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Thermal Expansion of Surface-Frozen Layers of Semi-Fluorinated Alkanes

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Surface freezing (SF), the formation of an ordered quasi-2D monolayer on the surface of a melt a few degrees *above* the bulk solidification temperature was discovered to occur in several families of chain molecules [1,2]. Our recent measurements show that some semi-fluorinated alkanes (SFA), $F(CF_2)_m(CH_2)_nH$ (abbreviated as F_nH_m) exhibit a SF effect for temperature ranges of order 4-5 ^oC. Such large ranges provide an opportunity to measure the thermal expansion of the quasi-2D crystalline SF monolayer in pure materials. X-ray grazing incidence diffraction measurements were carried out for F_8H_8, $F_{10}H_8$ and $F_{10}H_6$. Results for the molecular separation d vs. temperature T are shown in Fig. 1, yielding linear expansion coefficients of $(dd/dT)/d=(6.3\pm0.3)\times10^{-4}$, $(7.7\pm1.7)\times10^{-4}$ and $(7.7\pm0.2)\times10^{-4}$ $^oC^{-1}$ for $F_{10}H_6$, F_8H_8 and $F_{10}H_8$ respectively, close to the $(9\pm0.5)\times10^{-4}$ $^oC^{-1}$ of the fully protonated C_{20}-alkane SF monolayer[3]. The cross-sectional area of the F block is 28.3 $Å^2$/molecule [4], vs. only ~19.5 $Å^2$ for the H block [2]. Moreover, the F block is very rigid, and has a cross-section independent of length. Thus, one would expect the F blocks to dominate the structure and the expansion of the SF monolayer. Also, the expansion coefficient is expected to be independent of m and n. Contrary to these expectations, Fig. 1 clearly shows that increasing the F-block length by 25%, from F_8H_8 to $F_{10}H_8$, reduces the molecular separation, leaving the expansion coefficient unchanged. The reduced intermolecular distance reflects, most probably, the increased van der Waals attraction of the longer molecules. Surprisingly, a 33% increase in the H-block length, from $F_{10}H_6$ to $F_{10}H_8$, decreases not only the intermolecular distance, similar to the increase in the F block lengths, but also *increases* the expansion coefficient. This "softer" crystallinity can be understood perhaps as a shift in the balance between the H-H and the F-F interactions, towards lowering of the latter's dominance.

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References:

[1] X. Z. Wu *et al.*, *Science*, **261**, 1018 (1993); O. Gang *et al.*, *Phys. Rev. E*, **58**, 6086 (1998).
[2] B. M. Ocko *et al.*, *Phys. Rev. E*, **55**, 3164 (1997).
[3] B.M. Ocko *et al.*, *Phys. Rev. E* **63**, 32602 (2001).
[4] P. Lo Nostro, *Adv. Coll. Interface Sci.*, **56**, 245 (1995).

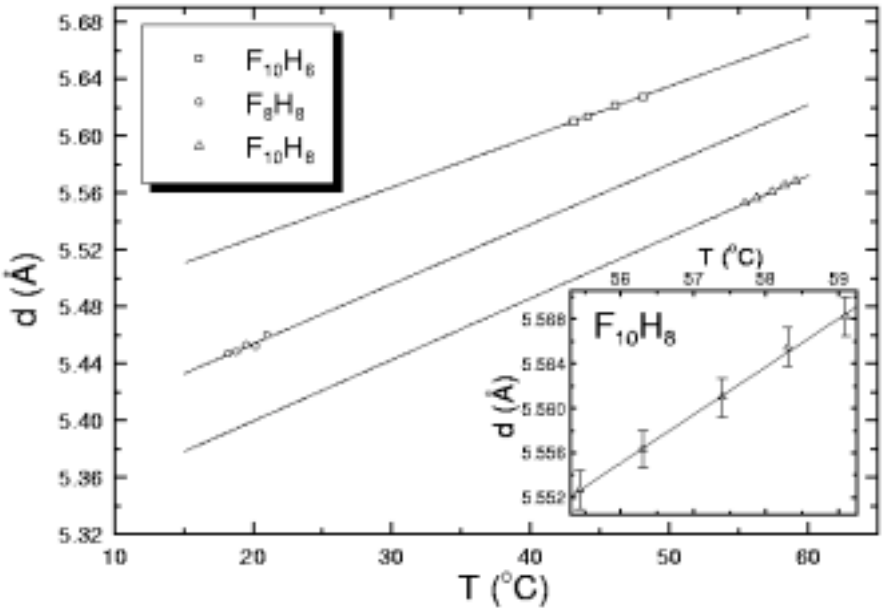

Fig. 1: The nearest-neighbor distances calculated from the GID peak positions (symbols) and their fits by straight lines. A magnified view is shown in the inset for $F_{10}H_8$. For a discussion see text.