Unifying Interfacial Self-Assembly and Surface Freezing

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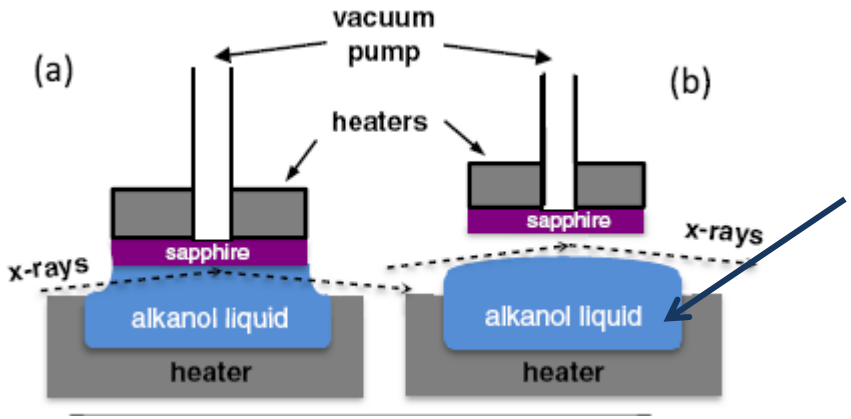
X-ray investigations reveal that the monolayers formed at the bulk alkanol-sapphire interface are densely packed with the surface-normal molecules hydrogen bound to the sapphire. About 30–35 °C above the bulk, these monolayers both melt reversibly and partially desorb. This system exhibits balanced intermolecular and molecule-substrate interactions which are intermediate between self-assembled and surface-frozen monolayers, each dominated by one interaction. The phase behavior is rationalized within a thermodynamic model comprising interfacial interactions, elasticity, and entropic effects. Separating the substrate from the melt leaves the monolayer structurally intact.



Alkanol molecule:
($C_nH_{2n+1}OH$, C_nOH)

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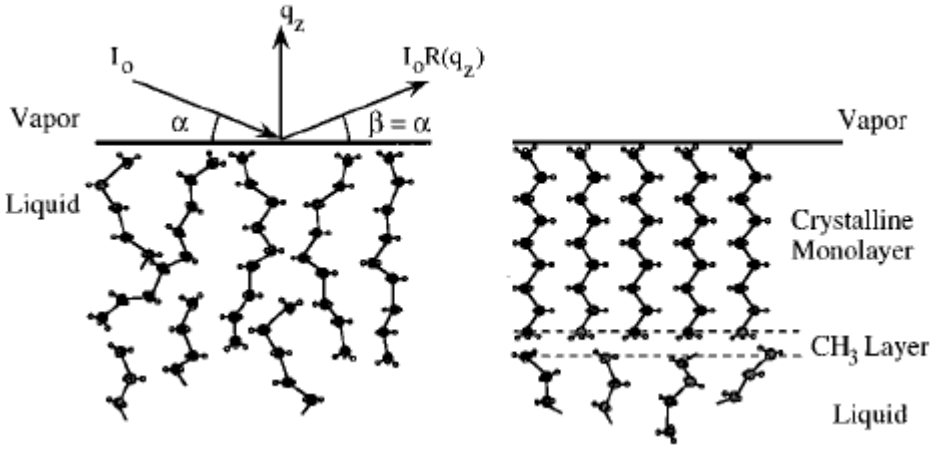
Surface freezing molecules in chain molecules : Normal Alkanes (vapor/liquid)

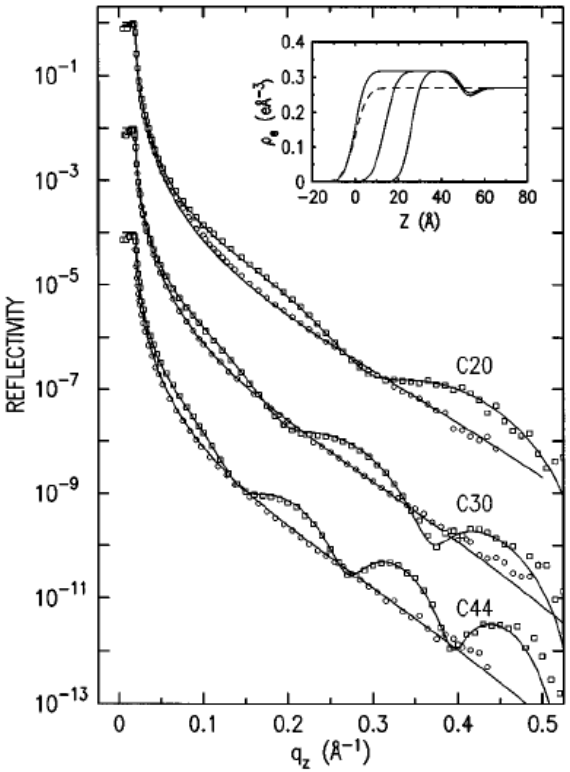
Normal alkanes → CH_3-$(CH_2)_{n-2}$-CH_3



Melting temperature

~ 3°C > bulk freezing temperature

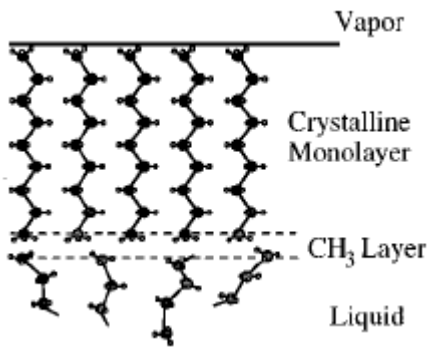
X-ray reflectivity results in normal alkanes



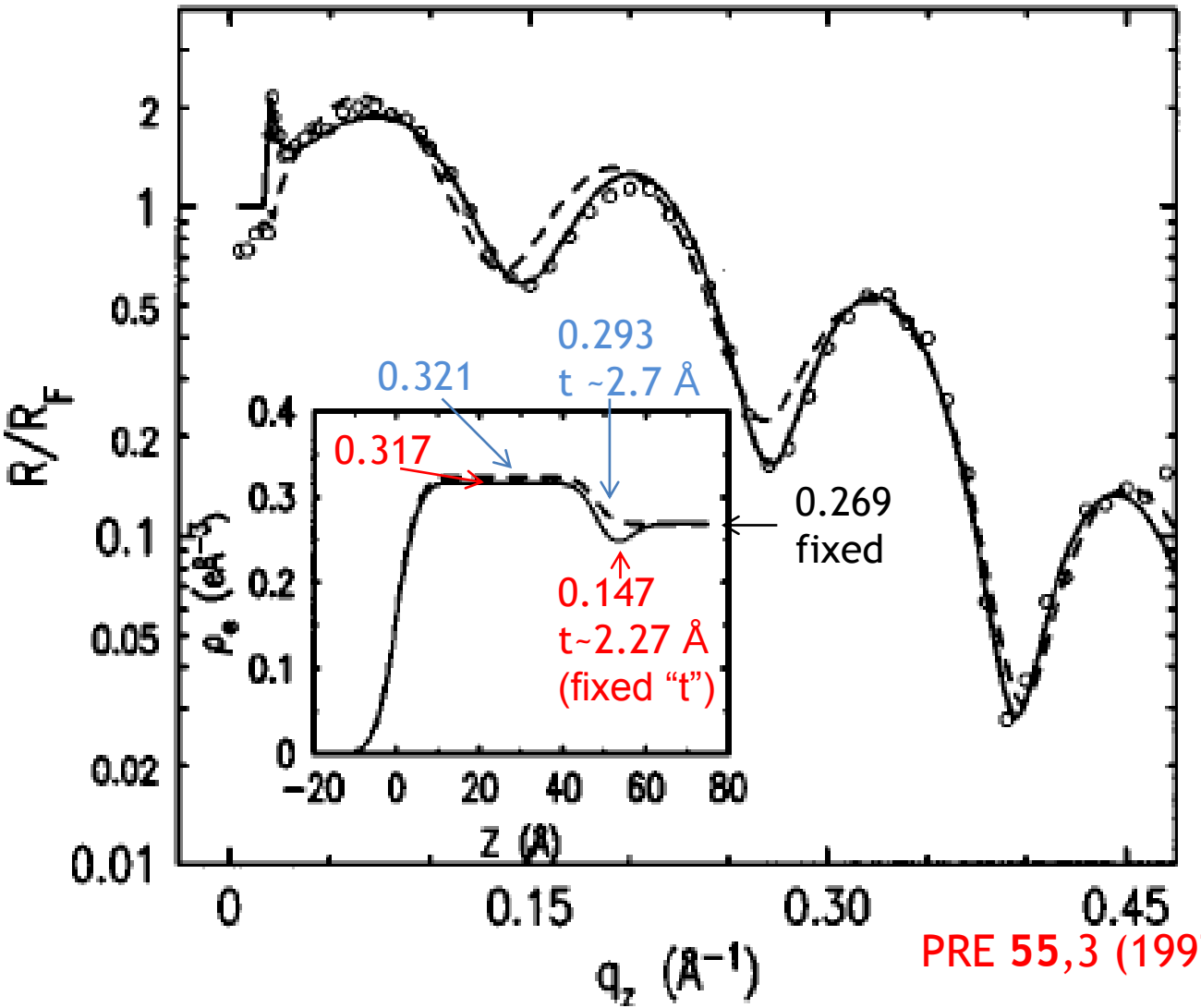
PRE **55**,3 (1997)

Surface freezing molecules in chain molecules : Normal Alkanes (vapor/liquid)

Electron density profiles:



One slab : dotted line
Two slab : solid line

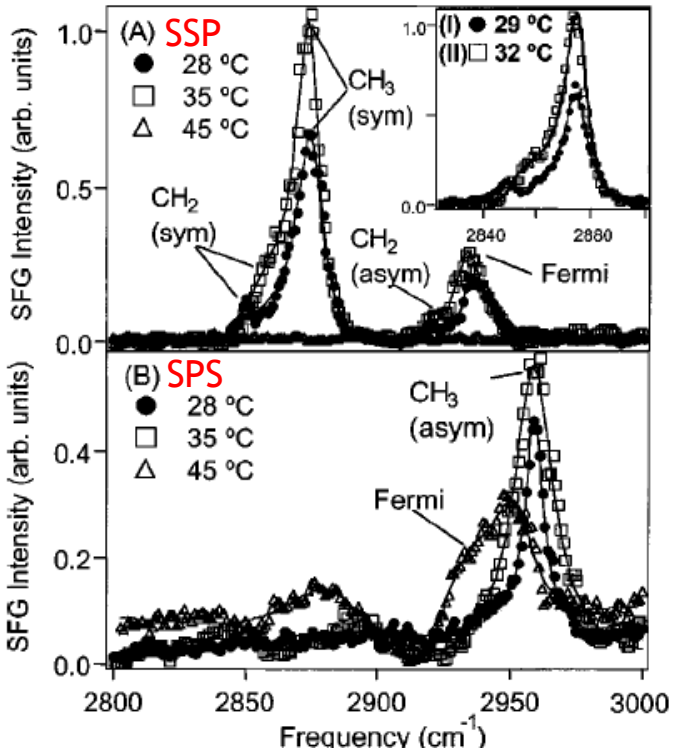


PRE **55**,3 (1997)

Surface freezing molecules in chain molecules : Normal Alkanes (solid/liquid)

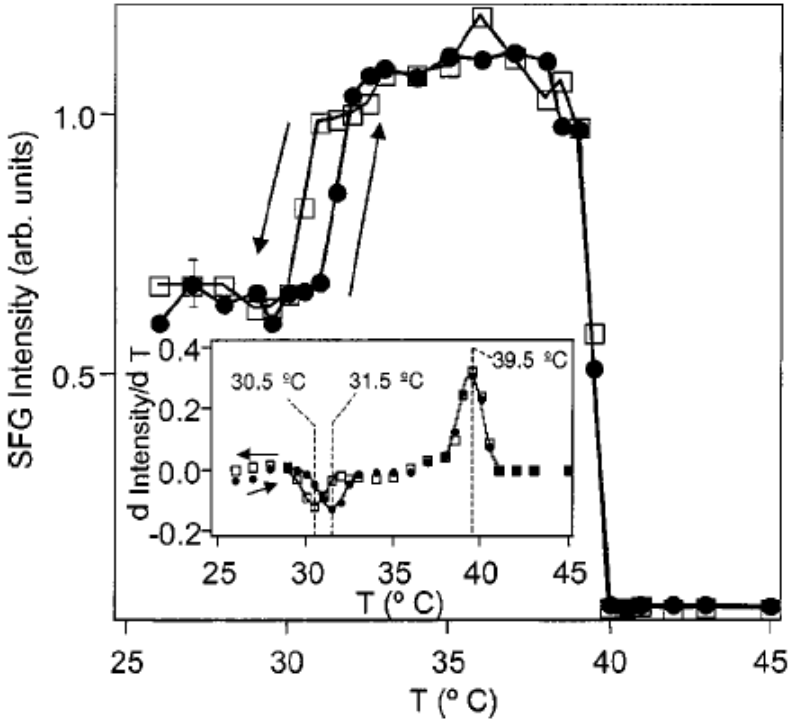
B. Ocko say that … For bulk *n* alkanes in contact with sapphire only surface parallel molecules were observed at the interface and surface freezing was not observed in optical measurement.

C_{21}/Al_2O_3 SFG spectra



Transition temperature:
bulk liquid-rotator → 39.5 °C
rotator-crystalline → 30.5 °C
crystalline-rotator → 31.5 °C

The variation in SFG signal intensity with temperature of the methyl sym. stretch of C_{21}/Al_2O_3 in SSP



PRE **66**,041607 (2002)

Surface freezing molecules in chain molecules : Normal Alkanes (solid/liquid)

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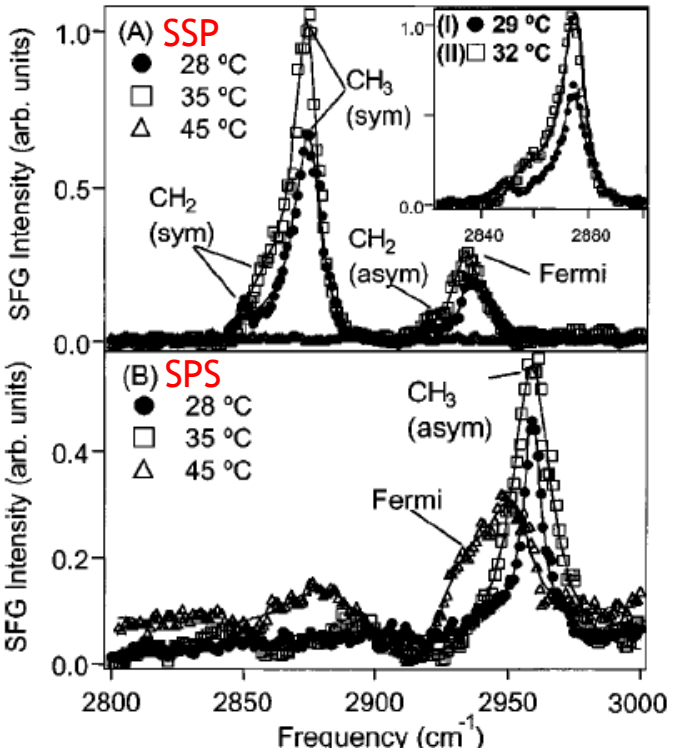
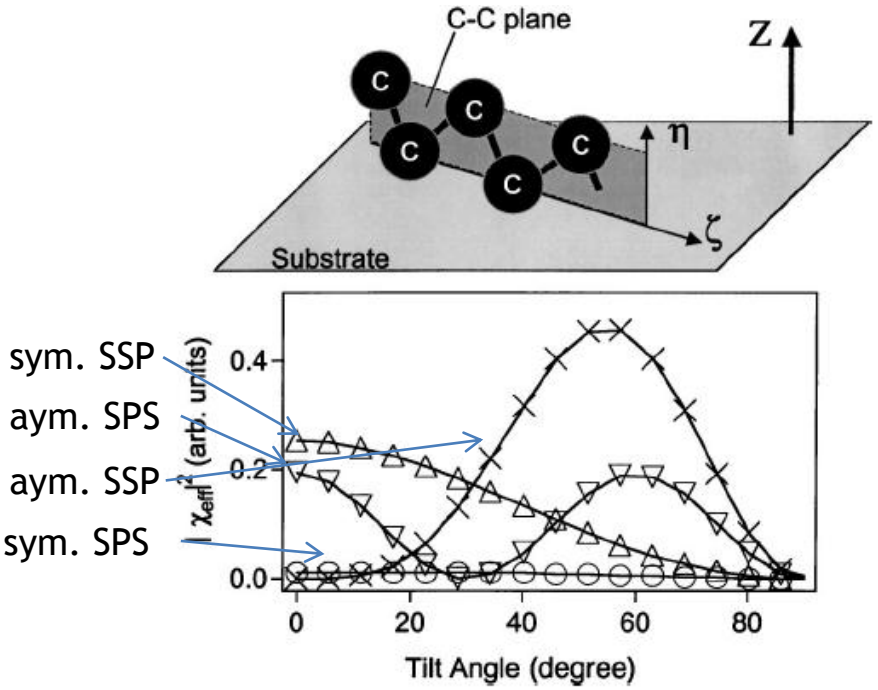
C_{21}/Al_2O_3 SFG spectra



Transition temperature:
bulk liquid-rotator → 39.5 °C
rotator-crystalline → 30.5 °C
crystalline-rotator → 31.5 °C

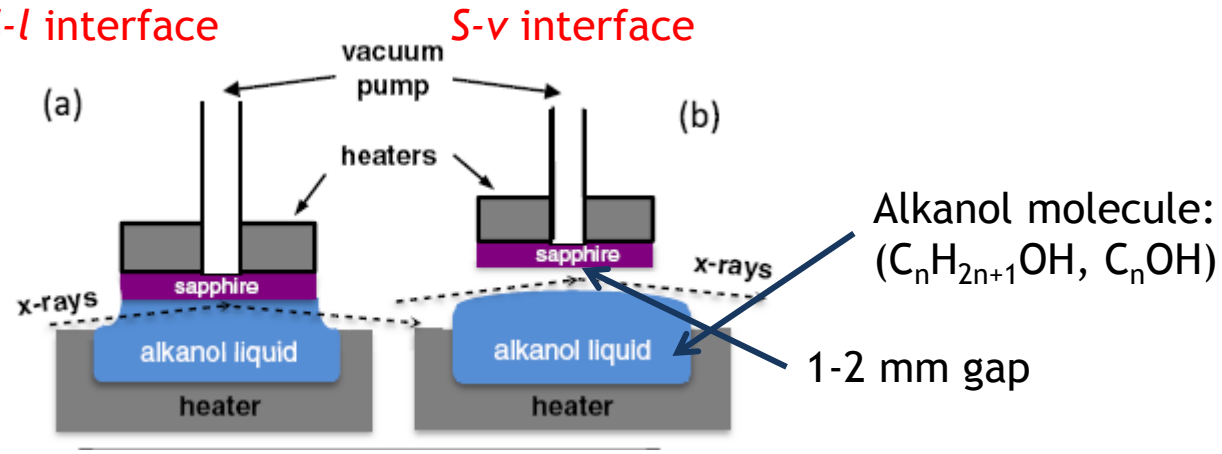
The calculated variation of the effective susceptibility of an odd *n*-alkane with tilt angle
(at below bulk-rotator temp. with methyl group)



PRE **66**,041607 (2002)

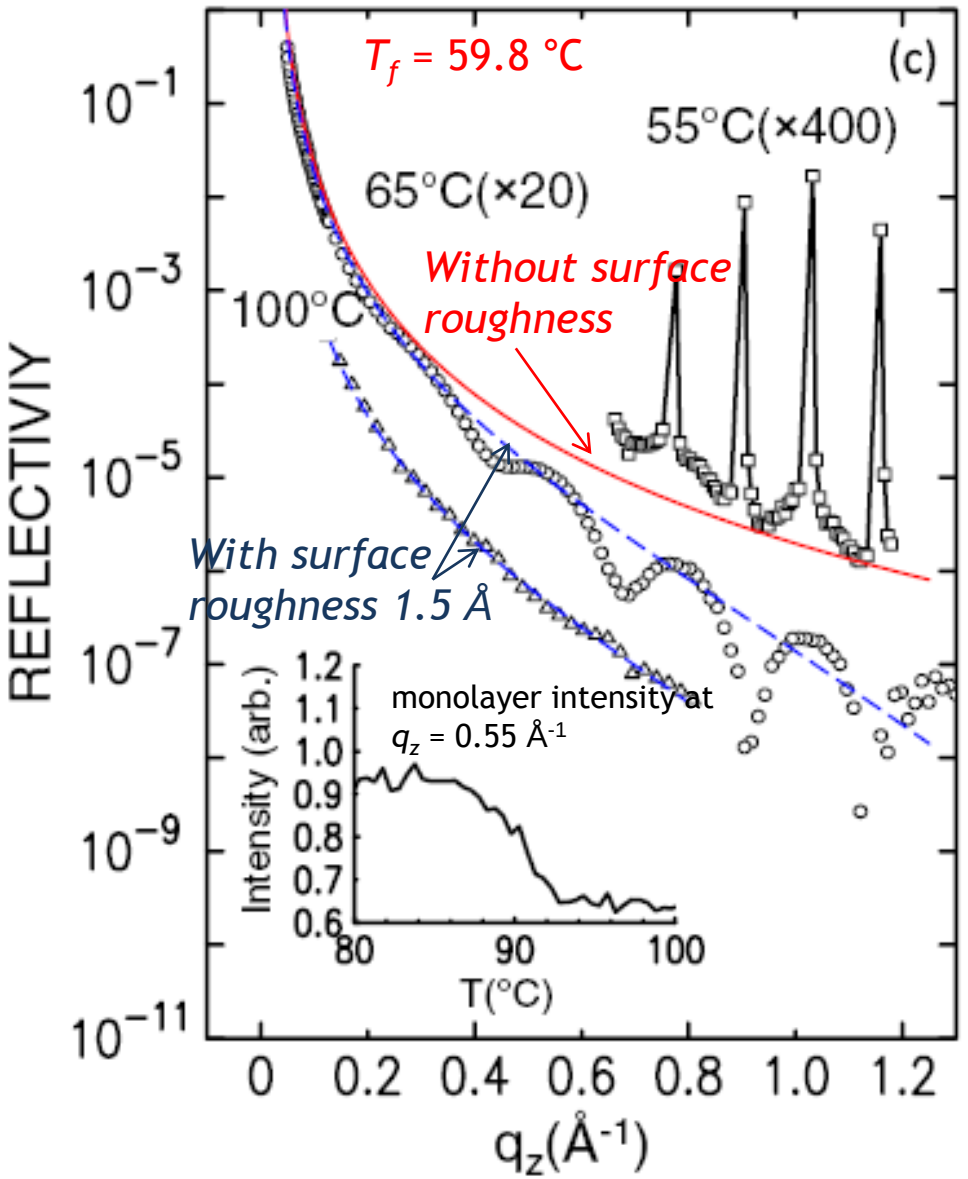
Surface freezing molecules in chain molecules : alkanol-sapphire interface

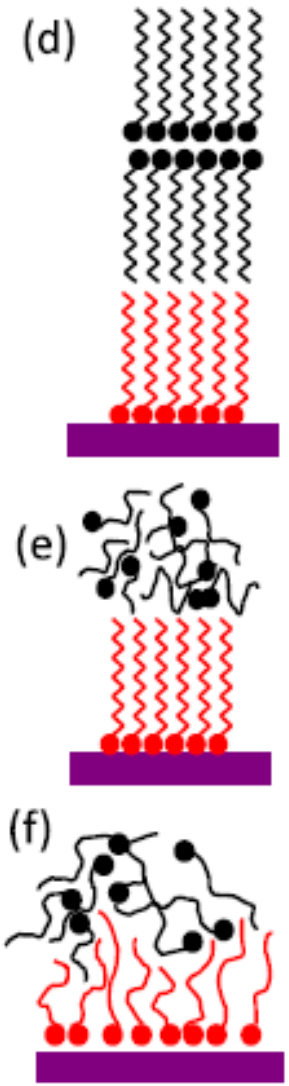
Experimental



X-ray reflectivity : 72.5 keV and 32 keV

Surface freezing molecules in chain molecules : alkanol-sapphire interface – X-ray reflectivity at *s-l*(sapphire/$C_{18}OH$)



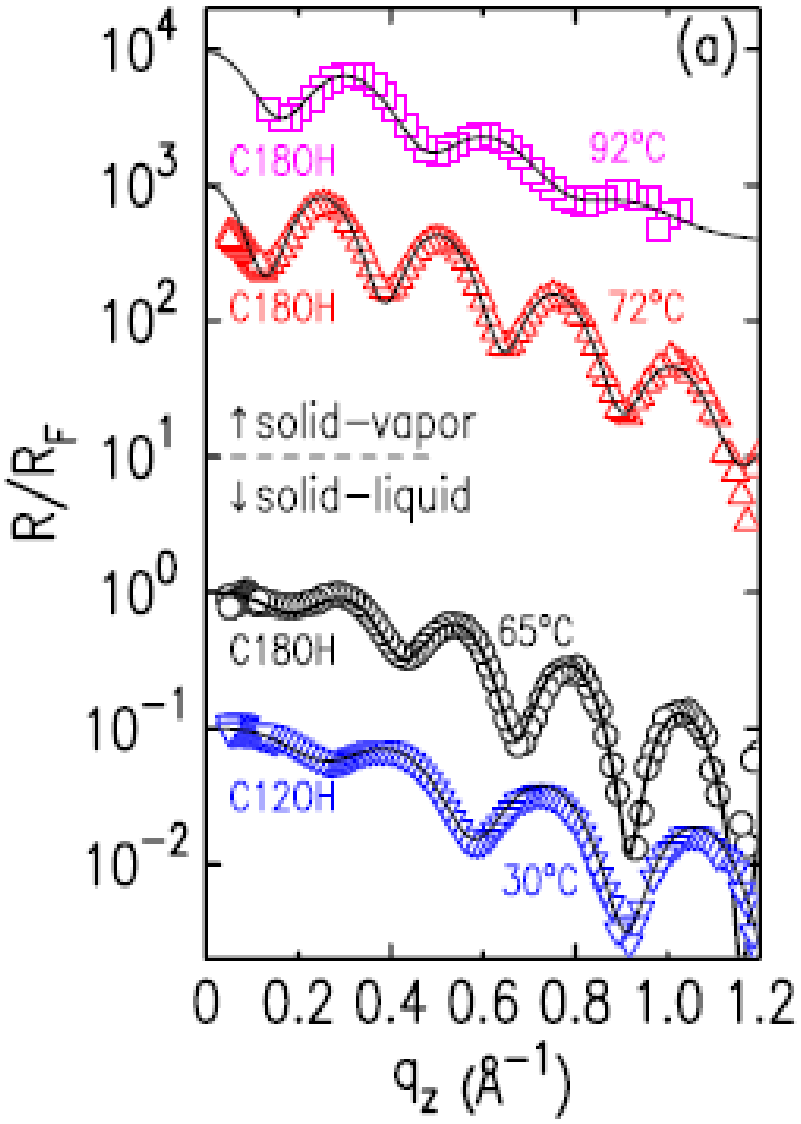


Crystalline : Bilayer spacing (~49 Å)

surface monolayer : q_z period is twice in crystalline

disordered

Surface freezing molecules in chain molecules : alkanol-sapphire interface – X-ray reflectivity at *s-l* and *s-v*



$C_{18}OH$ XR curves:

$\Delta q_z = 0.255$ Å^{-1}

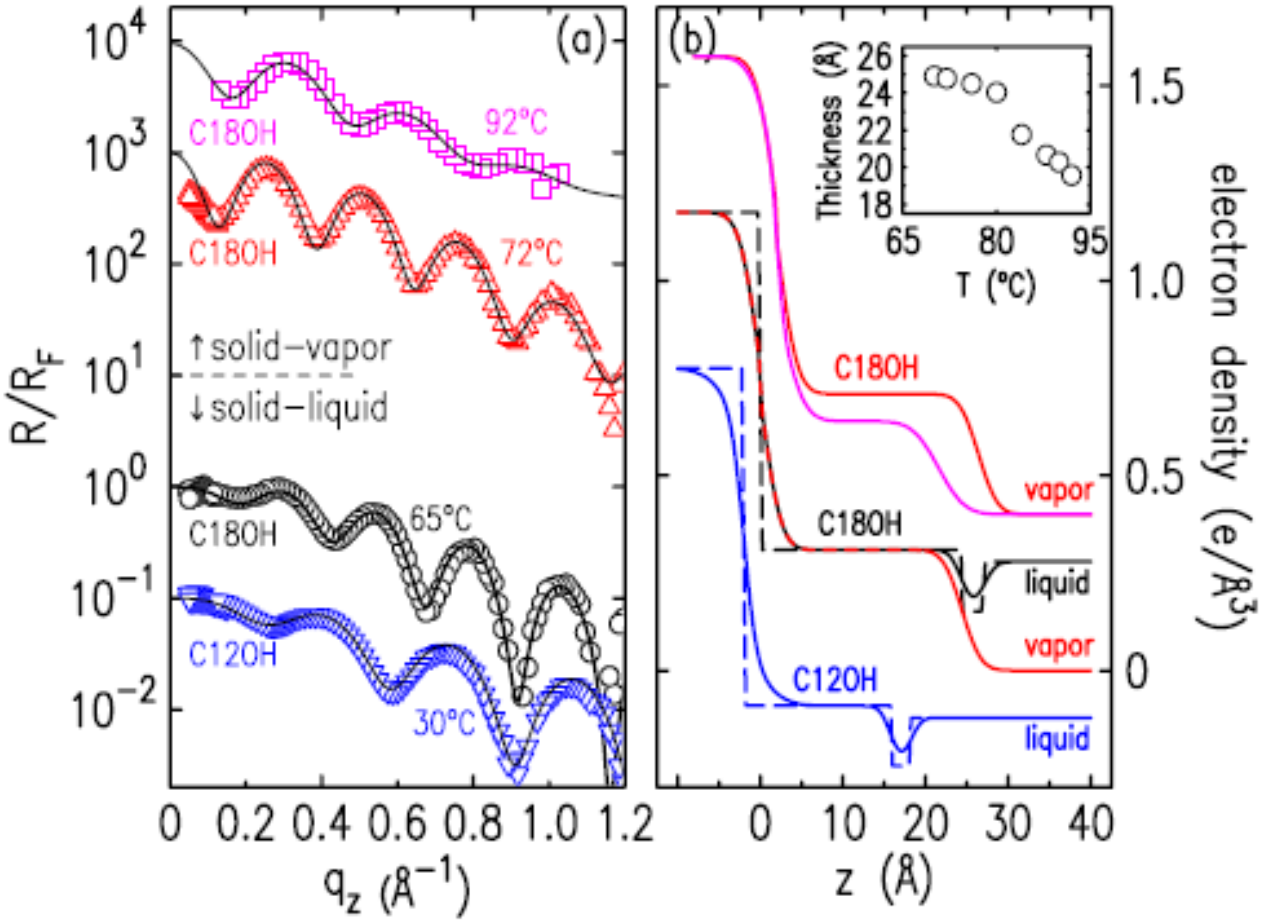
$d_{18} = 2\pi/\Delta q_z \sim 24.6$ Å

$C_{12}OH$ XR curves:

$\Delta q_z = 0.35$ Å^{-1}

$d_{18} = 2\pi/\Delta q_z \sim 18.0$ Å

Surface freezing molecules in chain molecules : alkanol-sapphire interface – X-ray reflectivity at *s-l* and *s-v*



electron density profiles

(a) sapphire, (b) hydrocarbon monolayer, (c) depletion region bet. the monolayer and bulk *n*-alkanol, (d) bulk liquid *n*-alkanol

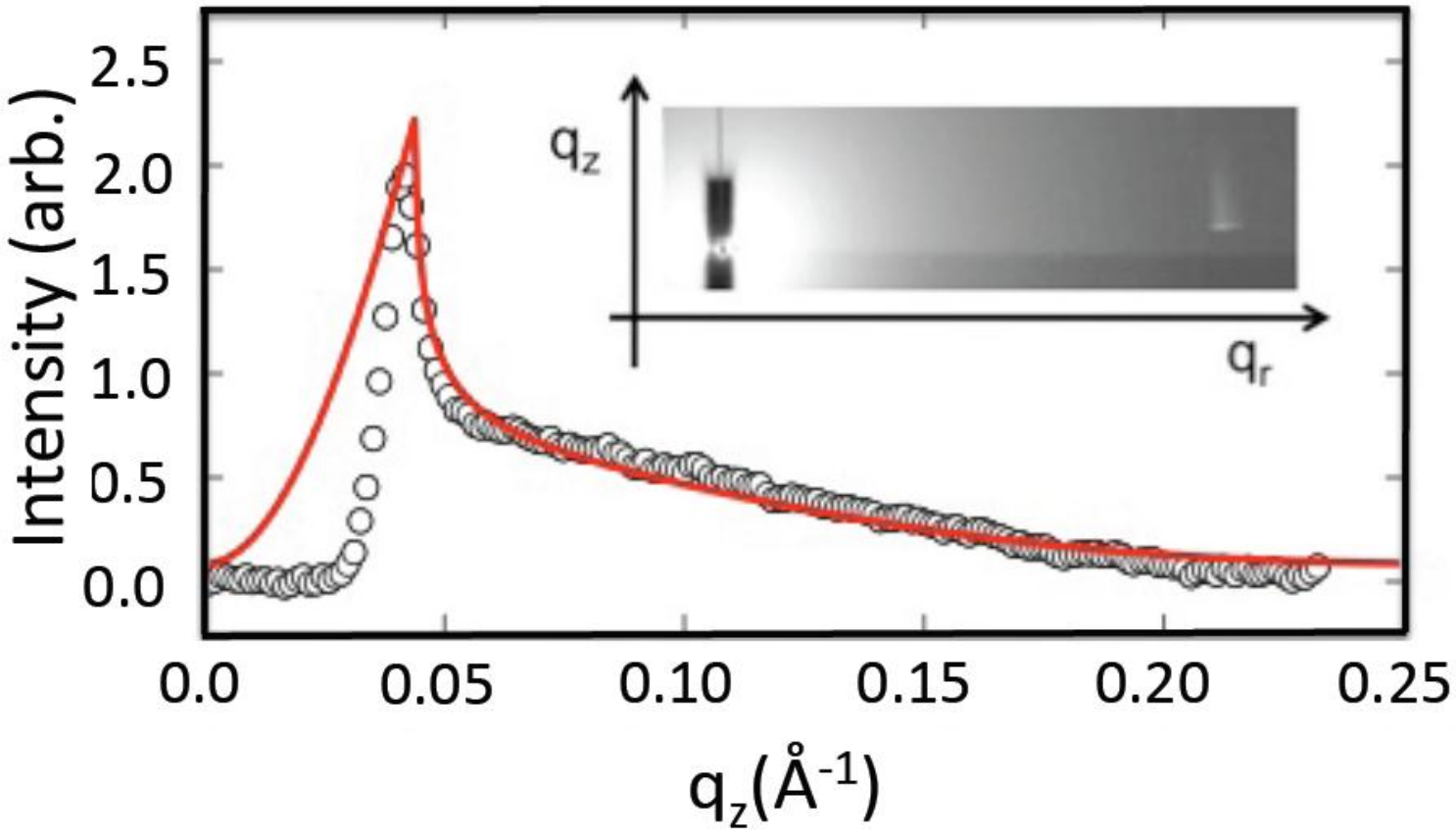
s-v interface

(c),(d)→0
electron density
sapphire : 1.175 e/Å^3
monolayer : 0.309 e/Å^3
liquid : 0.284 e/Å^3

s-l interface

For $C_{18}OH$
d = 24.4±0.2 Å
Δd = 2.6 Å
For $C_{12}OH$
d = 17.8 Å
Δd = 2.3 Å

Surface freezing molecules in chain molecules : alkanol-sapphire interface – Supplemental



measured Bragg Rod intensity of a C18OH solid monolayer at 60 °C on sapphire at the *s-v* interface (q_r = 1.52 ± 0.001 $Å^{-1}$)