

## Surface freezing in chain molecules. II. Neat and hydrated alcohols

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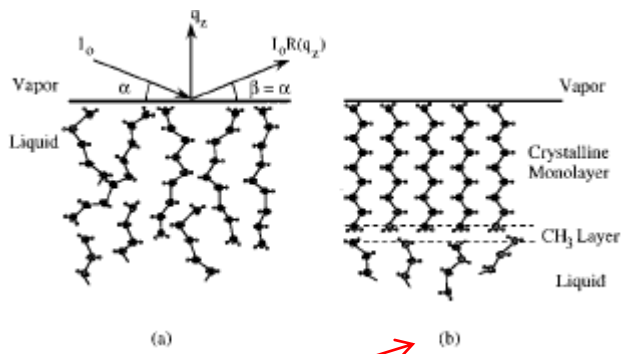
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Surface freezing is studied in dry and hydrated normal-alcohol melts by x-ray scattering and surface tensiometry. A single crystalline bilayer forms at the surface, for even carbon numbers only, at temperatures up to 1 °C (dry) or 2 °C (wet) above the bulk freezing, and persists without change down to bulk freezing. The packing is hexagonal, with untilted molecules for short chains and tilted molecules for long chains. The lattices of the upper and lower monolayers are shifted along the next-nearest-neighbor direction. Hydration is found to swell the bilayer by  $\sim 2.5$  Å due to water intercalation into the bilayer, at a molecular water:alcohol ratio of  $\sim 1:2$ . It also increases the transition temperatures, and the temperature and chain-length ranges for which surface crystallization is observed. These effects are accounted for quantitatively by considering the surprising *increase* in hydration upon freezing, and taking into account the Gibbs-rule-predicted water depletion at the surface in the liquid surface phase. [S1063-651X(98)15010-9]

SEOK, Sangjun, 08.28.2010

# Surface freezing in chain molecules. 1- Phys. Rev. E 55, 3 (1997)

The x-ray reflected specularly from the vapor-liquid interface of *n*-alkanes at high temp..



Experimental results of the x-ray

The surface crystalline layer of *n*-alkanes below surface freezing temperatures, but still above the bulk freezing point.

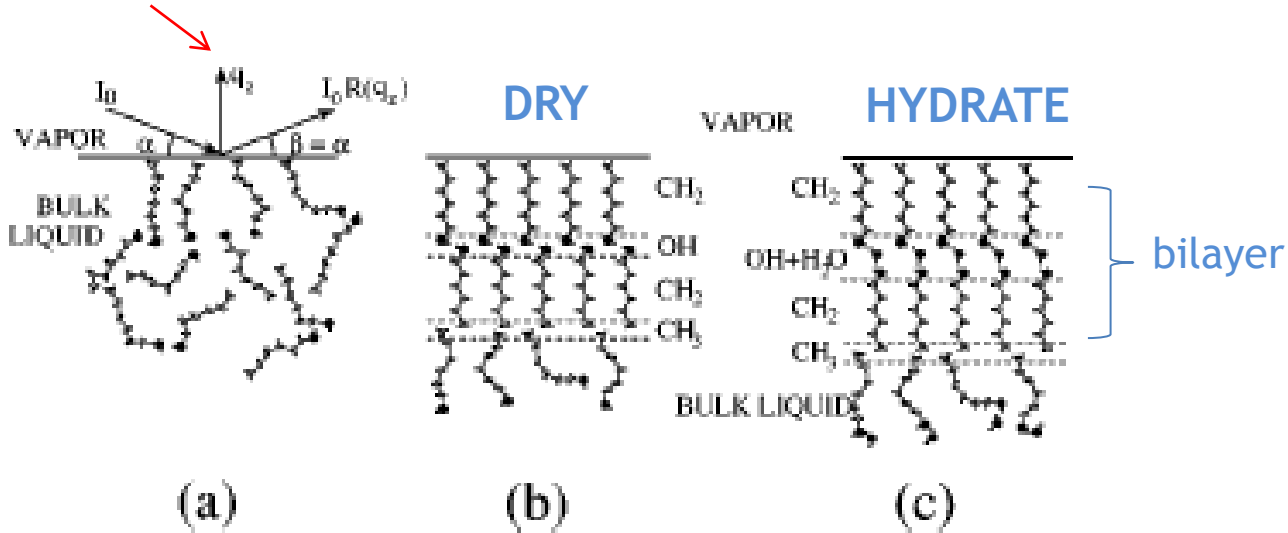
<i>n</i>	<i>D</i> (Å)	<i>q<sub>r</sub></i> (Å <sup>-1</sup> )	<i>q<sub>z</sub></i> (Å <sup>-1</sup> )	<i>T<sub>f</sub></i> (°C)	$\Delta T$ (°C)	$\delta$	<i>A</i> (Å <sup>2</sup> )	$\Delta S_s$ (mN m <sup>-1</sup> K <sup>-1</sup> )	$\Delta S_b$
14				4.50	0.00				
16				17.69	1.20			0.896	1.16
17				24.00	2.12			0.943	1.14
18	21.66	1.524		29.33	2.05	0.000	19.63	1.00	1.27
19				34.40	2.66			1.12	1.25
20	24.11	1.519	0.0	38.65	2.97	0.000	19.76	1.16	1.28
21	25.49	1.517	0.0	41.93	2.67	0.000	19.81	1.23	1.30
22	26.75	1.524		46.25	3.13	0.000	19.63	1.29	1.42
23	28.22	1.521		50.00	3.11	0.000	19.70	1.32	1.42
24	29.45			52.91	2.98			1.39	1.50
25				55.83	3.10			1.45	1.50
26	31.67	1.520		58.44	2.99	0.000	19.73	1.51	1.52
28				63.40	2.96			1.64	1.62
30	36.63	1.516		67.56	2.82	0.005	19.73	1.72	
32	38.43	1.510		70.69	2.52			1.76	
36	42.00	1.496	0.0 0.392	76.94	2.48	0.045	19.50	1.94	2.05
40	46.15	1.489		81.70	2.30			2.11	
44	50.34	1.476	0.356 0.740	85.70	1.30	0.106	18.71	3.02	3.45
46	49.1			88.05	0.55			3.29	
50				91.10	0.40			3.17	3.76

# Surface freezing in chain molecules. 2- *Phys. Rev. E* 58, 5 (1998)

**Samples** : normal 1-alcohol,  $\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}$ , denoted here  $\text{C}_n\text{OH}$

**X-ray wavelength** :  $1.54 \text{ \AA}$

Schematic molecular arrangement at the surface of an alcohol melt in its high-temp. liquid state.



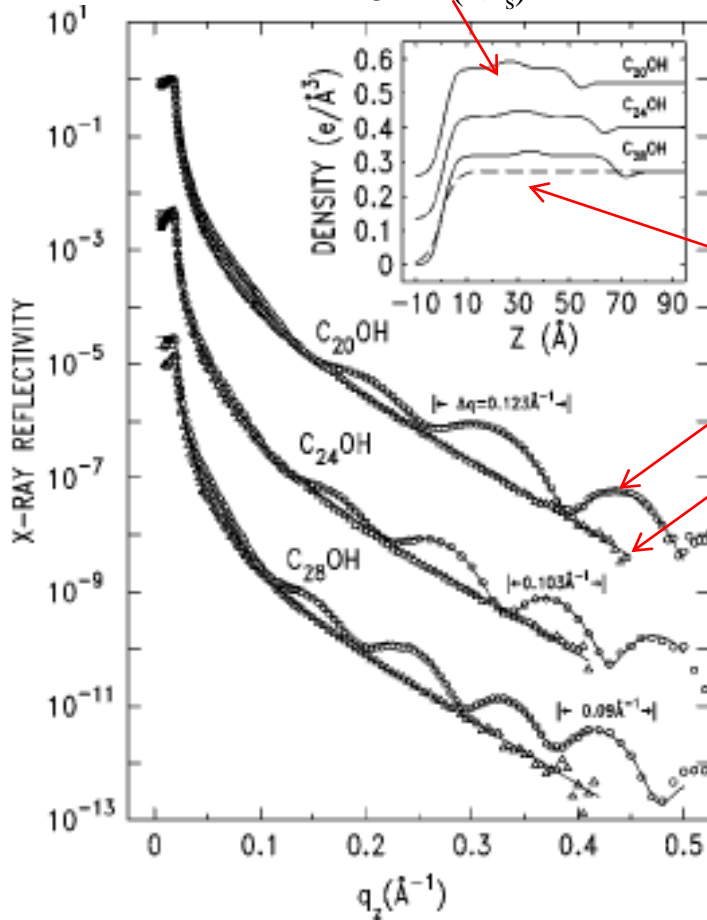
The surface-frozen phase, with the bulk remaining liquid, when dry and hydrated at water:alcohol ratio of  $\sim 1:2$ .

# Results and Discussion - Dry alcohol melt

## Surface-normal structure

X-ray reflectivity of  $C_{22}OH$  at a fixed  $q_z = 0.2 \text{ \AA}^{-1}$

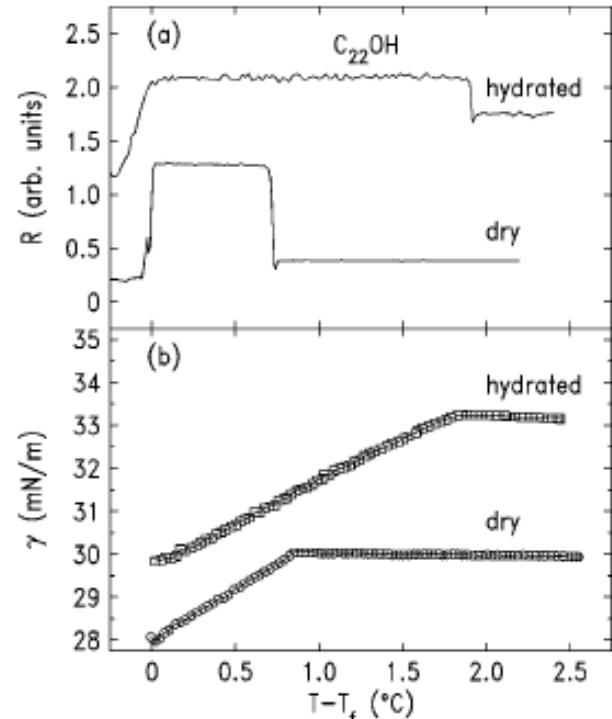
surface electron density =  $0.309 \pm 0.009 \text{ e/\AA}^3 (<T_s)$



Bulk electron density =  $0.279 \text{ e/\AA}^3 (>T_s)$

$<T_s$

$>T_s$

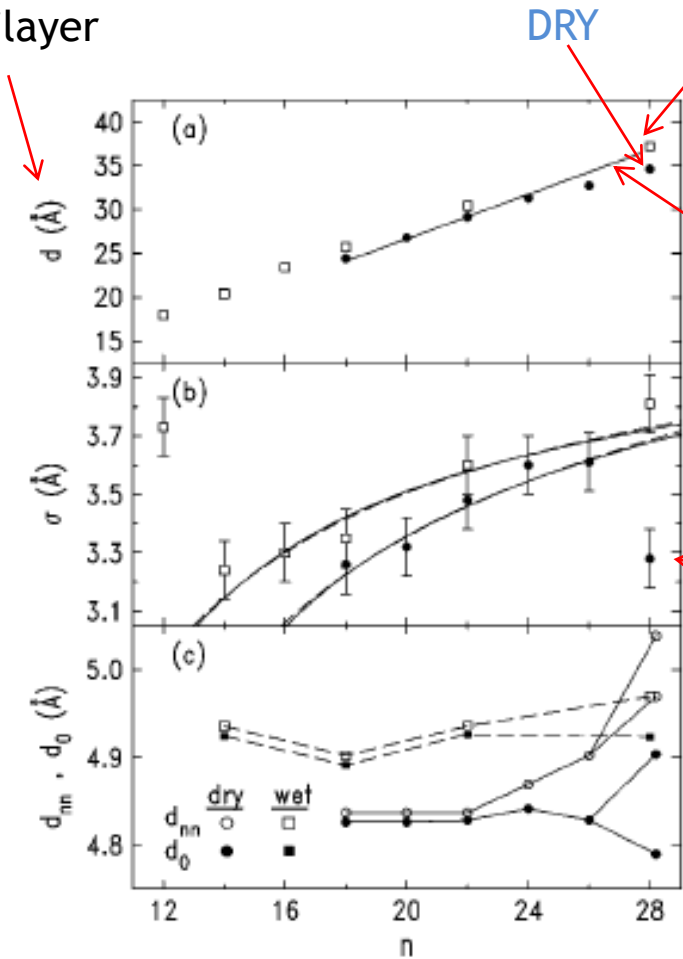


Bulk freezing temperature

# Results and Discussion - Dry alcohol melt

## Surface-normal structure

The half thickness of the bilayer



DRY WET

$n \leq 22$ , well agreed,  $n > 22$ , the bilayer are either tilted or not fully extended

the calculated fully extended lengths of the molecules ( $d_{\text{calc}} = 1.27 \times (n-1) + 2 \text{ \AA}$ )

Vapor interface roughness

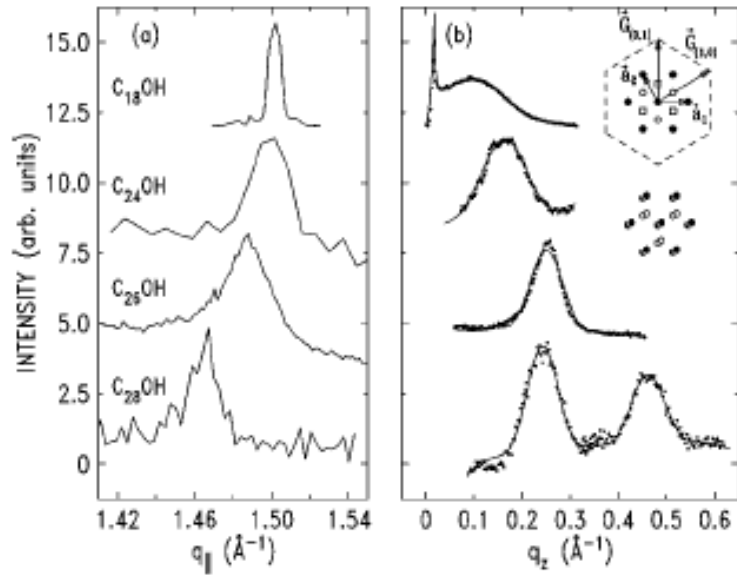
The transition from a plastic-crystalline to a crystalline phase???

( $d_{nn}$ ) the chain-chain spacing in the surface plane and ( $d_0$ ) in the plane normal to the molecular axis

$$\left. \begin{aligned}
 d_{nn} &= 2\pi / (q_{\parallel} \cos 30^\circ) \\
 d_0 &= 2\pi / (q \cos 30^\circ) \\
 q &= \sqrt{q_{\parallel}^2 + q_z^2}
 \end{aligned} \right\} \text{By Grazing incidence diffraction}$$

# Results and Discussion - Dry alcohol melt

## Surface-parallel structure



$n$	$D/2$ (Å)	$q_{  }$ (Å <sup>-1</sup> )	$q_z$ (Å <sup>-1</sup> )	$\theta$ (°)	$T_f$ (°C)	$\Delta T$ °C)	$\Delta S_x$ (mJ m <sup>-2</sup> K <sup>-1</sup> )	$\Delta S_b$
12					21.1			
14					37.0			1.33
16				< 5.0	49.0	0.15	1.4	1.66
18	24.42	1.50	0.1	< 5.0	57.15	0.6	1.7	1.82
20	26.75	1.50	0.1	< 5.0	63.7	0.8	1.75	2.18
22	29.15	1.50	0.09	< 5.0	69.8	0.9	2.3	2.40
24	31.29	1.49	0.16	12.0	73.95	0.8	2.4	2.70
26	32.71	1.48	0.26	22.0	77.4	0.65	2.75	2.96
28	34.61	1.46	0.24	17.0	81.2	0.9	2.6	
		1.44	0.47					
30					84.0			

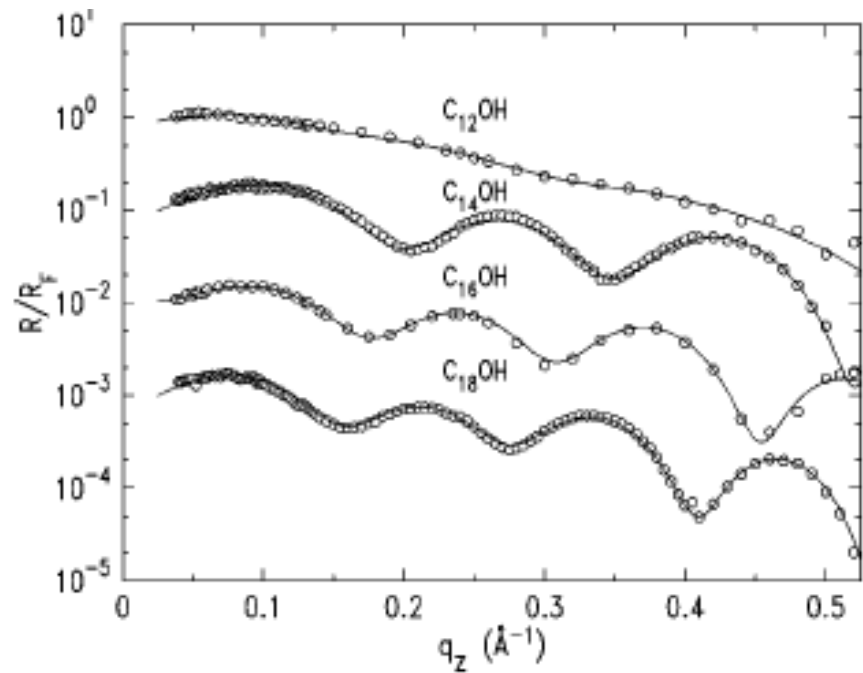
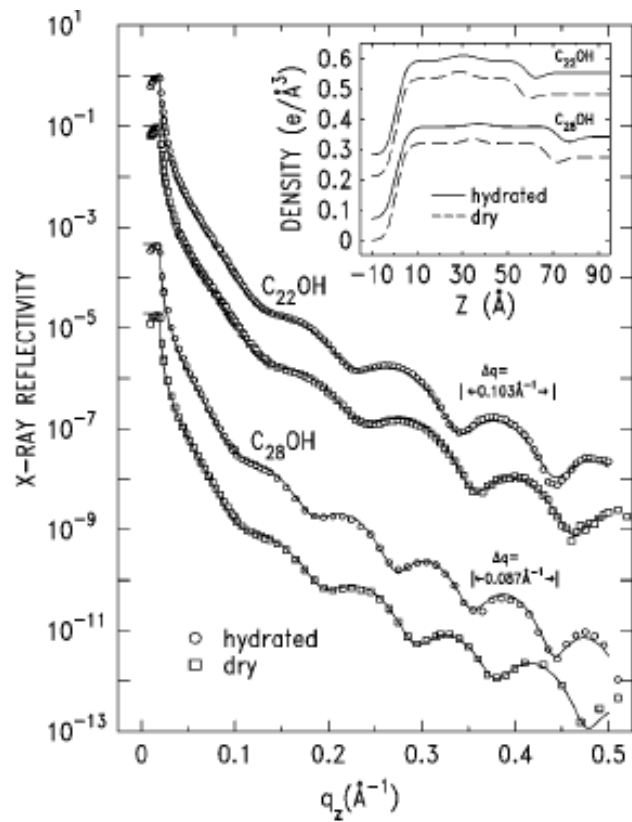
constant

Two in plane peaks

Gradually decrease

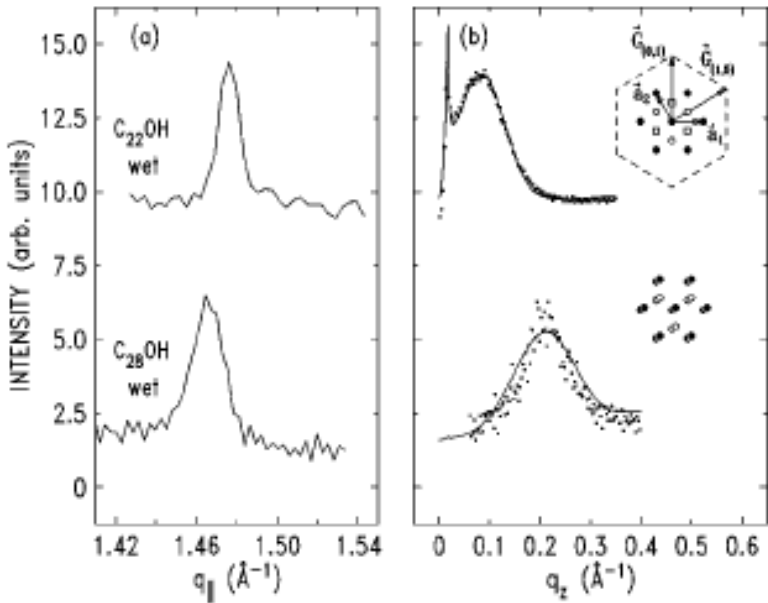
# Results and Discussion - Hydrated alcohol melt

## Surface-normal structure



# Results and Discussion - Hydrated alcohol melt

## Surface-parallel structure



$n$	$D/2$ ( $\text{\AA}$ )	$q_{\parallel}$ ( $\text{\AA}^{-1}$ )	$q_{\perp}$ ( $\text{\AA}^{-1}$ )	$\theta$ ( $^{\circ}$ )	$T_f$ ( $^{\circ}\text{C}$ )	$\Delta T$ ( $^{\circ}\text{C}$ )	$\Delta S_s$ ( $\text{mJ m}^{-2} \text{K}^{-1}$ )
12	17.91				23.4	1.7	0.82
14	20.38				39.5	1.7	1.28
16	23.38				51.6	1.8	1.38
18	25.72	1.48	0.1	<5.0	59.9	2.0	1.7
20					66.5	2.0	1.6
22	30.41	1.47	0.09	<5.0	72.8	1.8	1.95
24					76.35	1.9	1.8
26					80.2	1.4	2.8
28	37.16	1.46	0.2	19.0	83.7	1.6	2.45
30					86.5		