26$. However, unlike long chain alkanes, the tilt direction here is towards *next*- nearest neighbours. Furthermore, the hexagonal lattice of the upper layer is shifted in the next-nearest-neighbour direction by two-thirds of a layer spacing, putting each molecule in the upper layer at the center of the equilateral triangle formed by three adjacent molecules in the lower layer. This results in an efficient packing which minimizes the free volume in the bilayer. Fig. 1 shows that the reflectivity changes considerably upon the formation of the monolayer phase. Temperature scan at a fixed $q_z = 0.2$Å^{-1} (judiciously chosen from Fig. 1) are shown in Fig. 3(a) for C18 and C18O. The formation of the surface layer at T_s and the bulk freezing at T_f are clearly seen. No further transitions are observed. In statistical mechanics terms, the formation of the solid monolayer is a wetting effect and the solid layer is said to wet the liquid surface[19]. The lack of growth of more layers as the bulk critical point

is approached renders the wetting in this case strongly incomplete. Similar incomplete wetting was observed for the smectic surface layer on the bulk liquid for the 12CB liquid crystals[6]. However, the number of layers there increases to 5 as the critical temperature is approached, so that the wetting is less incomplete.

The surface tension scans for C18 and C18O are shown in Fig. 3(b). First note the sharp break in the slope, indicating the formation of the monolayer. The lack of any further breaks indicates, again, that no additional layers are formed. Since the surface tension γ is the excess free energy of the surface over that of the bulk, and since the free energy is given by $F = U - TS$, we obtain that $d\gamma/dT = -(S_s - S_b)$, where S is the entropy, and s, b denote surface and bulk, respectively. For $T > T_s$ the surface is liquid and, as discussed above, $S_s > S_b$ so that a negative slope is observed. However, the ordering of the surface at $T < T_s$ reduces S_s considerably so that $S_s < S_b$ and the slope becomes positive. The sharp change at T_s here, as well as in Fig. 3(a), indicate that within our temperature resolution of a few mK the transition is first order. However, unlike for the bulk freezing-melting effect, no hysteresis is observed in T_s. The slope change of C18O is about twice that of C18, indicating a twofold gain in entropy, in accord with the formation of a bilayer rather than a monolayer. The x-ray and surface tension measurements were repeated for a wide range of chain lengths n and temperatures T. We now discuss the chain length dependence found in these experiments.

For both alkanes and alcohols [9, 10, 20, 21] we find that the slope $d\gamma/dT$ at $T > T_s$ is practically n- independent and for alkanes it is equal to -0.09±0.01 dyne/cm/°C, in agreements with literature values[7]. For $T < T_s$ the slope is linearly increasing with n, and the slope is about twice larger for alcohols than for alkanes. This can be accounted for by chain-conformational entropy arguments[10, 20].

The measured temperature range of existence of the surface layer, $\Delta T = T_s - T_f$, is plotted in Fig. 4(a). Note that the range for alcohols is much smaller, both in n and ΔT, than that of alkanes, indicating a much reduced tendency for surface ordering. The shape of these curves can be rationalized using the following simple thermodynamical arguments. Since $d\gamma/dT = -(S_s - S_b)$, we have[10] $\Delta T = (\gamma_{T_s} - \gamma_{T_f})/(S_b - S_s)$. The measurements show that γ_{T_s} is practically independent of n. Using the known relations[7] $(S_b - S_s) \sim n$, and[22, 21] $\gamma_{T_f} \sim n^{-2}$, we obtain:

$$\Delta T = a/n - b/n^3, \qquad (1)$$

where $a < b$ are positive proportionality constants[21]. Eq. (1) clearly shows that for small n, ΔT is negative, and hence the surface layer is always disordered at temperatures above the bulk freezing temperature T_f. For very large n, the entropy reduces the ordered surface phase $\Delta T \to 0$ for $n \to \infty$. Only for intermediate n does an ordered surface phase exist with a significant temperature range ΔT. This simple surface energy model accounts for the vanishing of the ordered surface phase for low n. The transition from positive to negative ΔT can be interpreted as a transition from surface freezing to the common surface melting behaviour. Fitting Eq.(1) to the measured alkane data yields a satisfactory agreement, as shown by the solid lines in Fig. 4 (a). The faster-than-predicted falloff in the figure for large n is due to other disordering mechanisms, not accounted for in our simple model. These are most likely the internal degrees of freedom of the molecules such as the proliferation of *gauche* transformations and the associated loss of the average linearity of the molecule. For alcohols, additional interactions must be included to describe ΔT versus chain length[21].

Finally, the surface layer thickness and nearest neighbour distances are shown in Fig. 4 (b,c). The monolayer thickness D for alkanes (and bilayer half-thickness for alcohols) vary linearly with n, as expected. As the average slope of this variation is slightly smaller than the canonical 1.27Å per carbon found in bulk alkane crystals, small deviations from a fully extended, vertical chain conformation are likely to exist. A small but clear decrease of slope
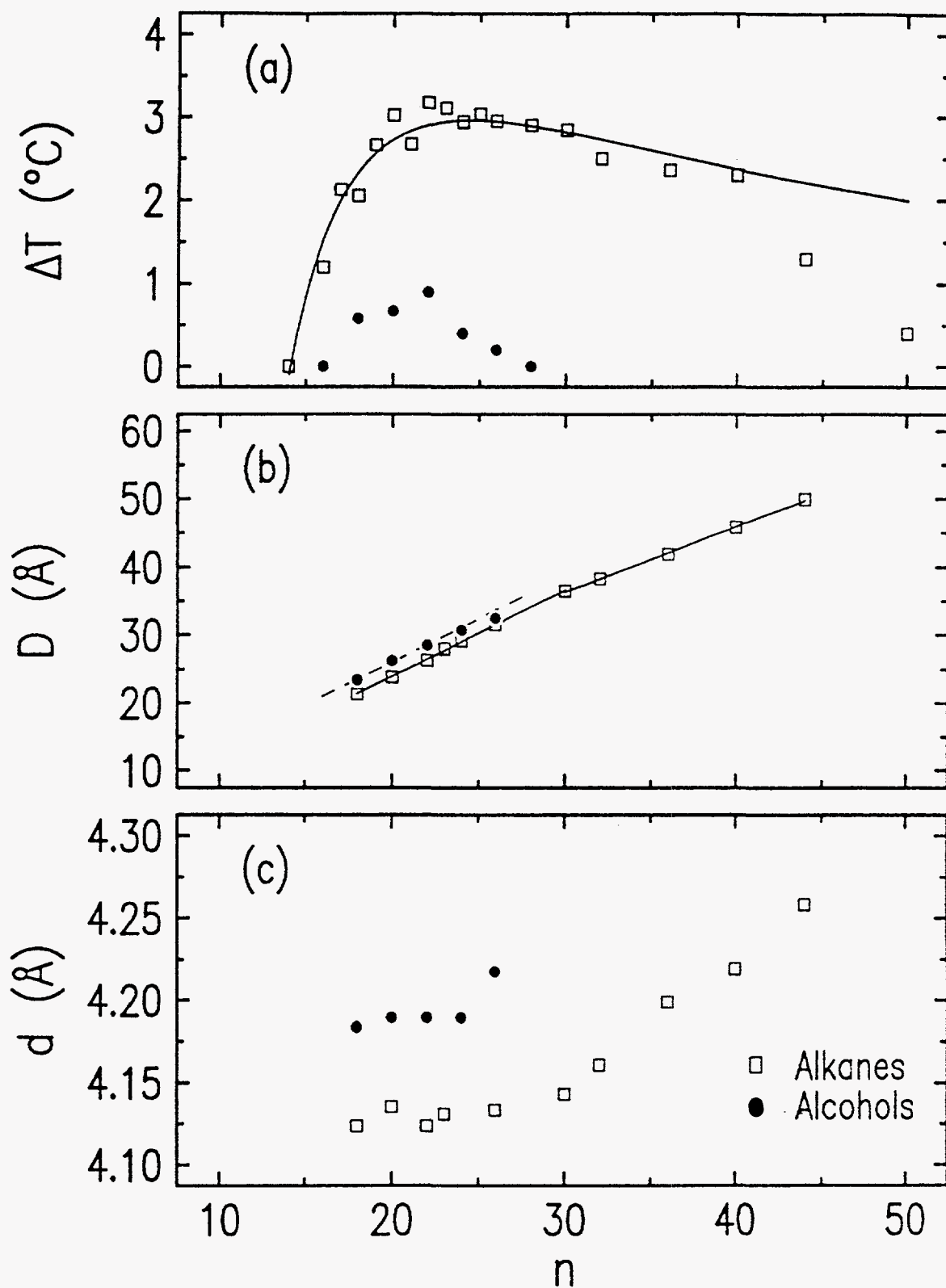
Figure 4: (a) The measured range of existence $\Delta T = T_s - T_f$ for the crystalline surface phase for alkanes and alcohols. The solid lines are fits to the theoretical expression in Eq. (1). (b) The reflectivity- measured monolayer thickness D for alkanes and half of the bilayer thickness of alcohols. (c) The GID-measured lattice spacing d of the hexagonally packed surface layer. the slope changes in (c) and (d) are discussed in the text.

is observed for $n \approx 30$ in alkanes and $n \approx 22$ in alcohols. At the same n we observe in Fig 4(c) the onset of a linear increase in the in-plane lattice spacing d, which is constant for smaller n. This marks the onset of a molecular tilt, while the onset of conformational disorder occurs for alkanes at a higher $n \approx 40$, destroying eventually the crystalline order. The BR measurements done on both substances clearly show the tilt for $n \geq 30$ in alkanes and $n > 22$ in alcohols. The existence or otherwise of an increased conformational disorder at these n can not be determined, however, by these methods. It is therefore possible that the proliferation of *gauch* defects in the chains above these n increases their average cross sections and decreases their average length as compared to the fully extended chains, thus contributing to the observed increase in d and the decrease in D, caused mainly by the tilt. This is an earlier, less developed, stage of the mechanism which is most likely responsible for the fast falloff in ΔT for large n in Fig 4(a). However, since ΔT is not a direct structural quantity it may not be as sensitive to conformational disorder as D and d. This may explain why the onset of the falloff in ΔT occurs only at $n \approx 40$ for alkanes and $n \approx 26$ for alcohols. A determination of the relative contributions of these effects will probably require additional GID and BR study using significantly higher resolutions than used for the present ones. An undulator source and a crystal analyzer will be required for these studies.

4   Conclusion

The novel surface phase, freezing and partial wetting effects presented here are not restricted to n-alkanes and alcohols. First measurements indicate that they exist in thiols and halogenated alkanes as well. Indeed they may be characteristic of a large class of molecules. Measurements on alkane mixtures also show a rich and unexpected surface phase behaviour[23]. At present no microscopic theory is available to account for the observed phenomena. It is hoped that further studies of related but progressively more complex chain molecules may reveal not only the origins of the surface behaviour detailed above, but also those of the surface behaviour of molecules incorporating such chains, like liquid crystals, and shed new light on the surface freezing *vs.* surface melting behaviour in condensed matter in general.

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