On sub-T_g dewetting of nanoconfined liquids and autophobic dewetting of crystallites

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Introduction:

❖ Rapid cooling results quenching to a metastable glassy state for some liquids. In the process the disorder structure of liquid is maintained.

❖ Through structural relaxation process molecules can be rearranged toward an equilibrium configuration near sub-T_g (glass transition temperature).

❖ Self diffusion occurs at T_g.

❖ Thermal stability of thin films is of technological importance for adhesion and lubrication.

❖ A relatively thick film dewets *via* the formation of dried holes as a result of thermal nucleation or heterogeneous nucleation initiated by defects, whereas thinner films form uniformly distributed surface undulations that exhibit a clearly defined wavelength.

❖ Molecular dynamics of liquids is slowed down dramatically during the glass transition.

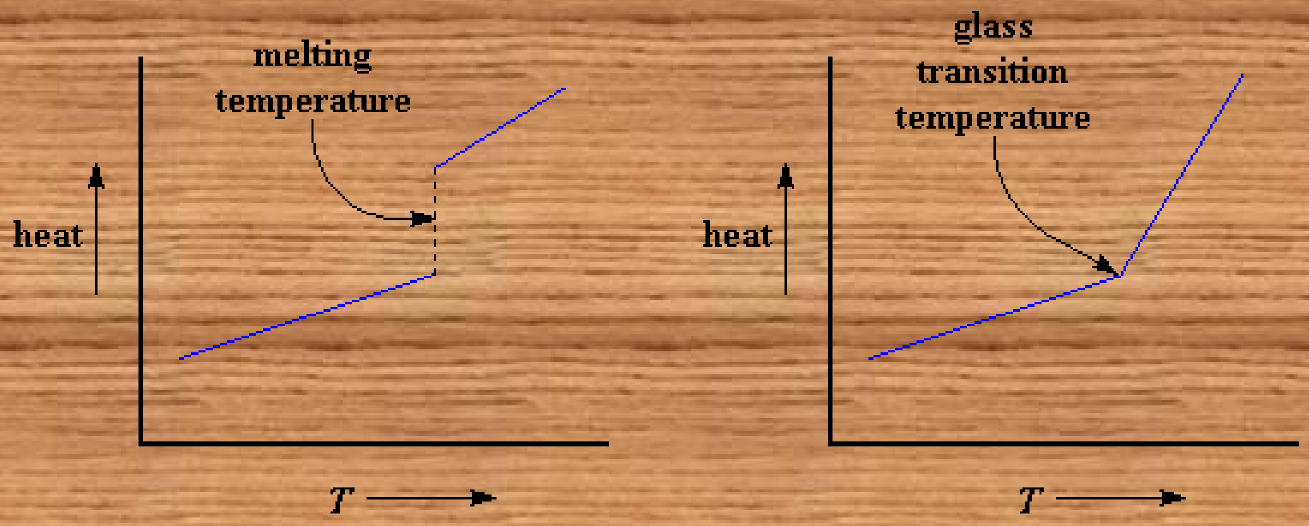
- The glass transition of polymers is assumed to be controlled by local segmental motion, but very little is known about the effect of the long-range center of mass motion (*i.e.*, translational molecular diffusion).

In this paper:

- Study of the effects of the free surface and substrate interface on the glass-liquid transition by monitoring dewetting of thin molecular-solid films using time-of-flight secondary ion mass spectrometry (TOF-SIMS) as a function of temperature.

- The dewetting behaviors of vapor-deposited *n*-pentane, toluene, and 3-methylpentane films are explored on substrates of silicon, graphite, amorphous solid water (ASW), and perfluoro-alkyl modified Ni.

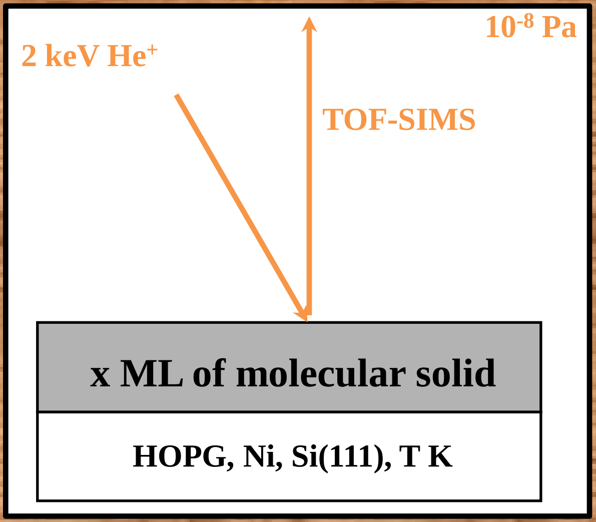
Relevance with polymer, T_g:



A heat vs. temperature plot for an crystalline polymer, on the left; and a amorphous polymer on the right.

http://pslc.ws/macrog/tg.htm#melt

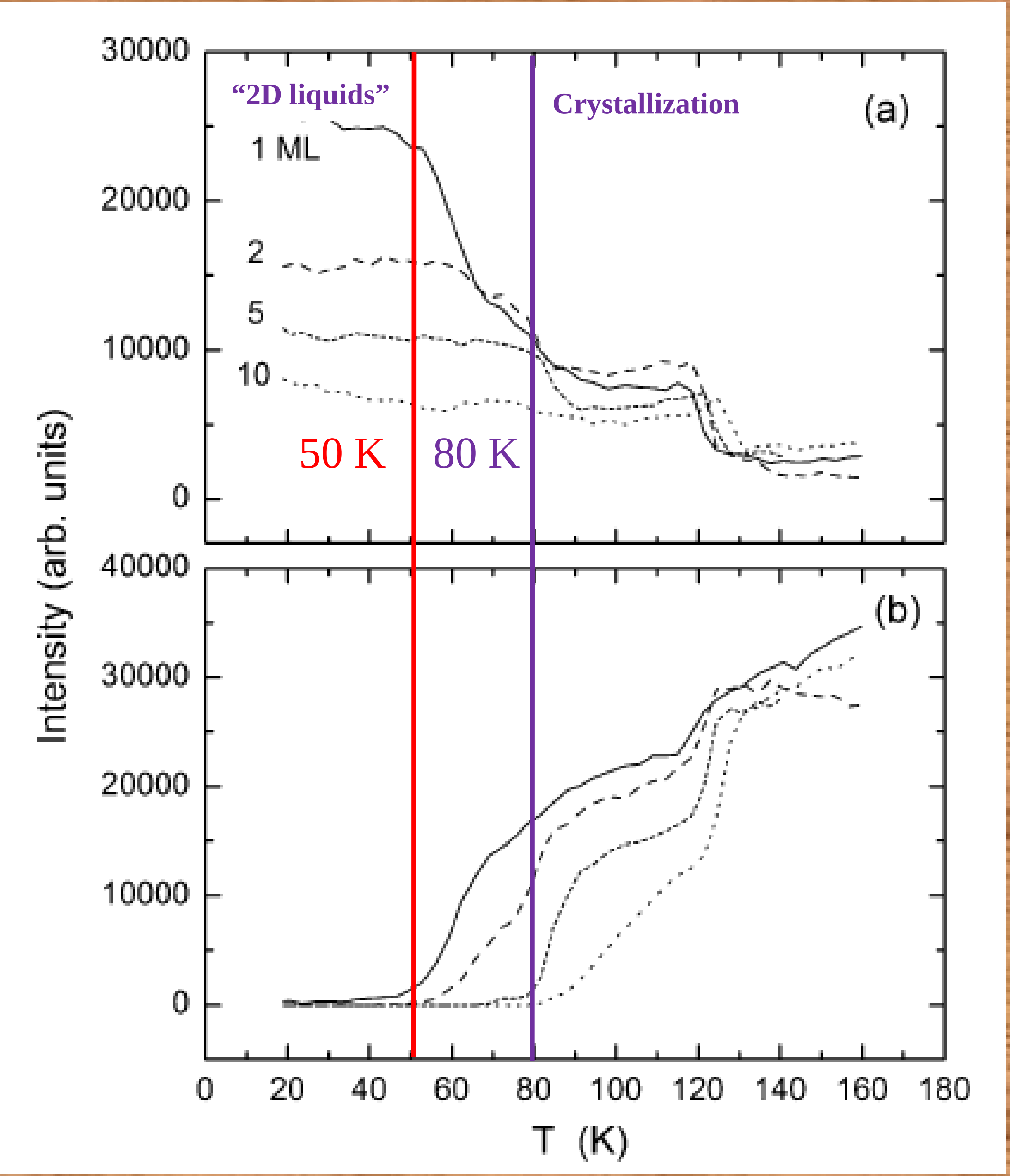
Experimental section:



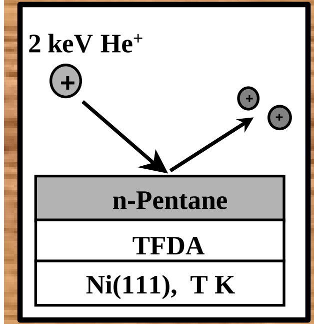
Preparation of substrate……

1. Si (111) wafer, p-type → Cleaned ultrasonically in water and ethanol → Etched using 40% NH_4F
2. Kept at N_2 atmos. and H_2-passivated (formation of Si(111):H)
3. Si(111):H irradiated using photon in air to form Si(111):OH
4. The mirror finished Ni substrate sample was first cleaned in the UHV chamber by several cycles of electronbeam heating (~ 1200 K) and ion-beam bombardment. After confirmation of surface cleanliness using TOF-SIMS, the substrate was extracted through a load-lock chamber purged with N_2 gas and immersed immediately in an ethanolic solution (0.04 mmol ml^{-1}) of tricosafluorododecanoic acid (TFDA: $CF_3(CF_2)_{10}COOH$).
5. A substrate of highly oriented pyrolytic graphite (HOPG) was cleaned by electron-beam heating to 1200 K in UHV.

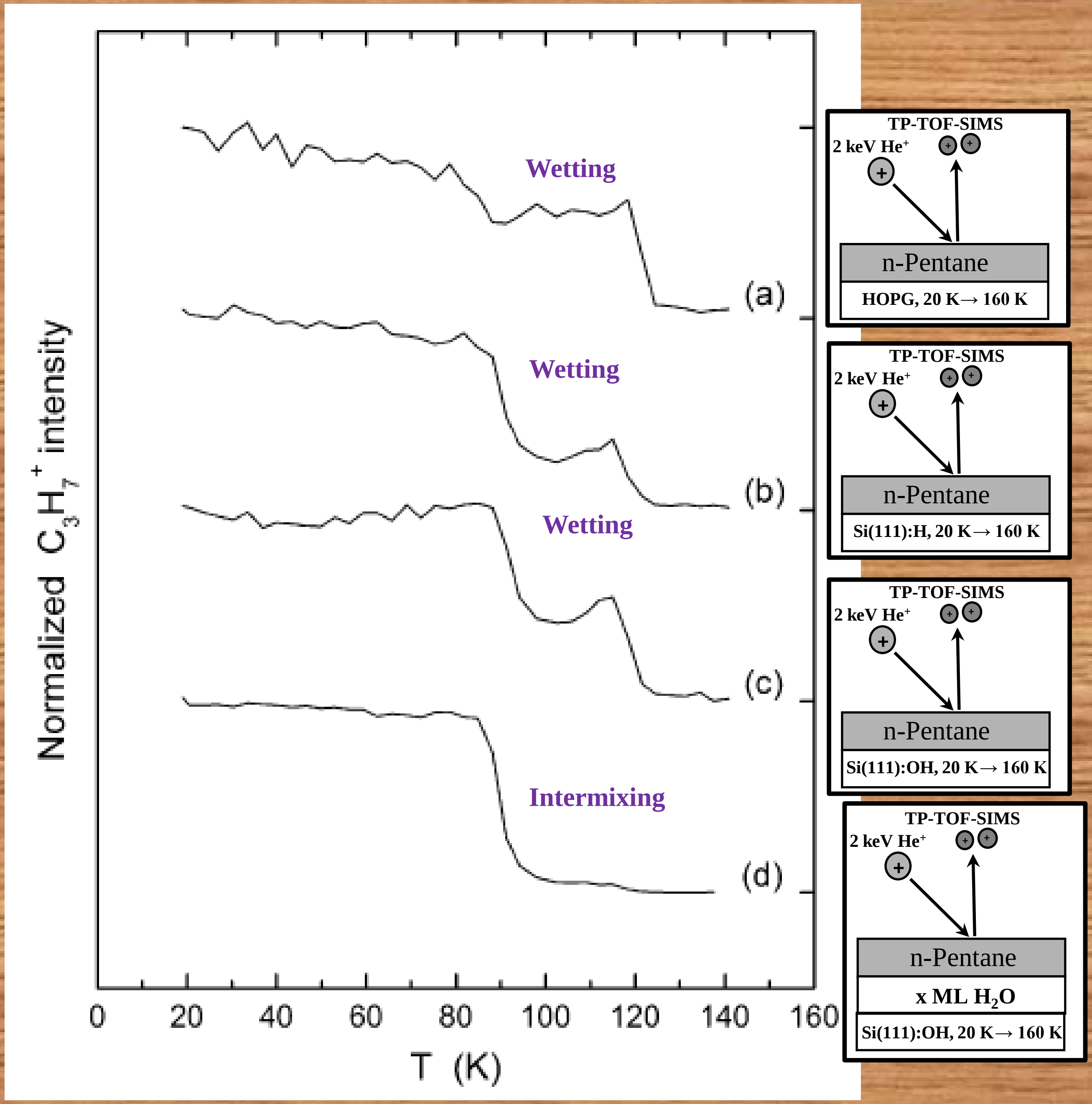
Results:

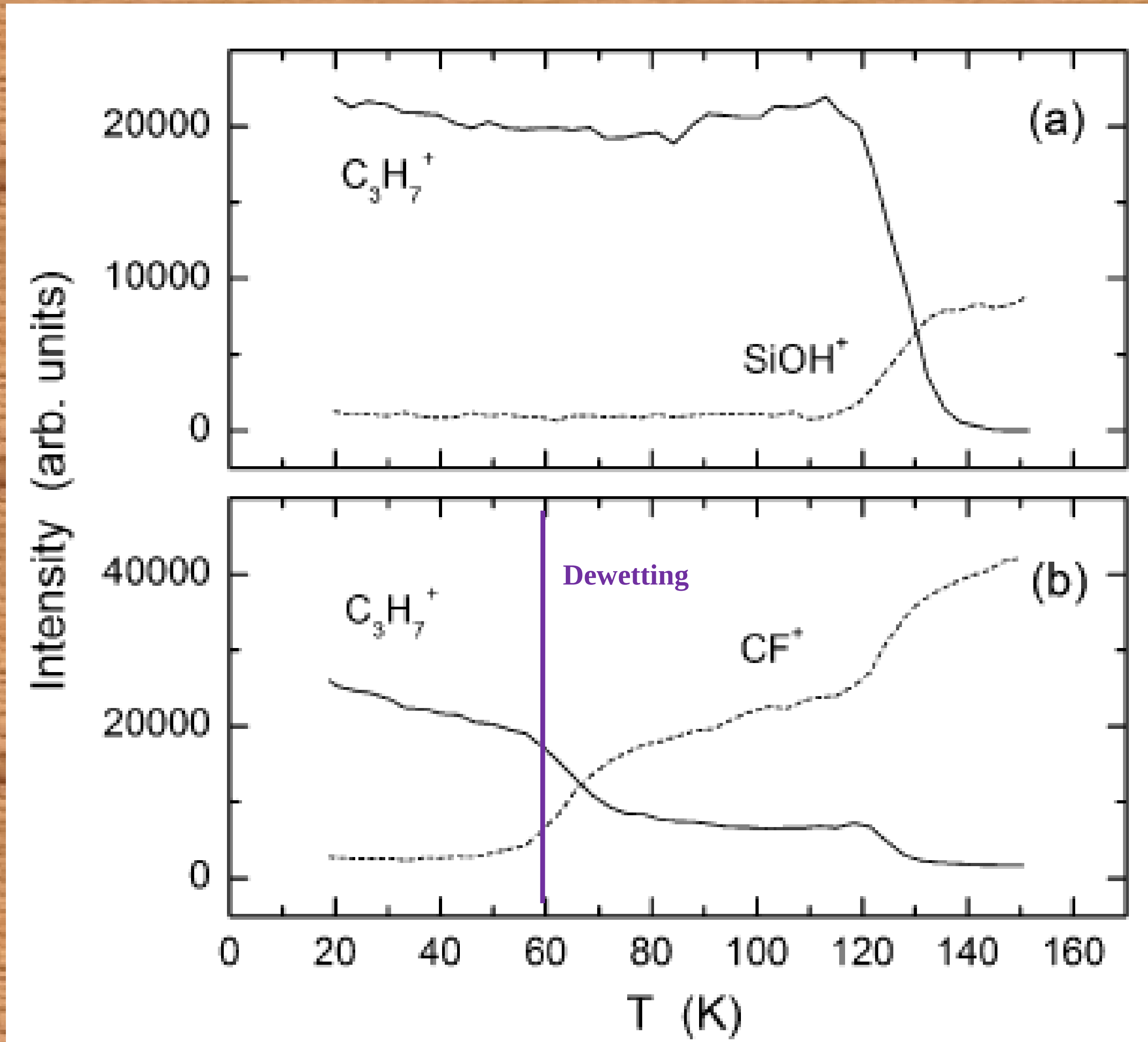


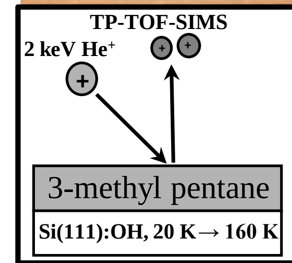
T_c (bulk) = 71.8 K

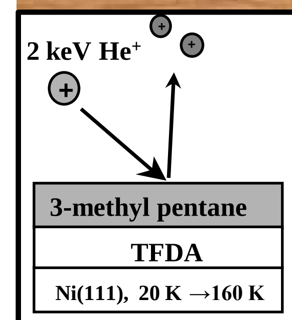


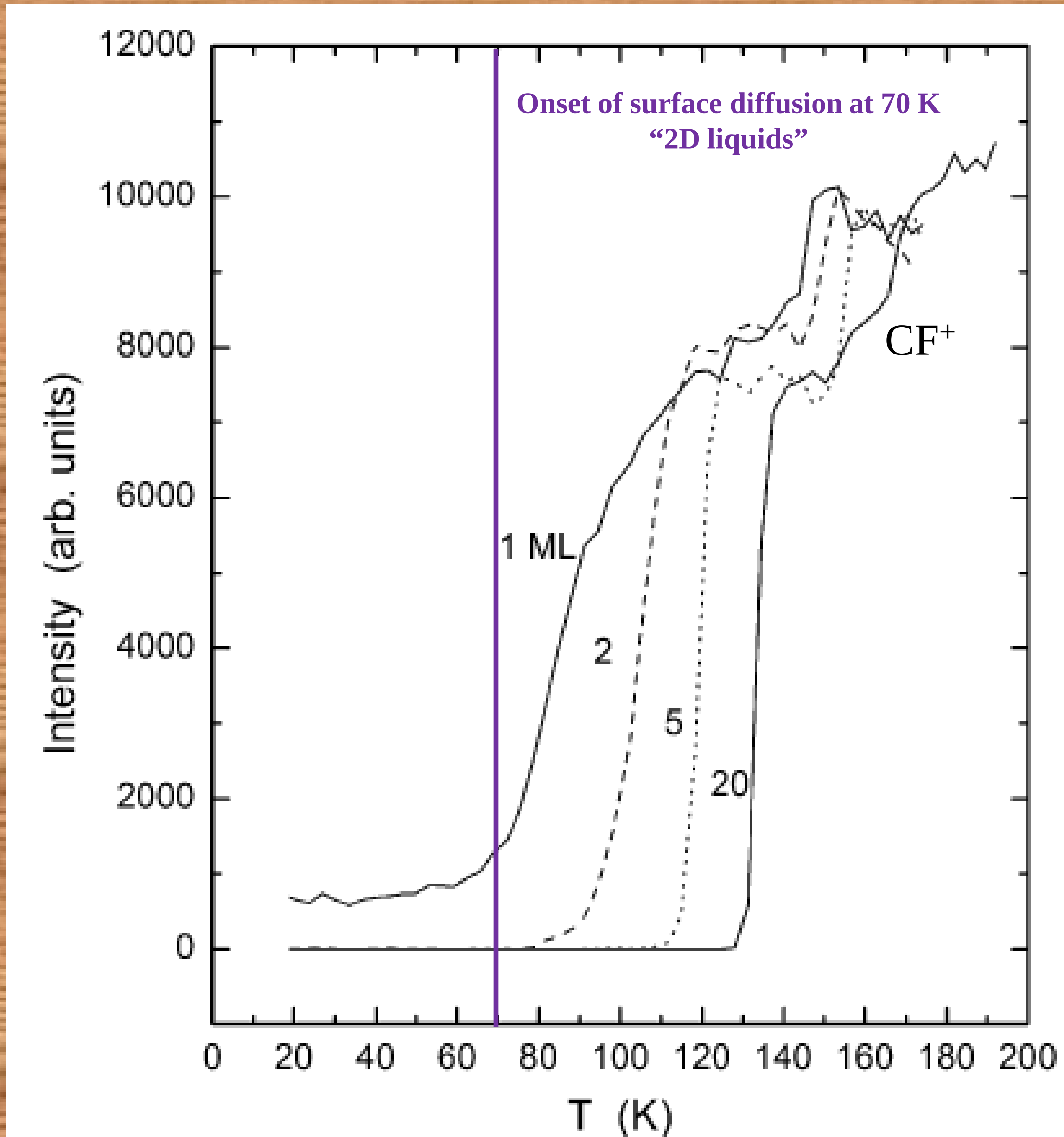
In the presence of the 2D liquid, sub-T_g dewetting is expected to occur when the cohesive force of the molecules overcomes the adhesive force, resulting in the 3D droplet formation without exhibiting long-range translational diffusion.


Normalized $C_3H_7^+$ intensity
T (K)
0
20
40
60
80
100
120
140
160
Wetting
(a)
Wetting
(b)
Wetting
(c)
Intermixing
(d)
TP-TOF-SIMS
2 keV He^+
n-Pentane
HOPG, 20 K→ 160 K
TP-TOF-SIMS
2 keV He^+
n-Pentane
Si(111):H, 20 K→ 160 K
TP-TOF-SIMS
2 keV He^+
n-Pentane
Si(111):OH, 20 K→ 160 K
TP-TOF-SIMS
2 keV He^+
n-Pentane
x ML H_2O
Si(111):OH, 20 K→ 160 K

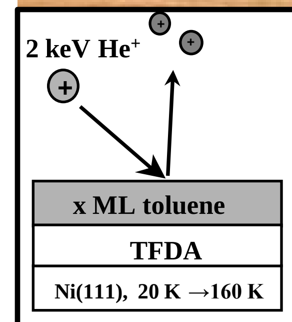

Intensity (arb. units)
(a)
C3H7+
SiOH+
(b)
C3H7+
CF+
Dewetting
T (K)
0
10000
20000
40000
0
20
40
60
80
100
120
140
160

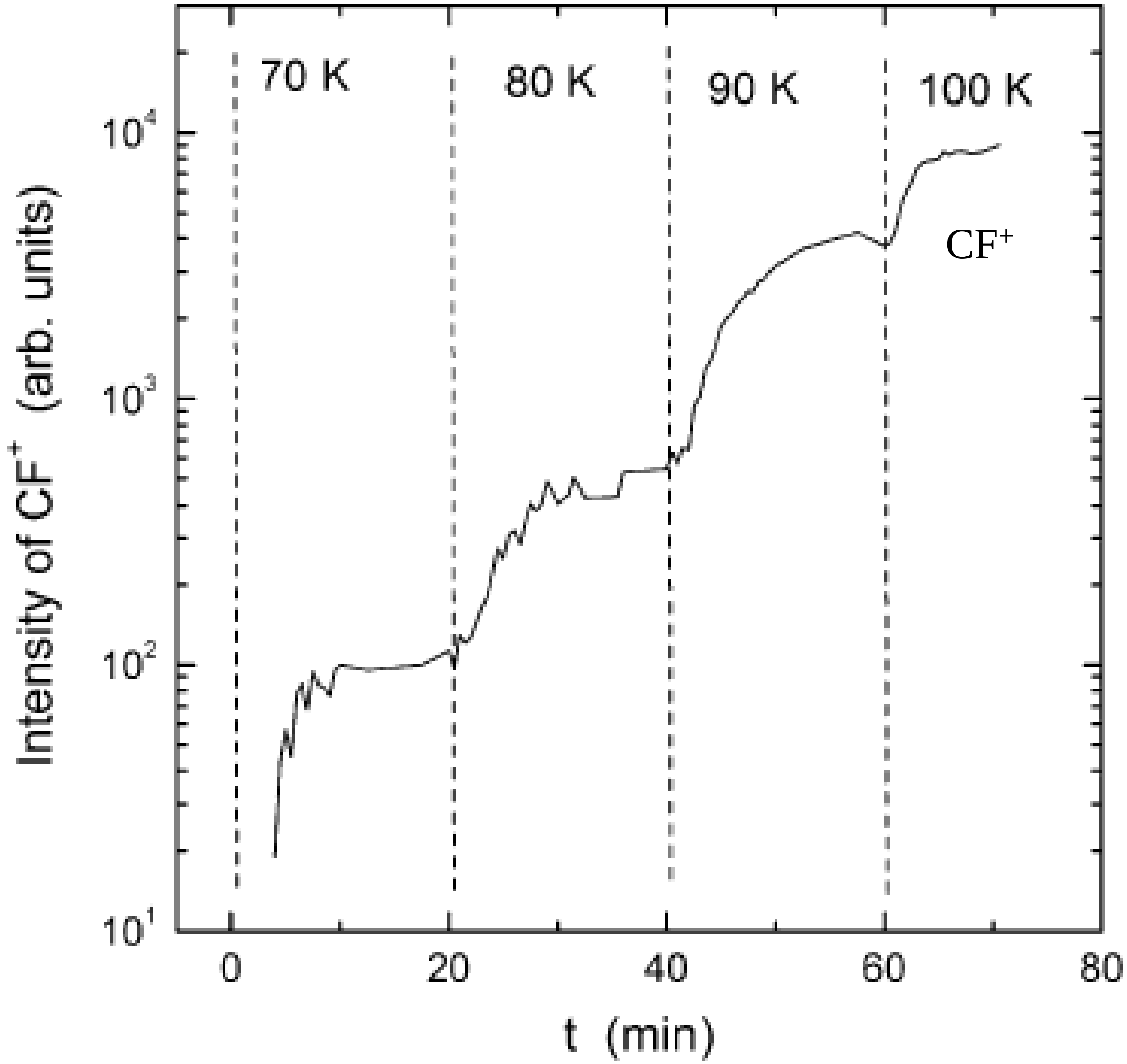

TP-TOF-SIMS
2 keV He+
3-methyl pentane
Si(111):OH, 20 K→ 160 K

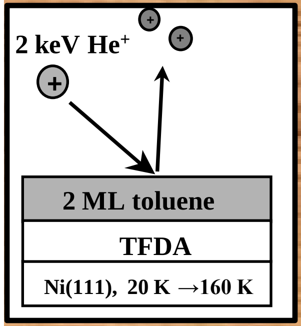

2 keV He+
3-methyl pentane
TFDA
Ni(111), 20 K →160 K

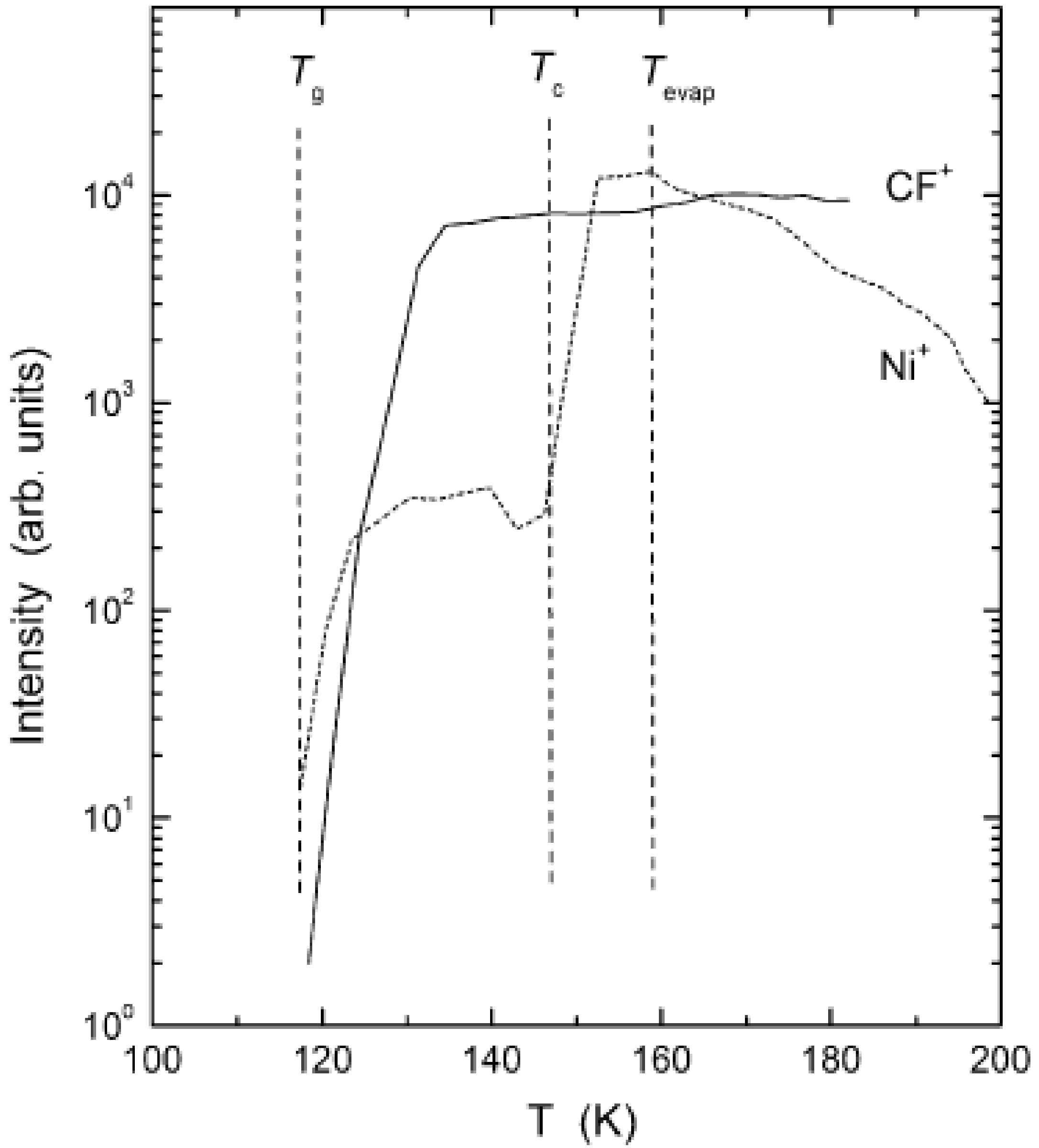

Onset of surface diffusion at 70 K
“2D liquids”
Intensity (arb. units)
12000
10000
8000
6000
4000
2000
0
0
20
40
60
80
100
120
140
160
180
200
T (K)
1 ML
2
5
20
CF+

T_g (bulk) = 117 K

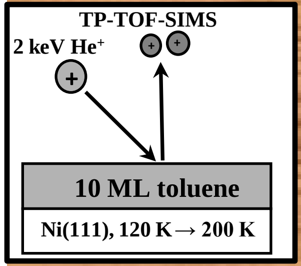

2 keV He+
x ML toluene
TFDA
Ni(111), 20 K →160 K


70 K
80 K
90 K
100 K
CF+
Intensity of CF+ (arb. units)
10^4
10^3
10^2
10^1
0
20
40
60
80
t (min)

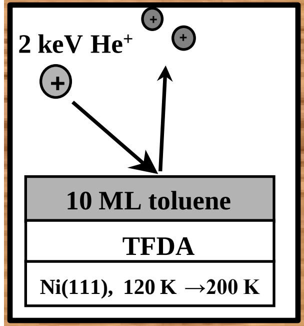

2 keV He+
2 ML toluene
TFDA
Ni(111), 20 K →160 K



Intensity (arb. units)
T (K)
T_g
T_c
T_{evap}
CF^+
Ni^+



TP-TOF-SIMS
2 keV He+
10 ML toluene
Ni(111), 120 K → 200 K



2 keV He+
10 ML toluene
TFDA
Ni(111), 120 K →200 K

Discussion:

- **The morphological stability of glassy films on Ni(111) up to bulk T_g can be attributed to the presence of an immobilized layer at the interface (a "dead layer").**
- **The stepwise evolution of the film morphology of toluene reflects how the liquid phase grows without the influence of a dead layer.**
- **The structural fluctuation of toluene monolayer can be induced by lateral diffusion of the 2D liquid at 70 K, resulting in undulation of the film.**
- **The contribution from 2D liquids ceases when 3D-like domains or puddles evolve.**
- **The higher the CF^+ intensity the deeper are the puddles are.**
- **The results show that the higher annealing temperature is necessary for the morphology change of deeper puddles.**
- **This is the reason for a high aging temperature (100 K) relative to the onset of the 2D liquid (70 K) in case of 2 ML toluene.**
- **The nanoconfinement effect that can be scaled by a puddle depth is responsible for this behavior.**

➢ **The dewetting of multilayer toluene films on the Ni(111) surface during crystallization is induced by hydrodynamic flow of supercooled liquid to the crystal nucleation sites without nucleation of dried holes.**

➢ **On the perfluoro-alkyl terminated surface, crystallization occurs in the preexisting droplets of supercooled liquid, but no further evolution in morphology (automorphism) is clearly identified at T_c.**

Conclusion:

❖ In order to understand the origins of T_g reduction of nanoconfined liquids, the effects of free surface and substrate interface on dewetting of *n*-pentane, 3-methylpentane, and toluene films, the various studies were performed.

❖ It was found that these molecules become mobile in the first monolayer at temperatures considerably lower than the bulk T_g as revealed from the droplet formation on the perfluoro-alkyl terminated Ni substrate.

❖ This behavior can be attributed to surface diffusion and cohesion of mobile molecules in the 2D liquid.

❖ The *n*-pentane monolayer fundamentally wets the substrates of graphite, silicon, and ASW, and dewetting occurs upon crystallization.

❖ The presence of the premelting layer is identified from disappearance of the *n*-pentane crystallites on the ASW surface via intermixing. This behavior, together with autophobic dewetting of crystallites, suggests that the properties of quasiliquid differ significantly from those of the 2D liquid.

Conclusion:

1. Surface modification is an important step of investigation in any surface sensitive study.
2. Glass transition temperature and the intermixing of A-B system can be studied by using other tools.
3. Projectile induced reaction can be studied on the liquid like layer.
4. Can the molecular volcano come out at lower temperature if the temperature at T_g?