Premelting of Ice (冰的预融)

Theory, methods and more

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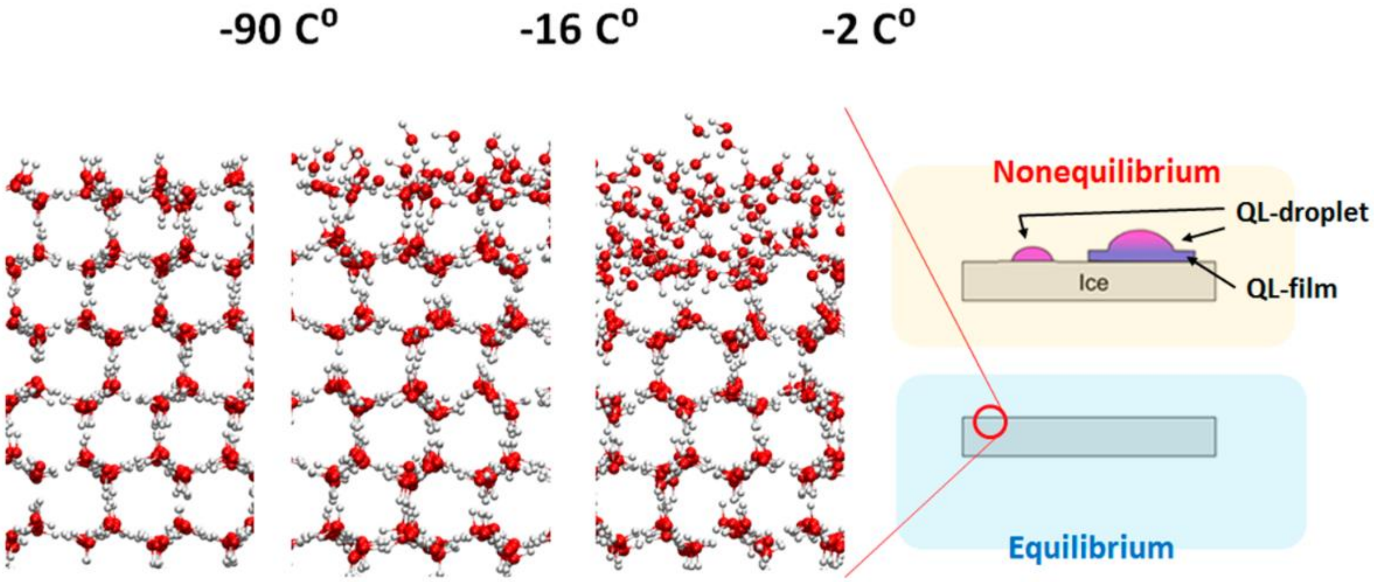
Premelting是什么?

- Premelting是指在温度低于熔点时,固体表面出现熔化/融化(类似液体结构)的现象



- Premelting的基本原因是表面分子结合力低于体相分子

> 缺陷(点缺陷/位错/…)

> 悬键

> …

预融研究中都关心些什么?

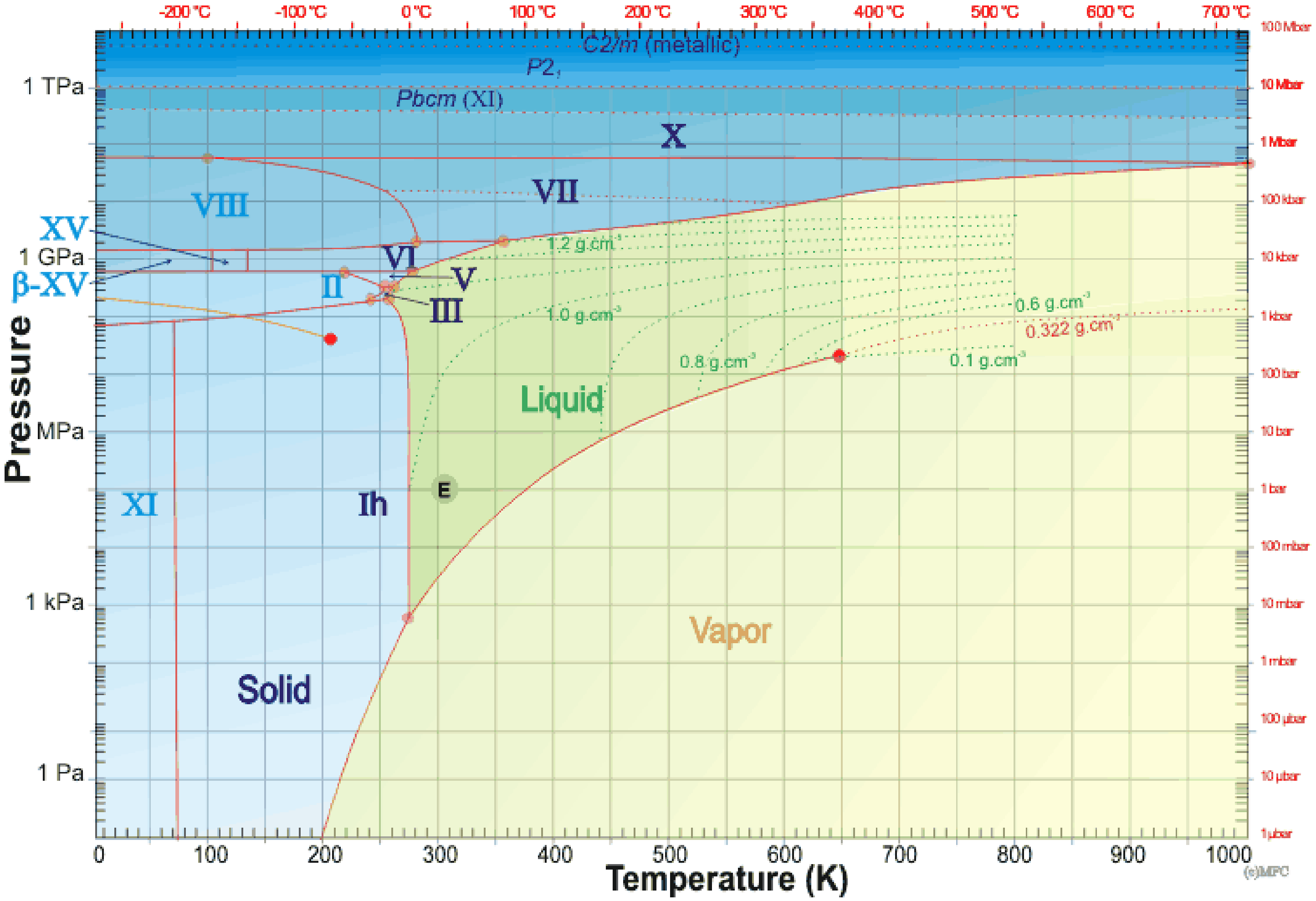
预融从什么温度开始发生?

预融层的深度是多少? 预融层的深度与温度有什么关系?

预融层的结构是什么样的?

其它因素(例如表面晶面,溶质等等)对于预融层有什么影响?

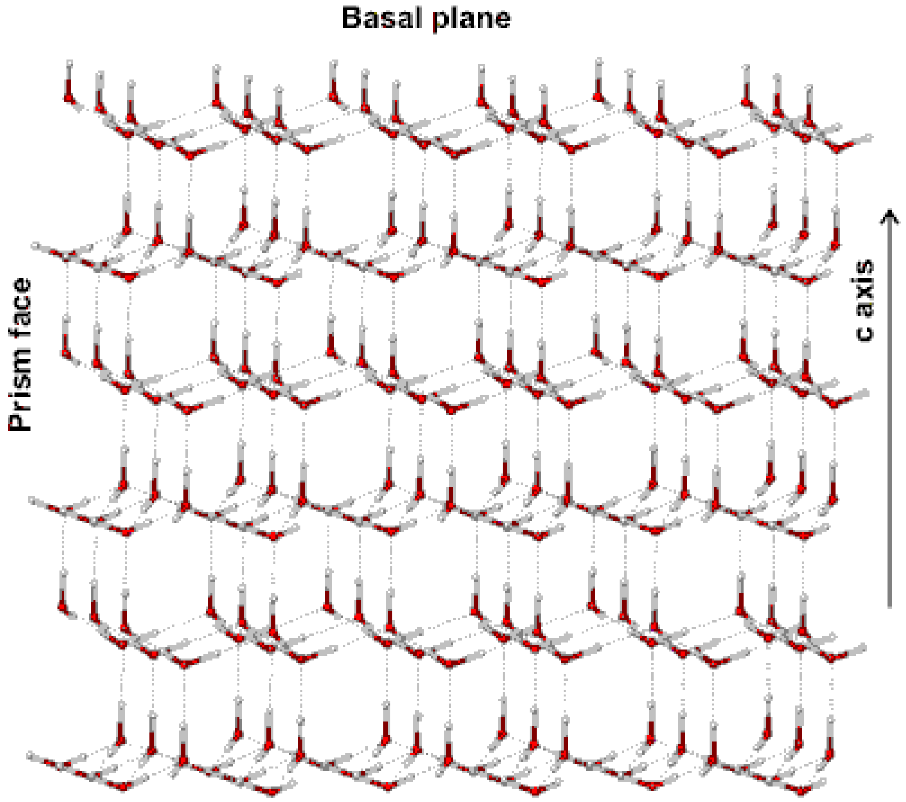
冰(H_2O)的相图



H_2O的相图，其中冰相有十多种

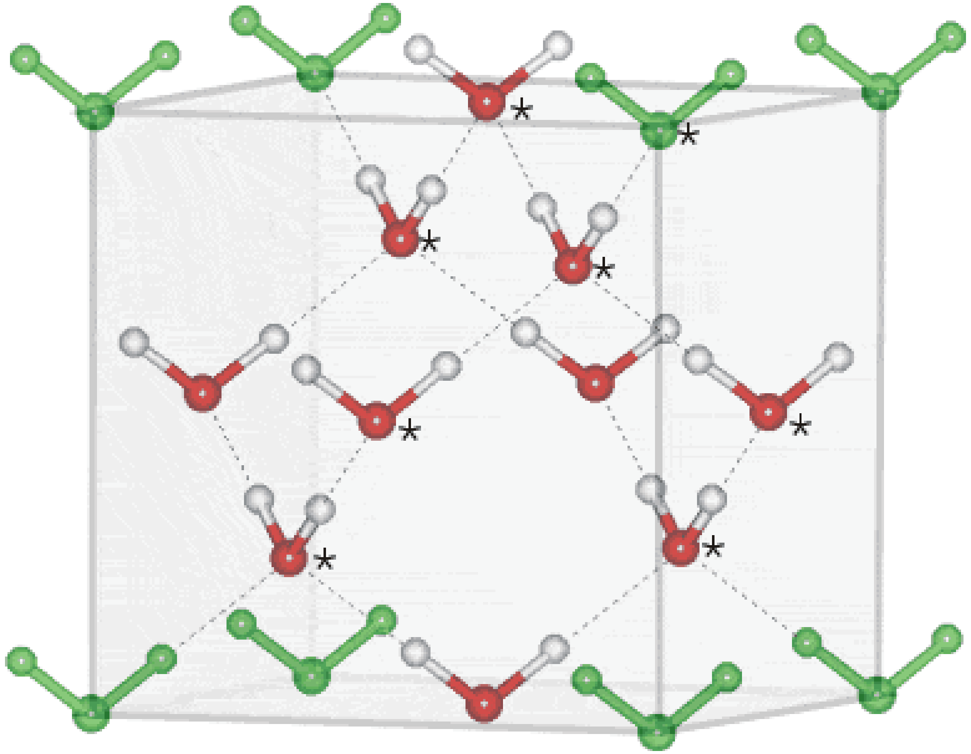
最常见的冰相: I_h与亚稳态I_c

Hexagonal Ice (ice I_h)



六方晶系, a=b=4.5181Å, c=7.3560Å

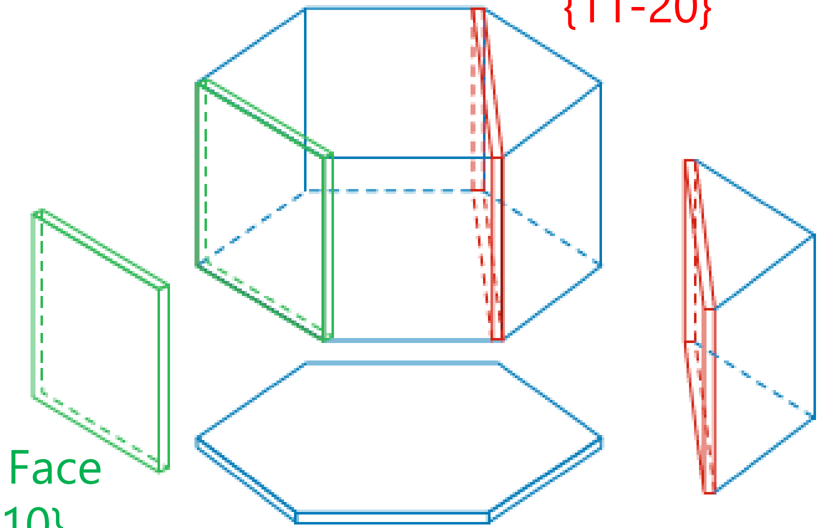
Cubic Ice (ice I_c)



立方晶系, a=b=c=6.358 Å

I_h冰的晶面和结构

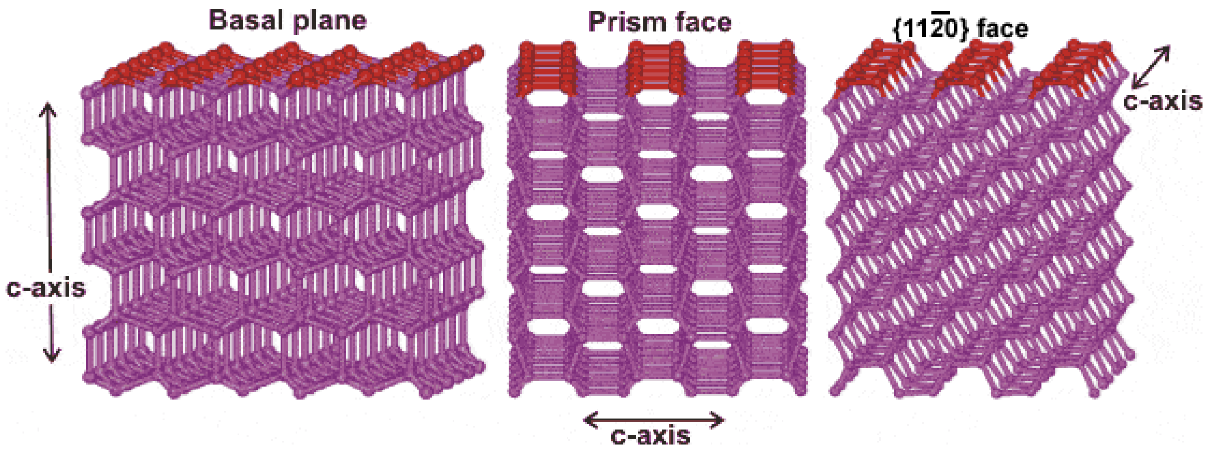
- I_h冰的表面通常是一些特定的晶面，包括{0001}, {10-10}和{11-20}



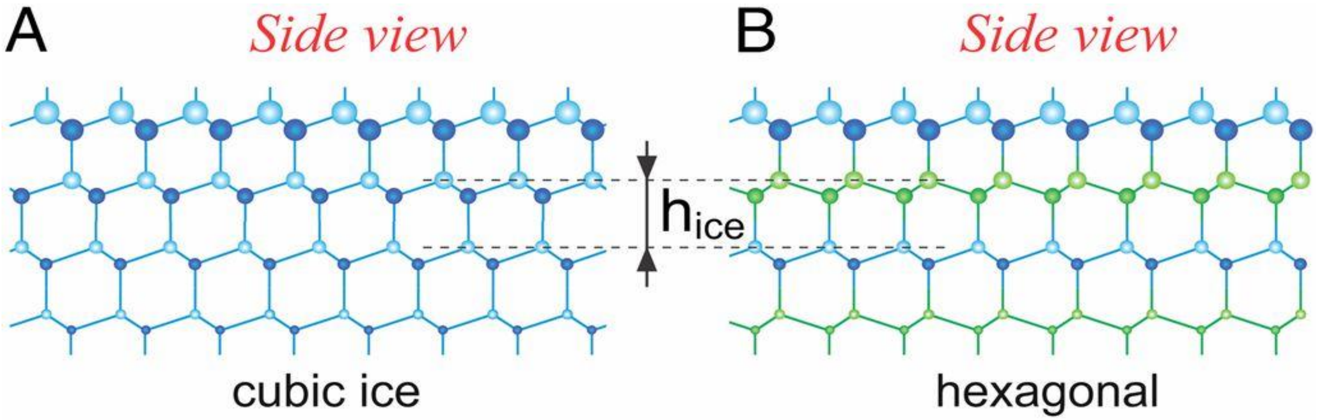
Secondary Prism Face
{11-20}

Prism Face
{10-10}

Basal Plane
{0001}



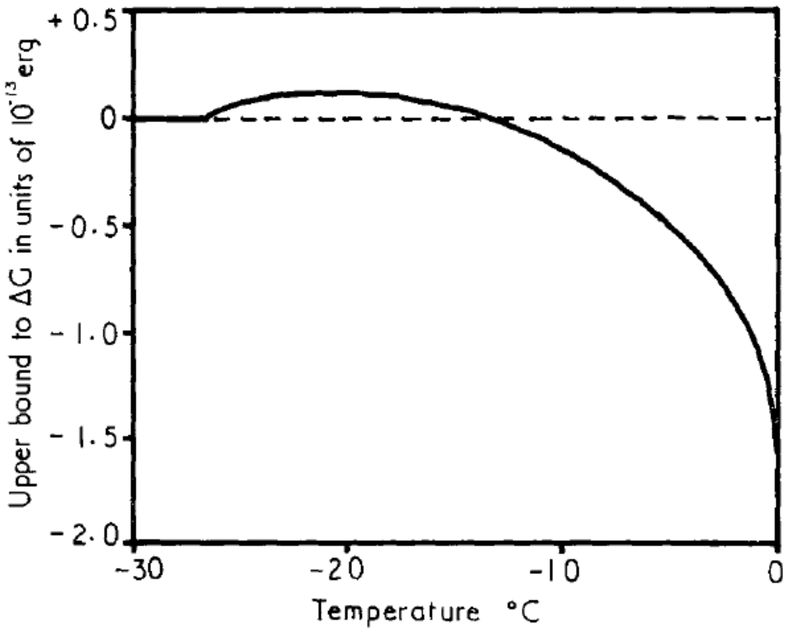
- 冰晶体的分层通常以两排水分子为一个单位，即bilayer



预融的温度与深度

- 分析预融引起的自由能变化
  可以估算预融开始的温度

Fig. 3



Fletcher估计的预融自由能变化上界

$$\Delta G \approx \Delta S_F \Delta T d + \frac{kT}{2\gamma}(\alpha_0 - \tfrac{1}{2})^2[1 - \exp(-2\gamma d)] + \delta\gamma(\alpha_0 - \tfrac{1}{2})^2 - (\alpha_0 - \tfrac{1}{2})[\epsilon_1 - \epsilon_2 \exp(-\gamma d)].$$

- 热力学方法分析预融层深度

在液相远远大于原子尺寸时
液相深度与温度系数t($t = (T_0 - T)/\,T_0$， T_0代表熔点温度，T代表实际温度) 呈现指数-1/3的关系：

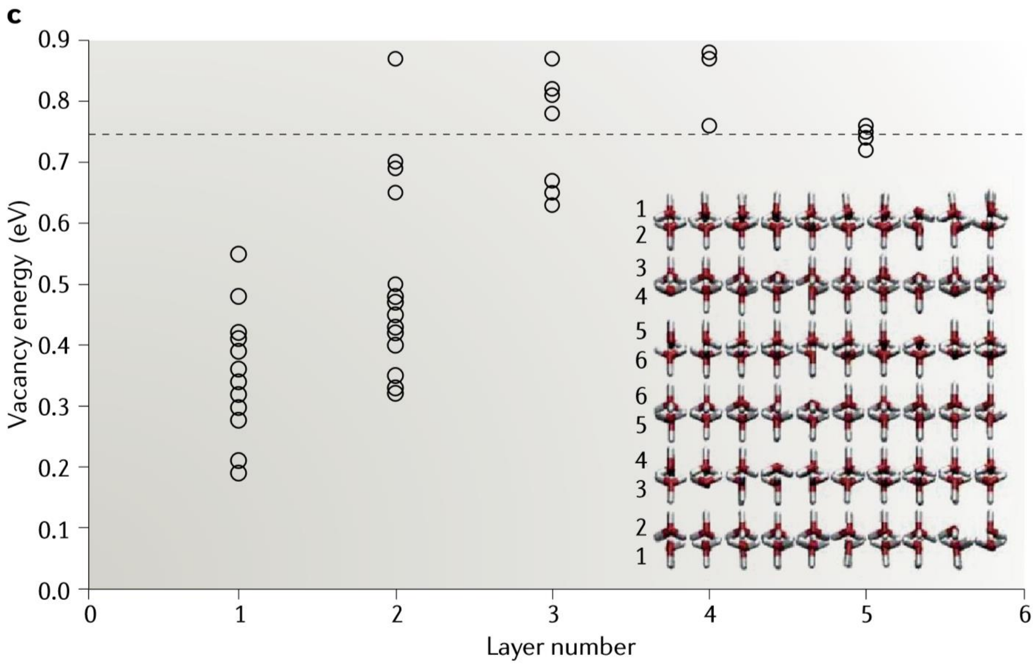
$$d = \left(-2\sigma^2 \frac{\Delta\gamma}{\rho_l q_m}\right)^{1/3} t^{-1/3}$$

液相的深度与原子尺寸相当时
预熔层的深度与温度呈现对数关系：

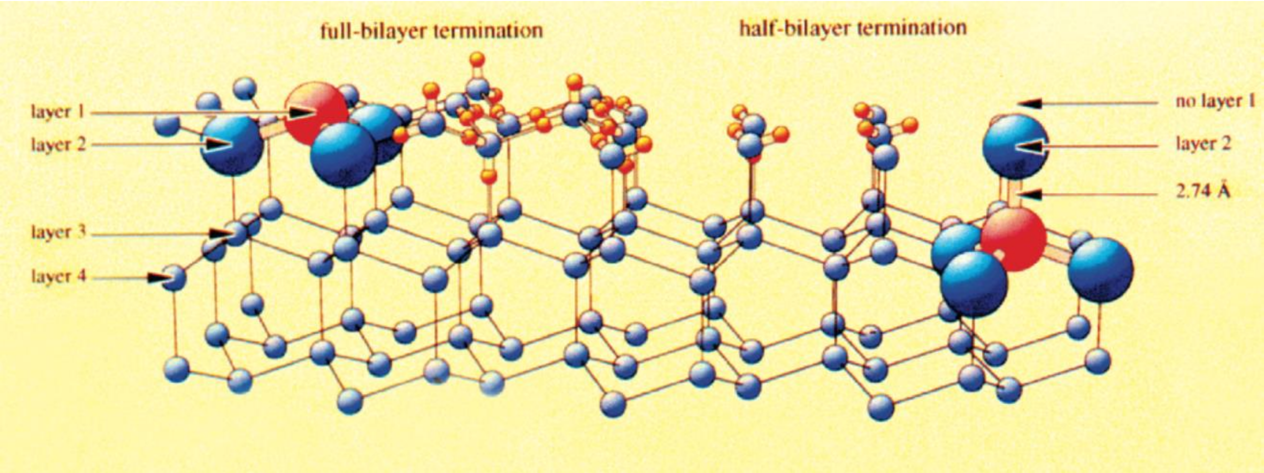
$$d \propto |\ln t|$$

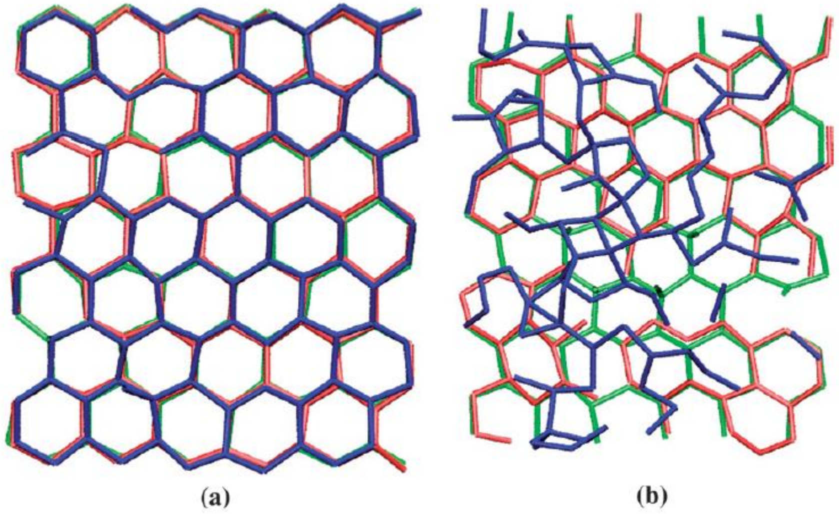
预融层的深度: 分子层次

- 预融一般是以双层(bilayer)为单位
- 预融通常包括一到两个bilayer



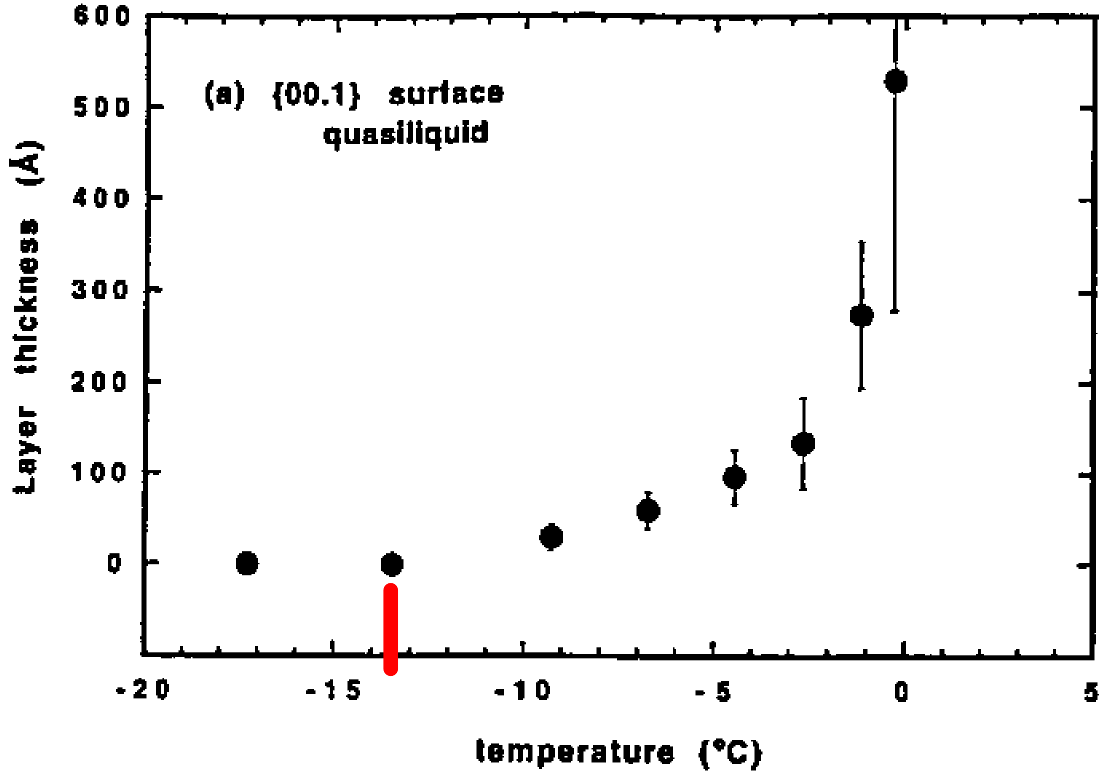
冰表面各层的空位形成能
冰最表面的bilayer空位形成能较低，预示着预融容易发生



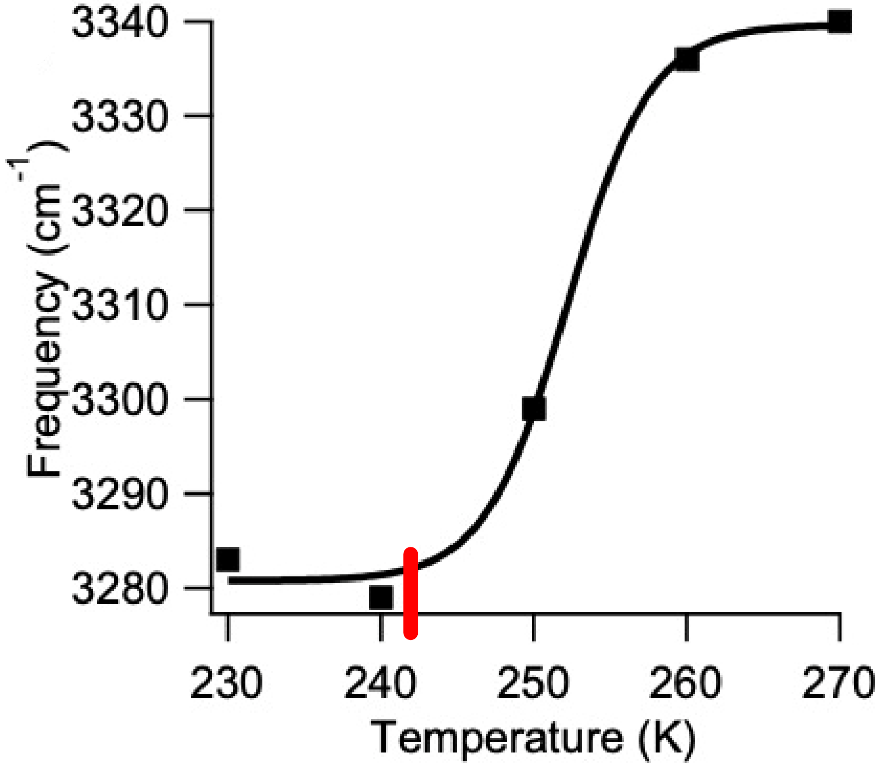


预融中冰表面的两个bilayer(蓝/橙)结构散开
而第三层(绿)仍保持基本正常的结构

预融的温度与深度

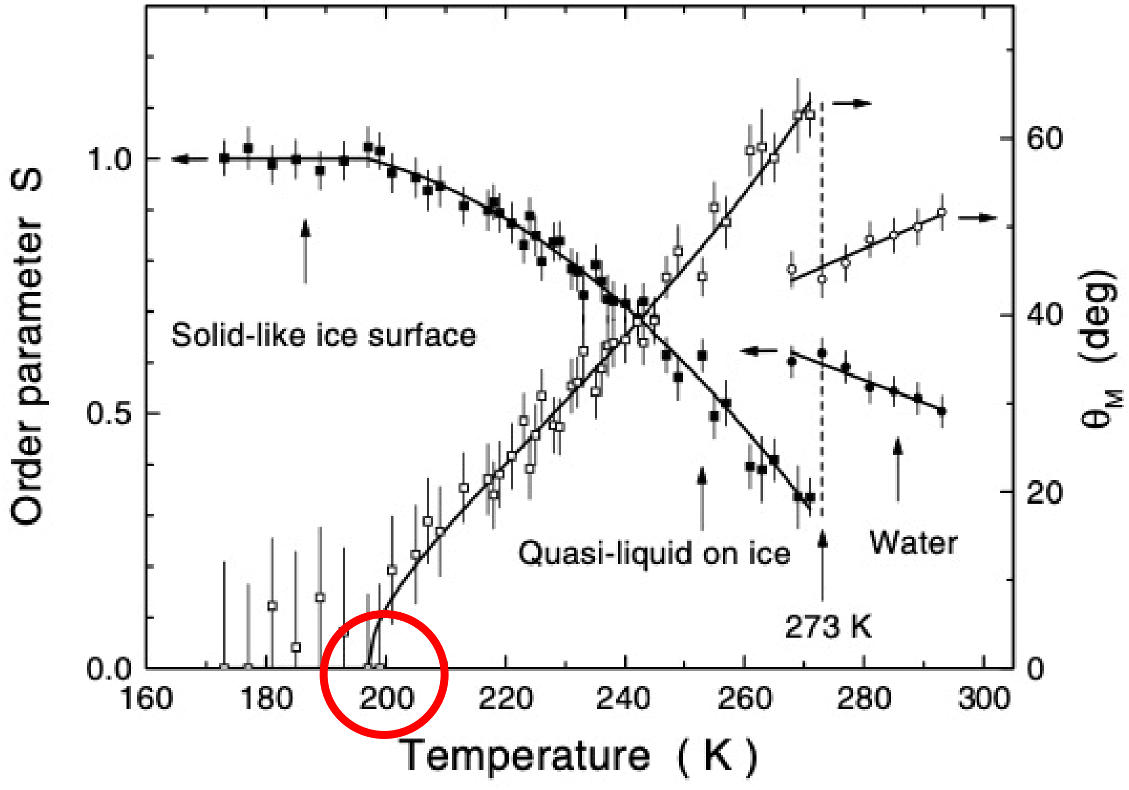


掠射角XRD(Glancing-angle X-ray scattering)
测得的预融深度与起始温度

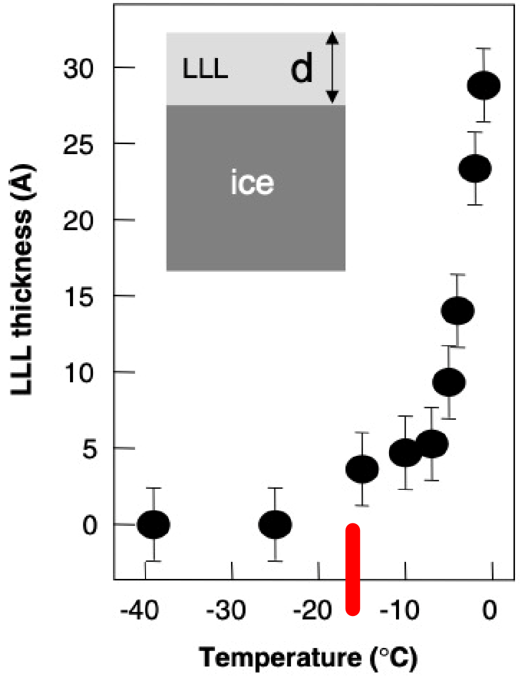


和频光谱(SFG spectroscopy)
测得的预融起始温度

预融的的温度与深度

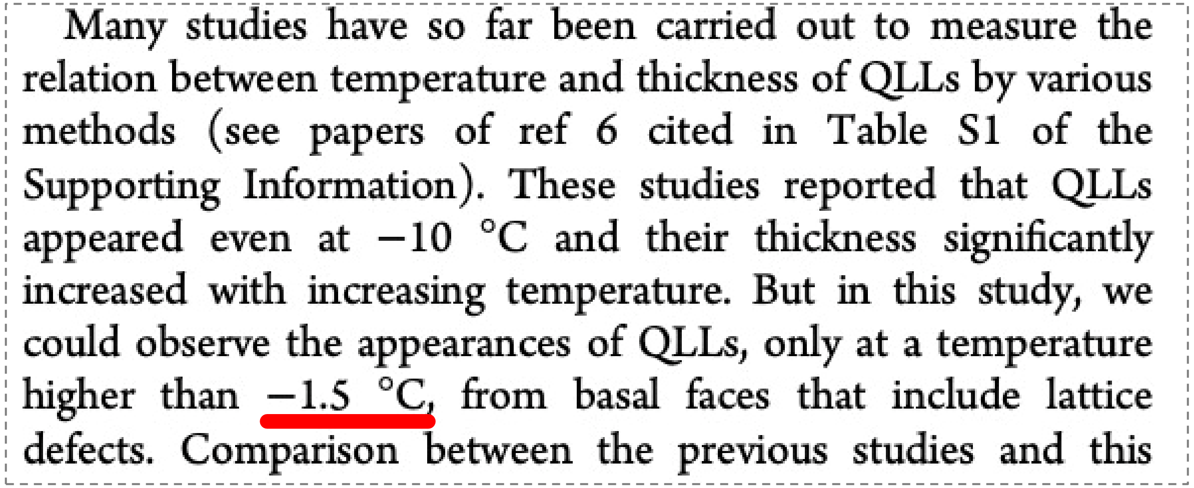


表面振动光谱(Surface vibrational spectroscopy)



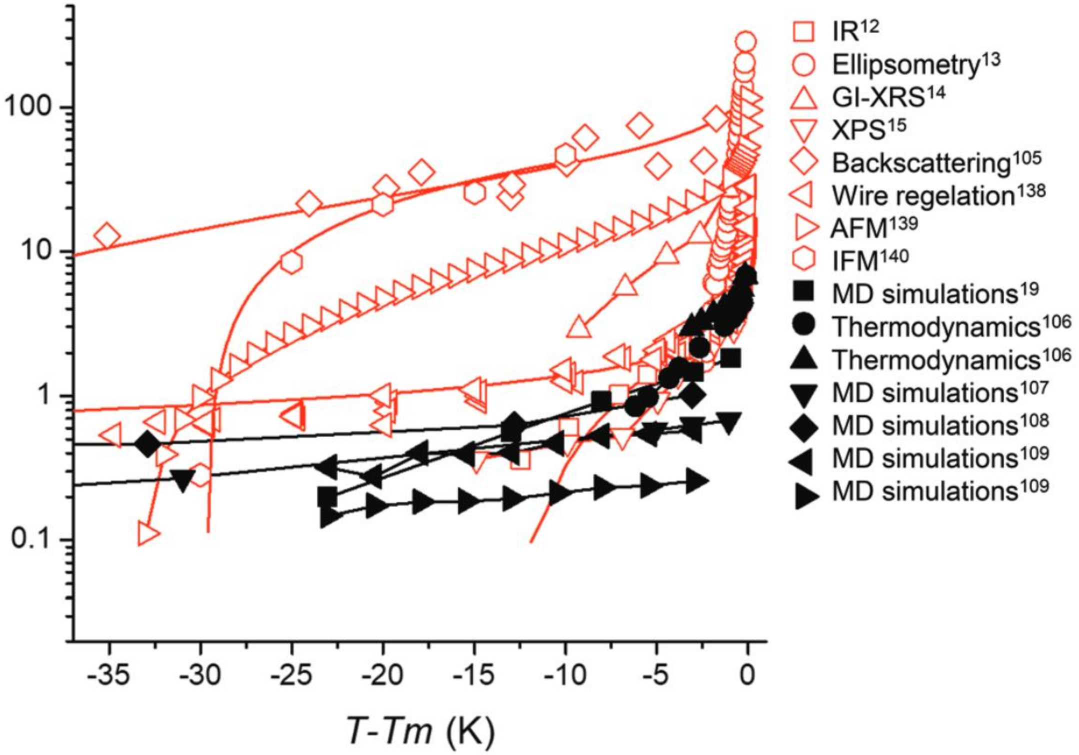
近边X射线吸收精细结构
(Near-edge x-ray absorption fine-structure, NEXAFS)

光学显微镜的观察


Many studies have so far been carried out to measure the relation between temperature and thickness of QLLs by various methods (see papers of ref 6 cited in Table S1 of the Supporting Information). These studies reported that QLLs appeared even at −10 °C and their thickness significantly increased with increasing temperature. But in this study, we could observe the appearances of QLLs, only at a temperature higher than −1.5 °C, from basal faces that include lattice defects. Comparison between the previous studies and this

预融层的深度和温度的关系

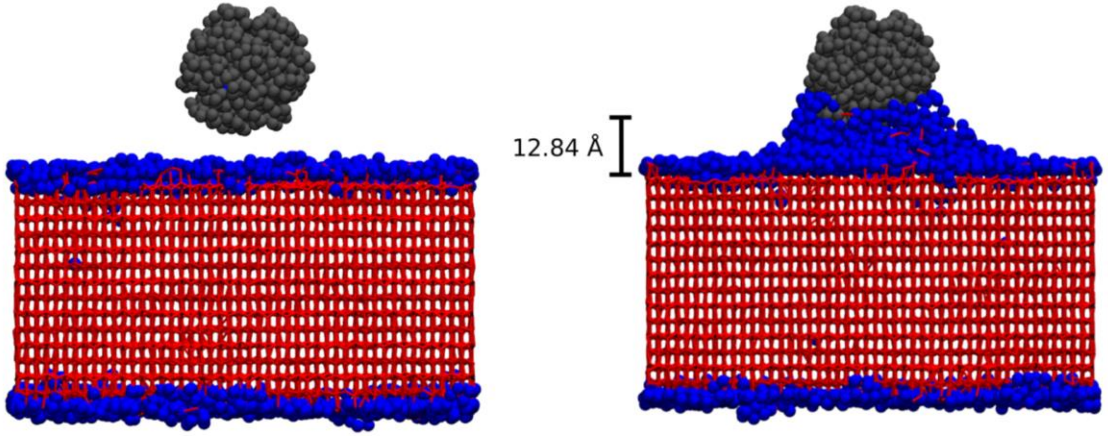
- 随着温度接近融点,预融层的深度逐渐增加
- 但是不同实验或计算方法测得的结果差异很大
- 为什么会这样?



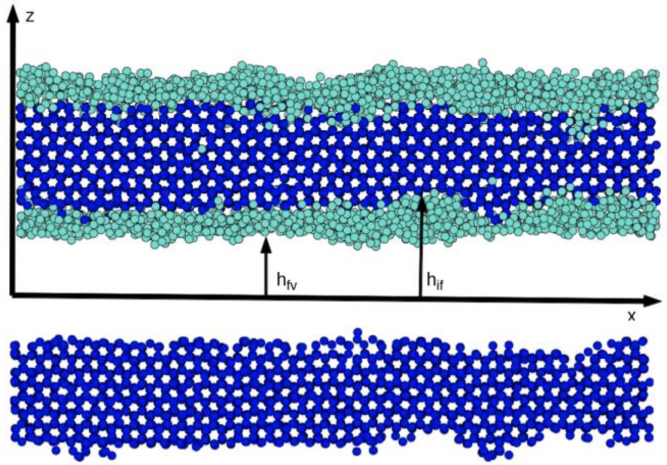
- 实验方法带来的问题

AFM tip at 8 Å from the surface

AFM tip at 7.5 Å from the surface

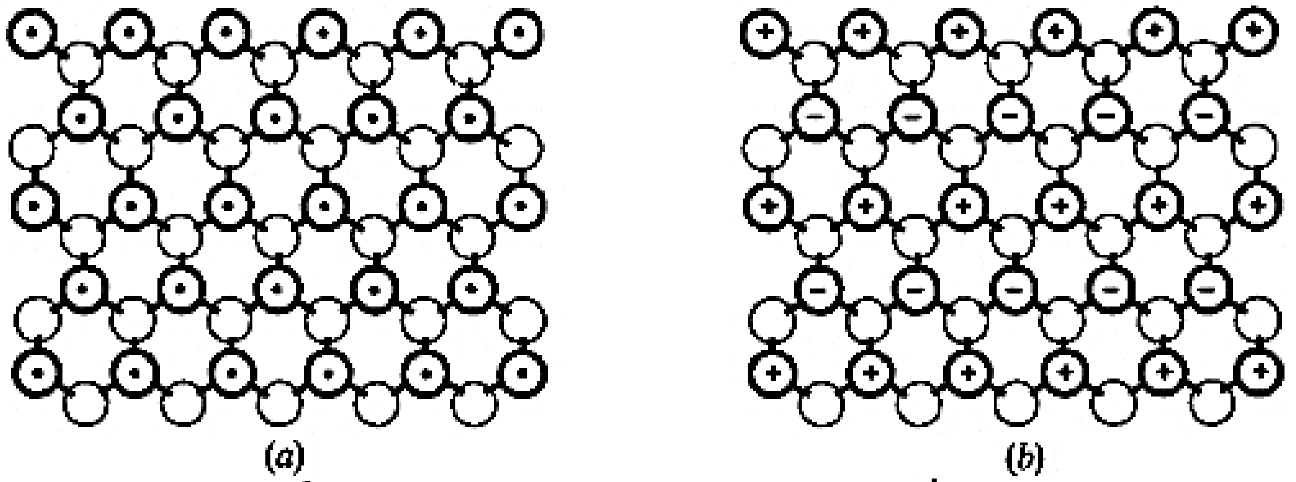


- 预融层的深度是well-defined的吗?



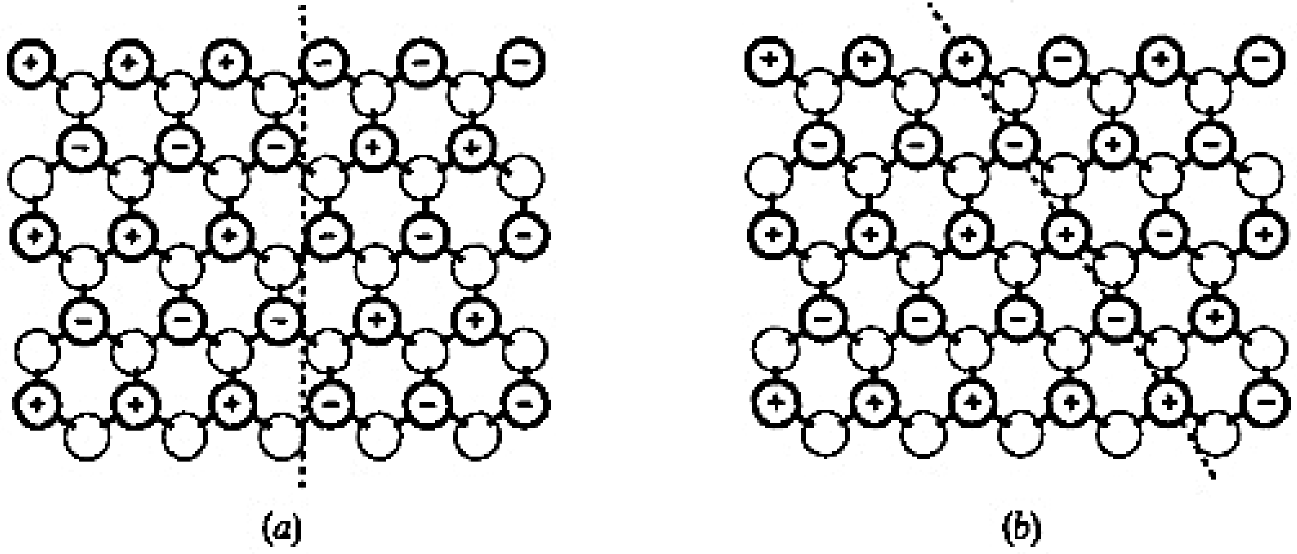
预融层(QLL, quasi-liquid layer)中分子的排列

表面质子的排列倾向


(a) (b)

表面分子粗黑体，细棍是O-H，黑点可能是质子也可能是孤对电子，排列是随机的，但是要求质子键和电子键数量相等 (ice rule)

(b)是表面能最低的表面重构排列：每个键有四个相反符号的最近近邻，只有两个相同符号的最近近邻 (Fletcher Stripe)


(a) (b)

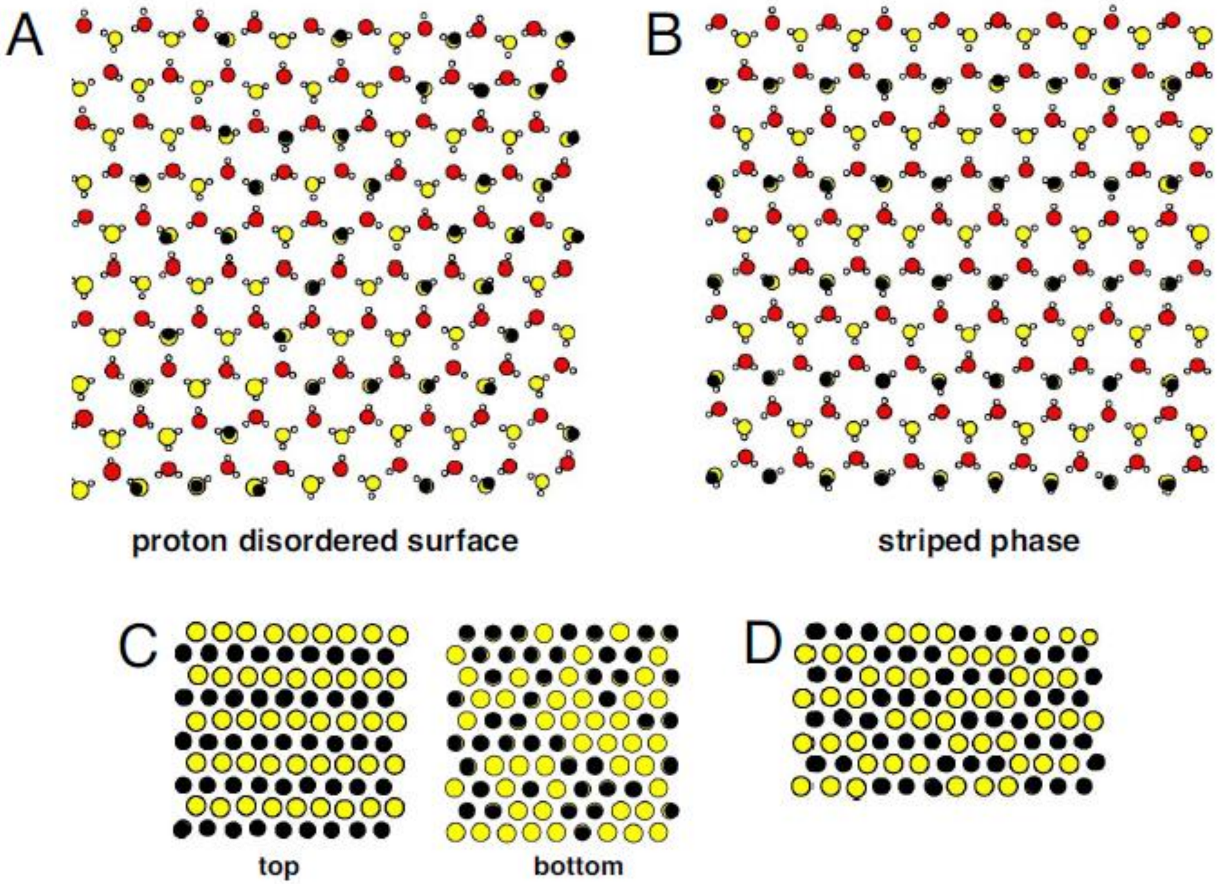
冰的正棱柱面(10-10)的结构

(a)所示的滑动重构和(b)所示的镜像重构的能量损失基本上为零，因此它们可以在表面自由发生

其他类型的域边界通常会消耗大量的能量，因此极少形成其他的重构结构。

QLL的表面结构

预融伴随着水分子表面质子的重构，表面会倾向于形成Fletcher条纹结构，右图经过一段时间的演化表面的质子形成了许多条纹结构。这种结构也是为了使表面的能量最低



proton disordered surface

striped phase

top

bottom

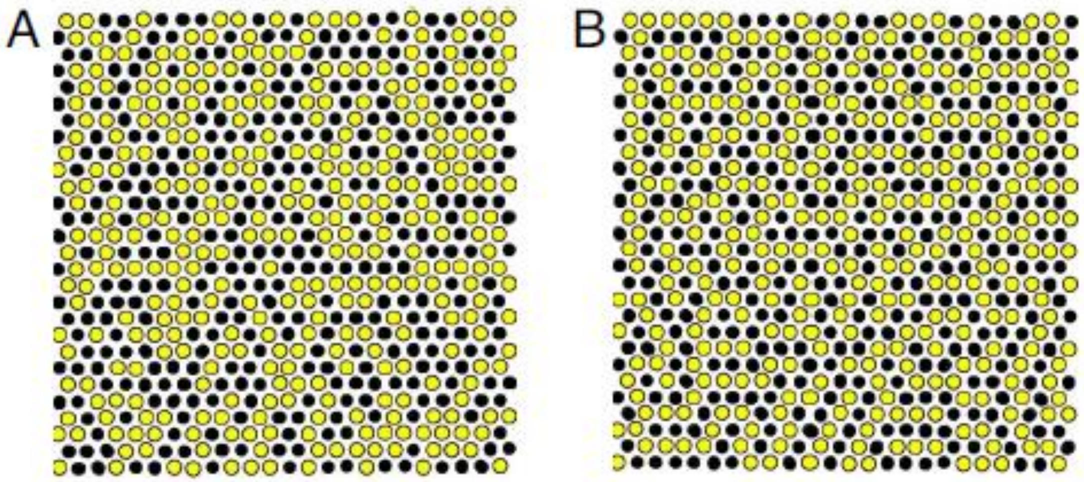
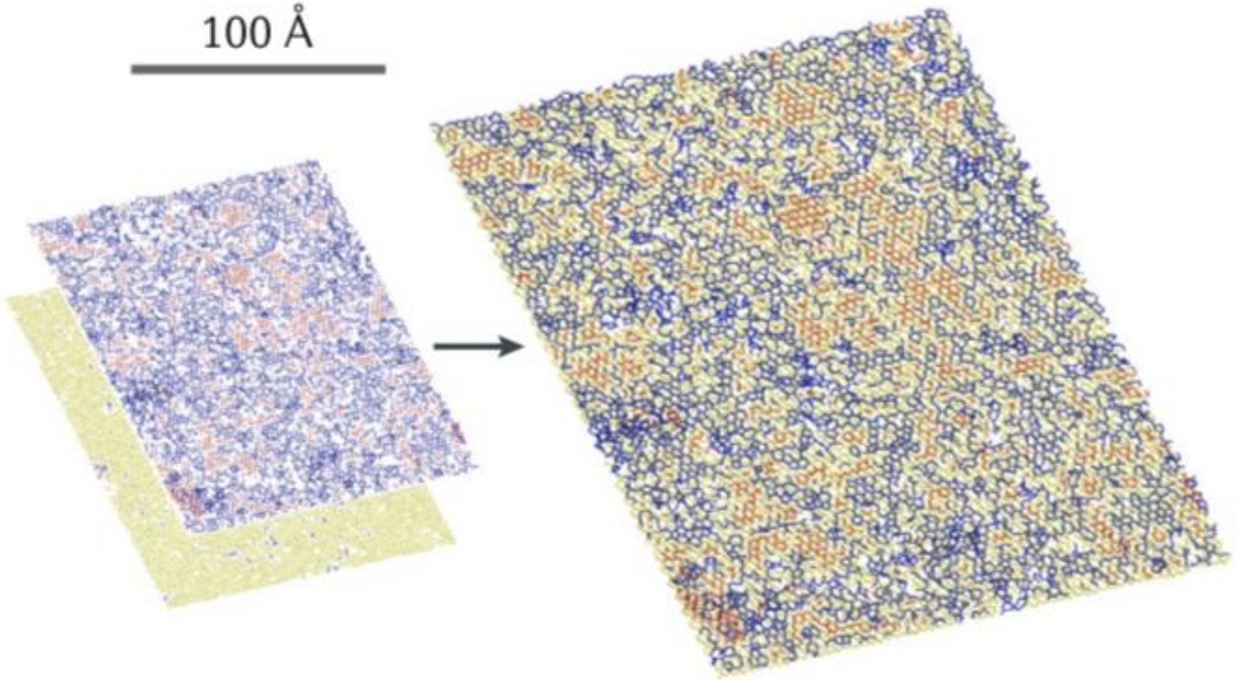


Fig. 3. Initial (*A*) and final (*B*) surface snapshots of the MC quench applied to the initially totally disordered top ice bilayer. d-H and d-O atoms are in black and yellow, respectively. Note the small striped areas, or domains ("mosaic tiles"), in the quenched *B* configuration.

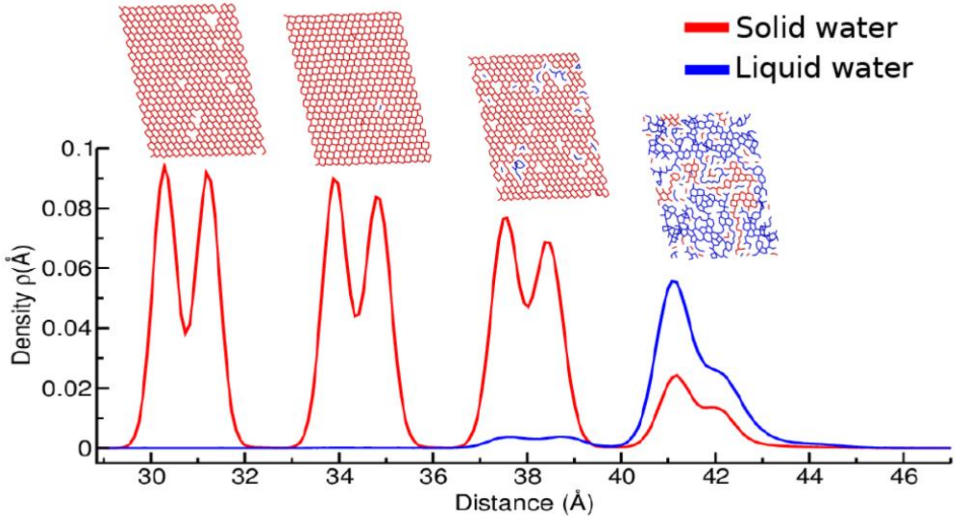
表面水分子的排列情况
黑色——表面是(有悬键的)氢原子
黄色——表面是(有悬键的)氧原子

QLL的不均匀性

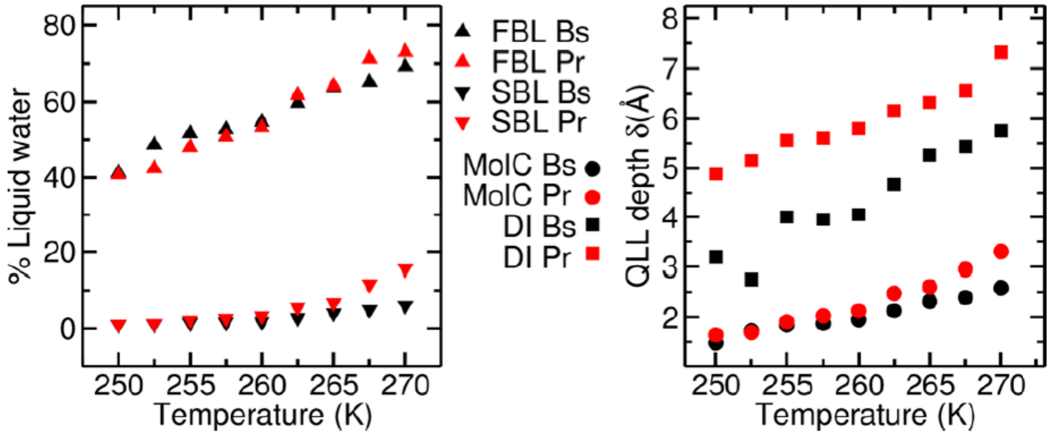
- QLL层其实是晶体和液体混合的
- 温度越高,液体的成分越大



液态水——蓝色
第一个bilayer冰——红色
第二个bilayer冰——黄色



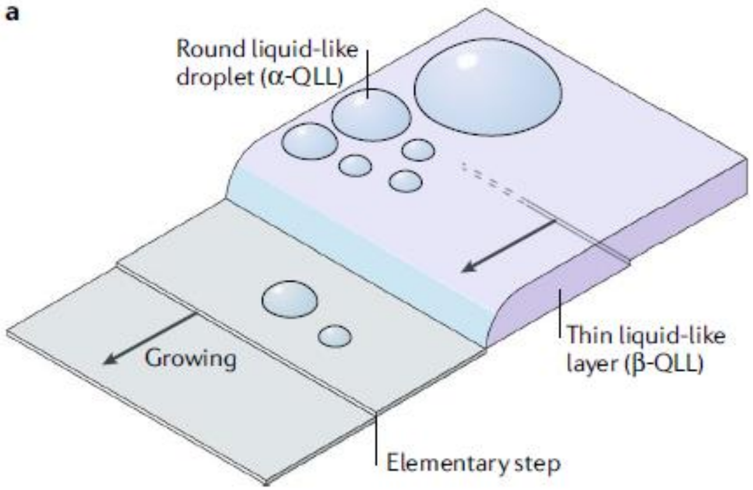
随着接近表面，bilayer中的液体成分增加

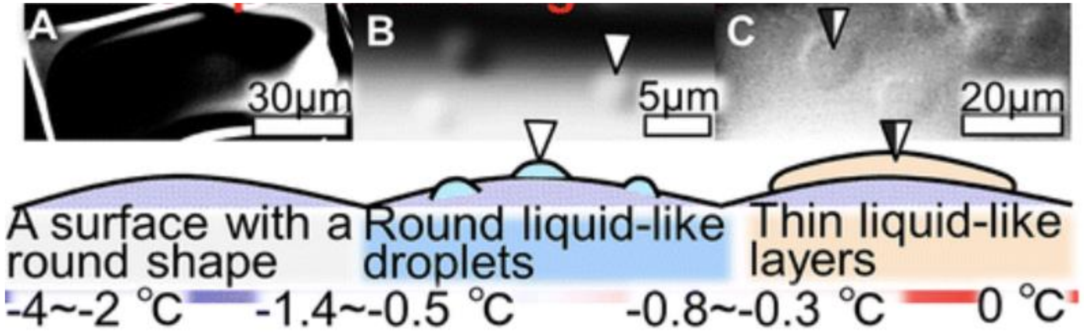


随着温度上升，表面层液体成分增加

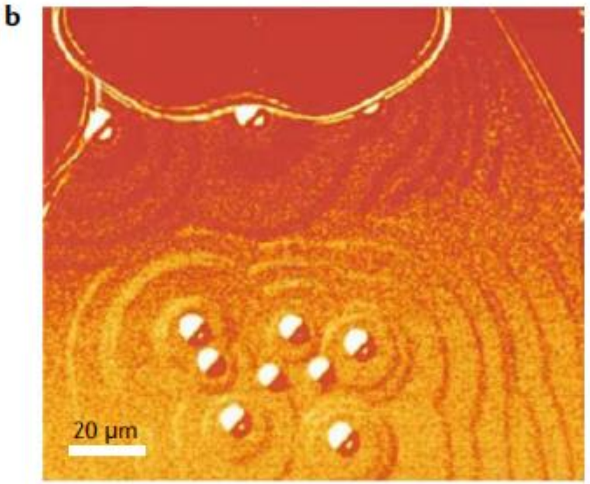
QLL的两种类型

- QLL分为两种, 即α-QLL(水滴状)和β-QLL(表面延展)
- 具体生成哪种QLL和多种因素有关

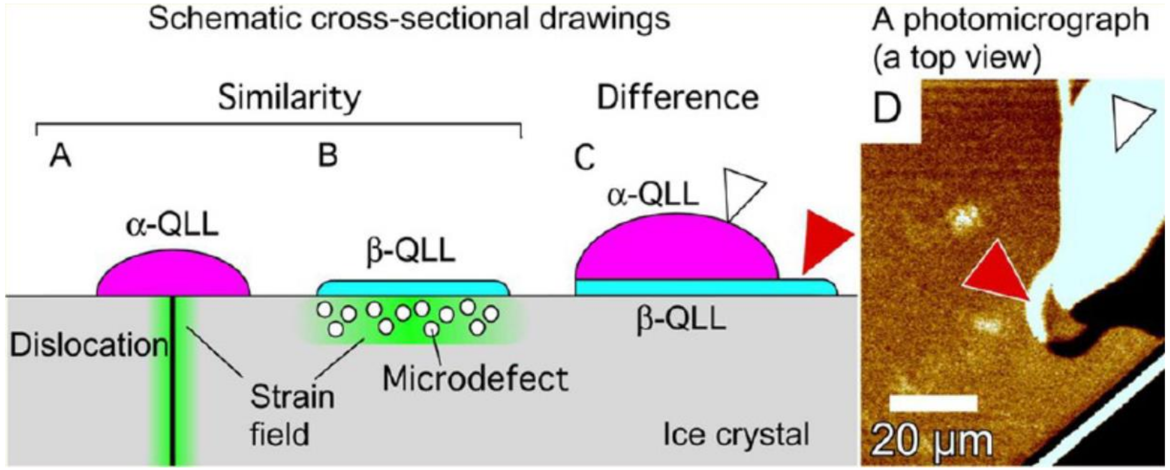




QLL的形成类型似乎和温度区间有关



α-QLL很大，可以直接在光学显微镜下观察到

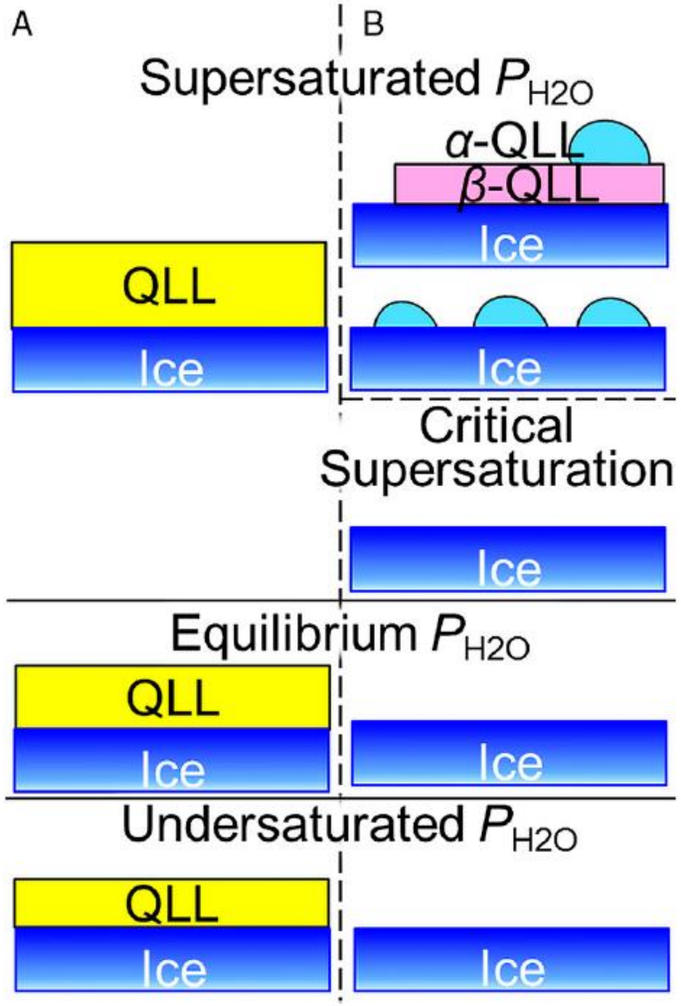


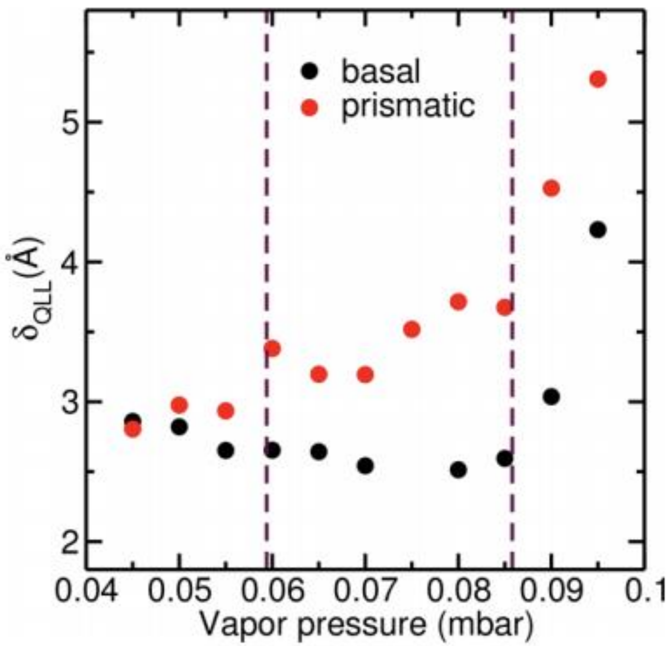
有研究认为位错会引发α-QLL，而局域缺陷引发β-QLL

蒸汽压对QLL的影响

两种QLL相的产生要满足水蒸气的蒸汽压大于饱和蒸汽压，这可能说明两种相是主要是水蒸汽沉积而不是冰表面水分子融化占主导的结果。

蒸汽压也会影响表面是被α相修饰还是β相修饰： β相产生的蒸汽压又显著大于α相，β相更不稳定，但是β相与固相接触更大，浸润角更大，这与我们的直觉相反…

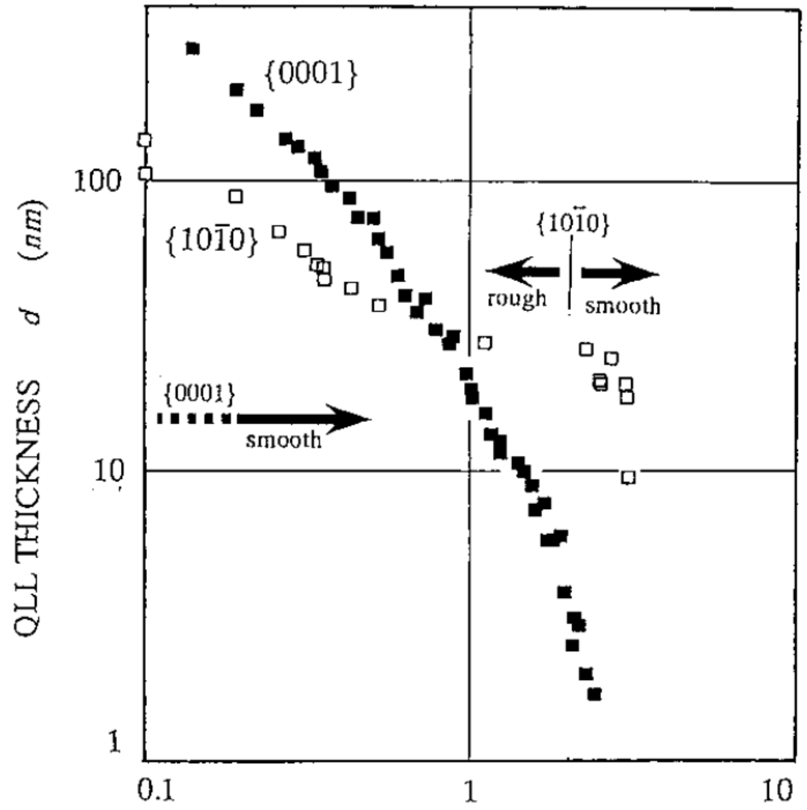




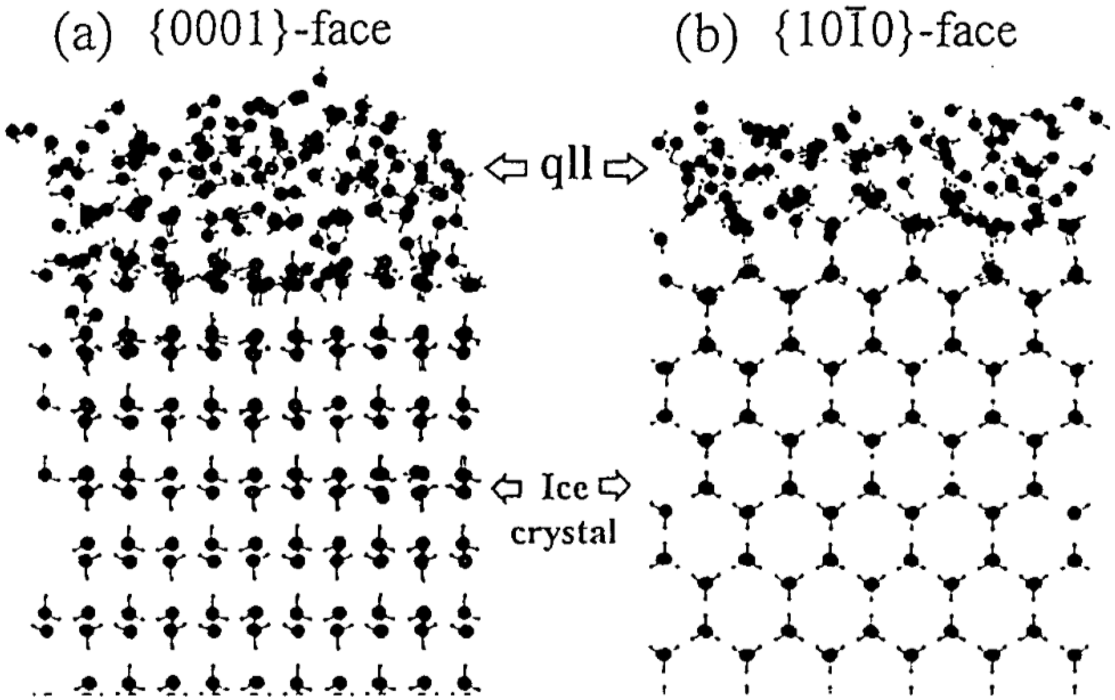
270K下QLL层深度在平衡蒸汽压附近与蒸汽压的依赖关系

晶面对QLL的影响

可以看到不同的晶面预融层深度随时间的变化关系都大致呈现对数关系，但是斜率不同，{0001}面变化更快。许多实验也观测到{0001}面的起始预融温度更低。



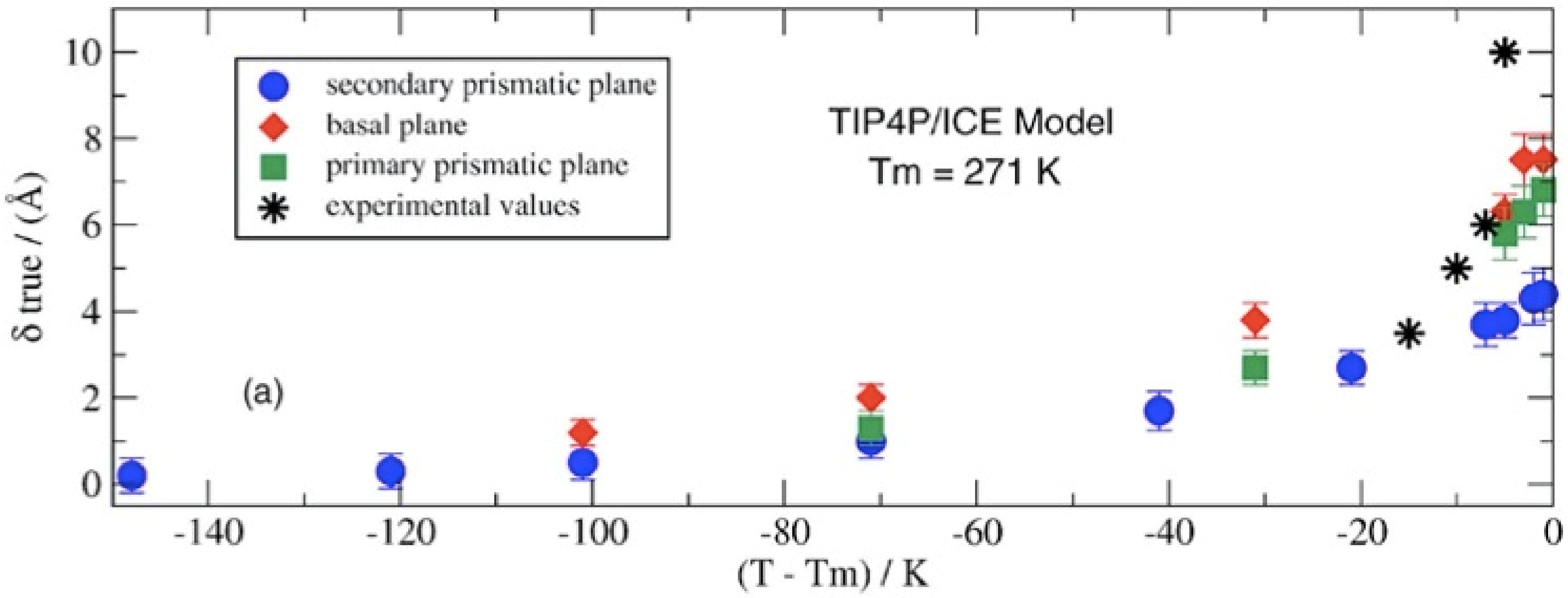
实验观测{0001}与{10-10}两个晶面预融层深度与温度关系

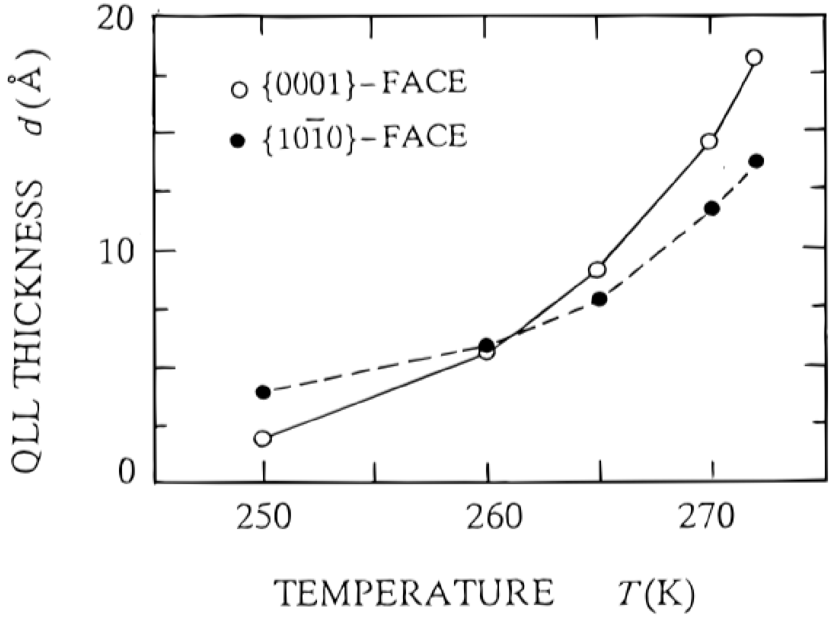


265K下不同晶面QLL的微观结构(计算)

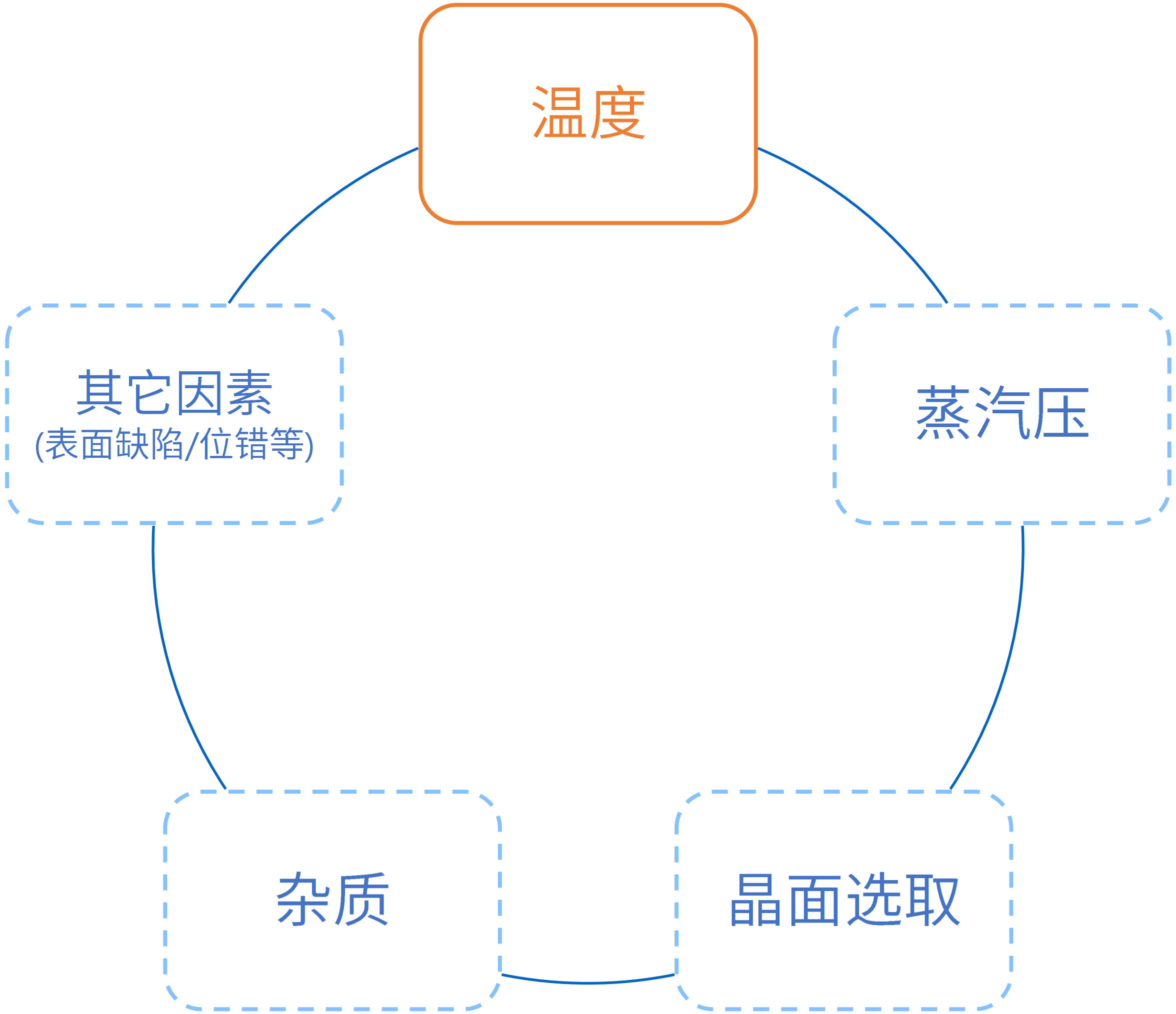
晶面对QLL的影响

计算得到的各晶面QLL深度-温度关系





预融的影响因素总结



温度

蒸汽压

晶面选取

杂质

其它因素
(表面缺陷/位错等)

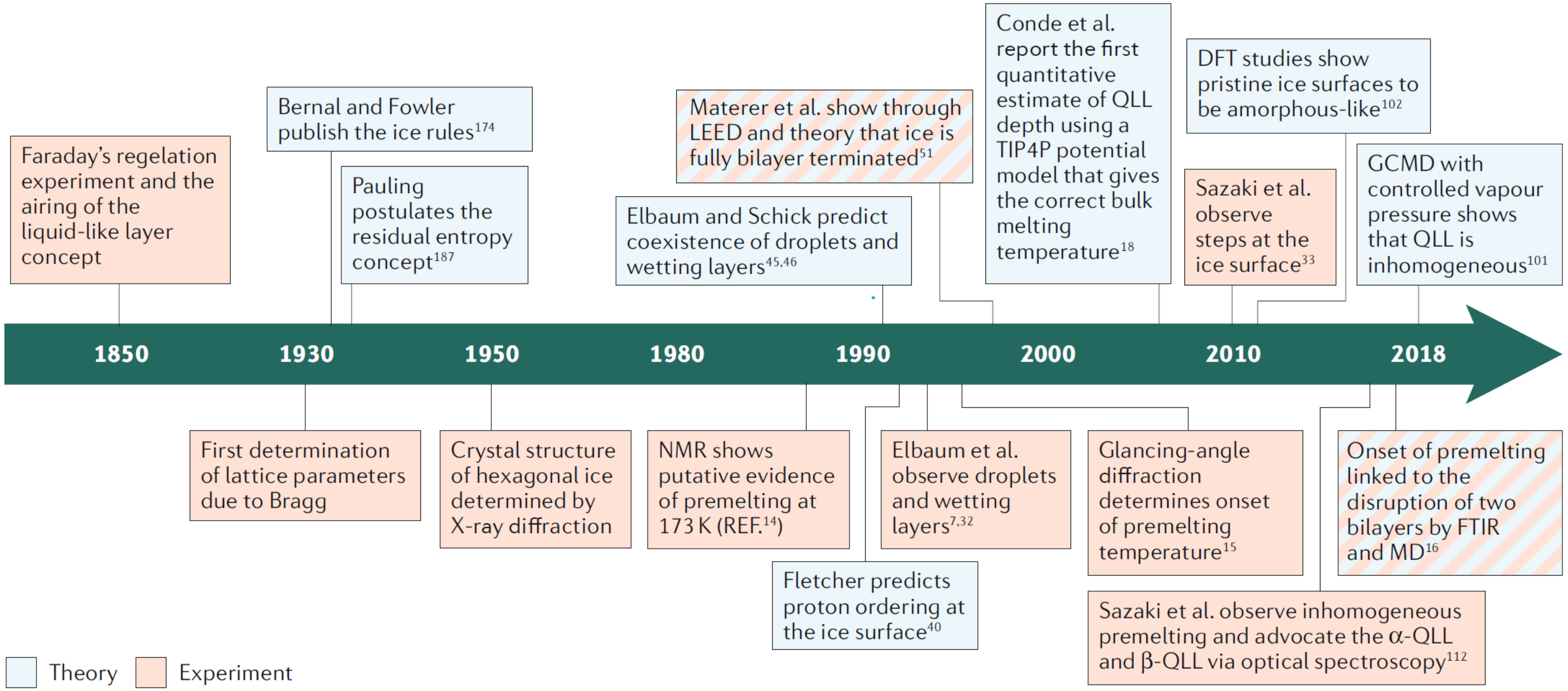
Premelting的研究方法

实验

计算

温度/深度

结构


Faraday's regelation experiment and the airing of the liquid-like layer concept

Bernal and Fowler publish the ice rules[174]

Pauling postulates the residual entropy concept[187]

Elbaum and Schick predict coexistence of droplets and wetting layers[45,46]

Materer et al. show through LEED and theory that ice is fully bilayer terminated[51]

Conde et al. report the first quantitative estimate of QLL depth using a TIP4P potential model that gives the correct bulk melting temperature[18]

DFT studies show pristine ice surfaces to be amorphous-like[102]

Sazaki et al. observe steps at the ice surface[33]

GCMD with controlled vapour pressure shows that QLL is inhomogeneous[101]

First determination of lattice parameters due to Bragg

Crystal structure of hexagonal ice determined by X-ray diffraction

NMR shows putative evidence of premelting at 173 K (REF.[14])

Elbaum et al. observe droplets and wetting layers[7,32]

Glancing-angle diffraction determines onset of premelting temperature[15]

Onset of premelting linked to the disruption of two bilayers by FTIR and MD[16]

Fletcher predicts proton ordering at the ice surface[40]

Sazaki et al. observe inhomogeneous premelting and advocate the α-QLL and β-QLL via optical spectroscopy[112]

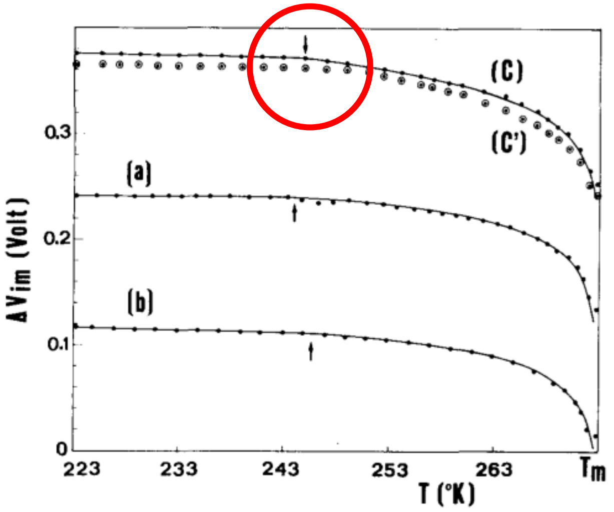
☐ Theory 🟧 Experiment

早期实验

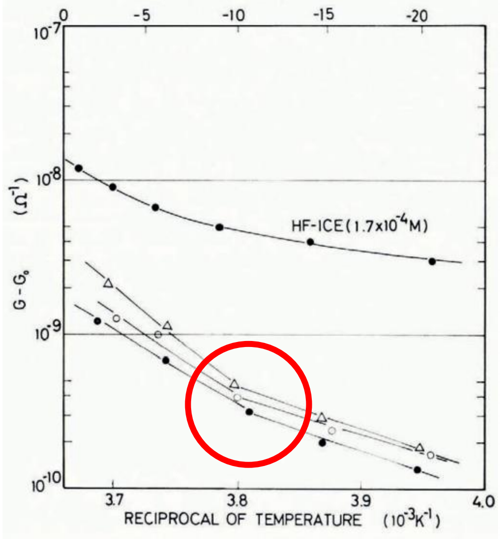
- 1850 法拉第 (两块潮湿的冰(moist ice)能粘在一起)

- 1967-1978 表面电学性质测量（电位差、电导率等）
- 1974 光电发射（Photoemission）
- 1978 卢瑟福背散射光谱（Rutherford backscattering spectrum）

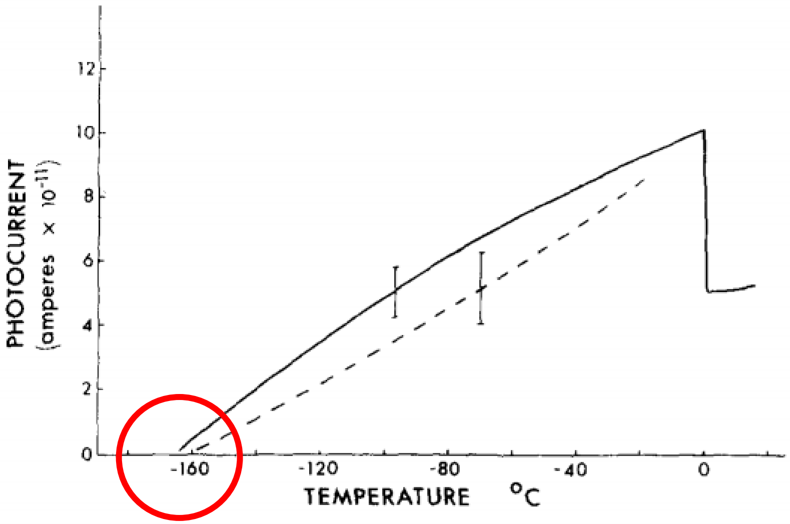
>> 实验数值分散度很大



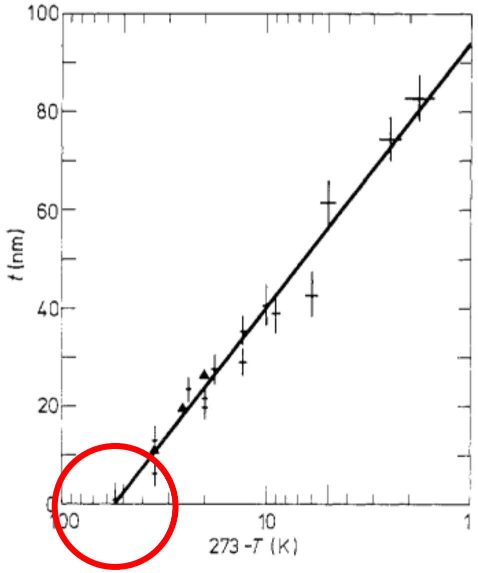
电位差



电导率



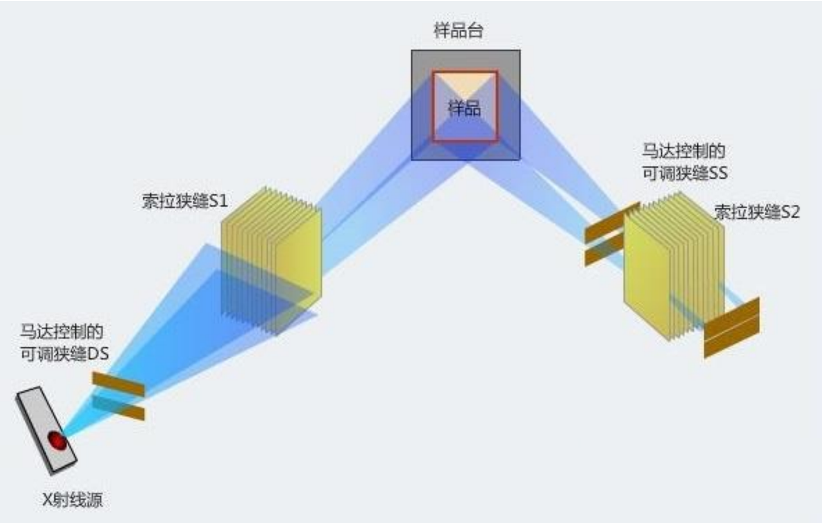
光电发射

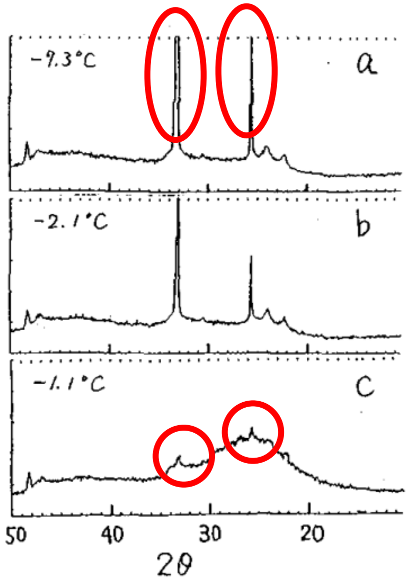


卢瑟福背散射光谱

X射线衍射

- 从衍射图样识别晶体/非晶 >> 测定预融温度

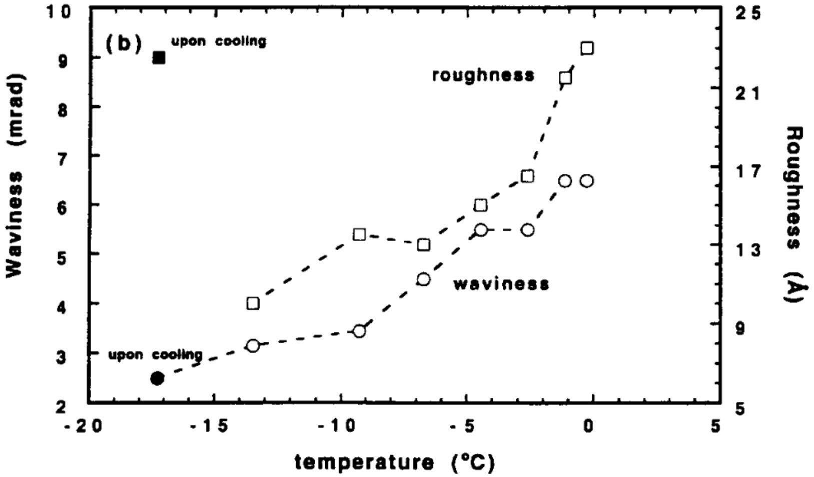


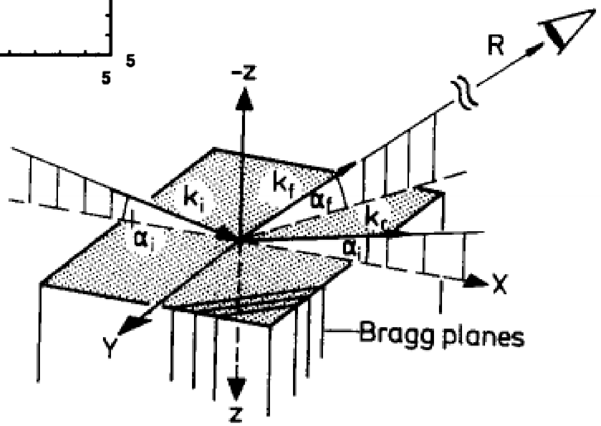


- 掠射角X射线衍射（Glancing-angle X-ray scattering）

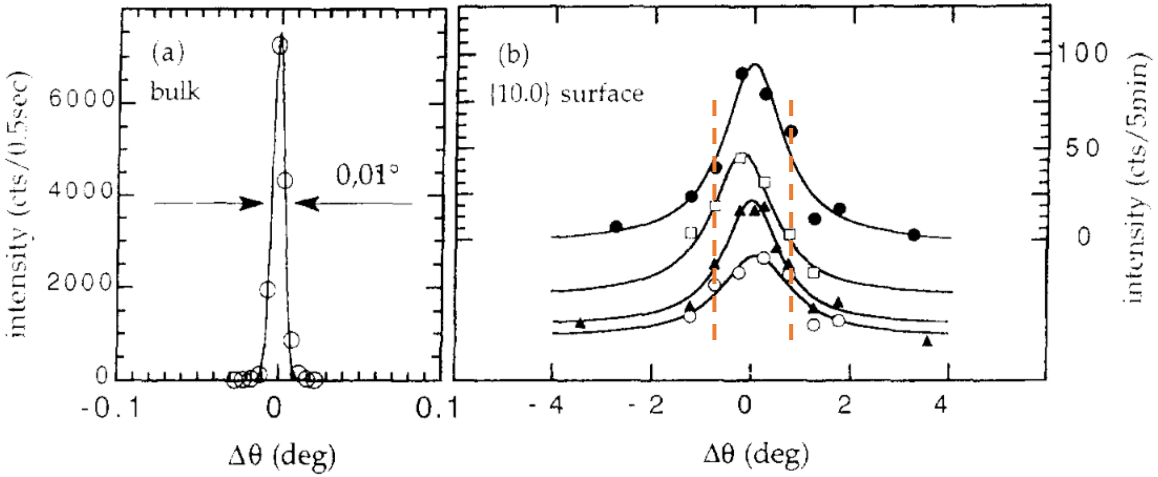
>> 针对表面性质

>> 预融深度 / 表面粗糙度





衍射峰宽度 >> 表面结构的有序度(缺陷)



更多实验方法

- 核磁共振 (Nuclear magnetic resonance, NMR)

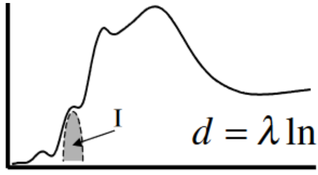
\>> 表面分子的**动态信息**

- 椭圆偏振技术 (Ellipsometry)

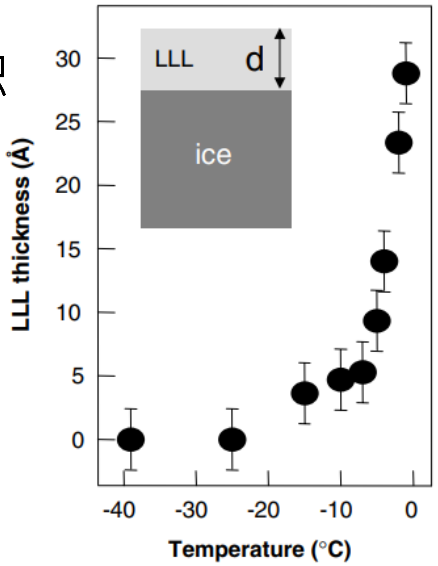
\>> 折射率/表面膜深度

- 近边X射线吸收精细结构 (Near-edge X-ray absorption fine-structure, NEXAFS)

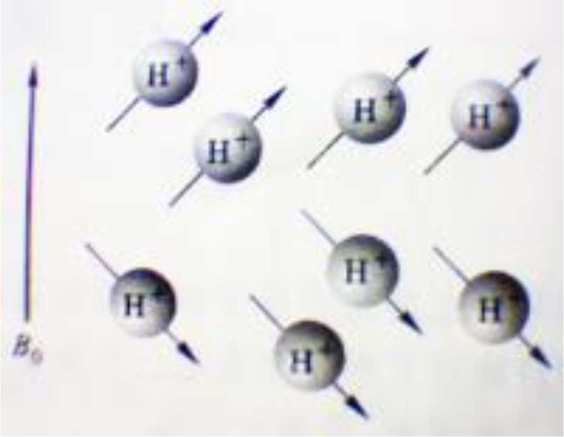
NEXAFS测定自由氢的峰面积给出QLL的深度

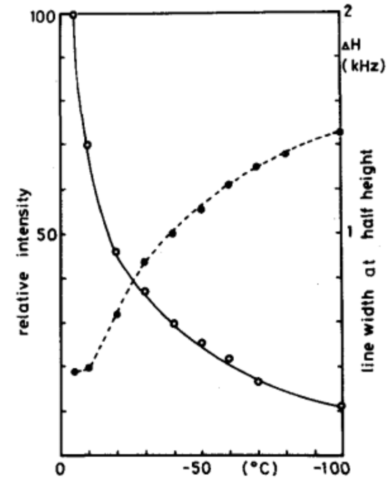


$$d = \lambda \ln\left(1 - \frac{I - I_{ice}}{I_{water} - I_{ice}}\right)$$

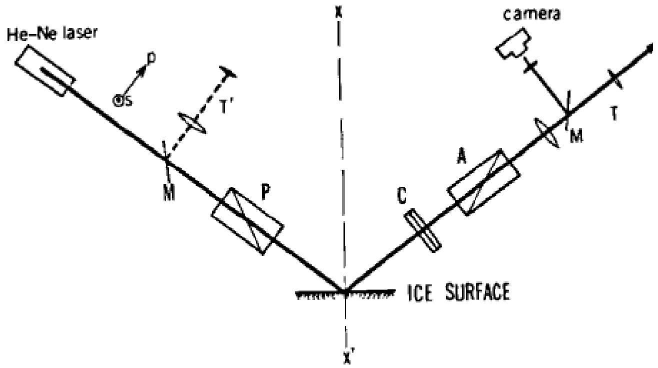


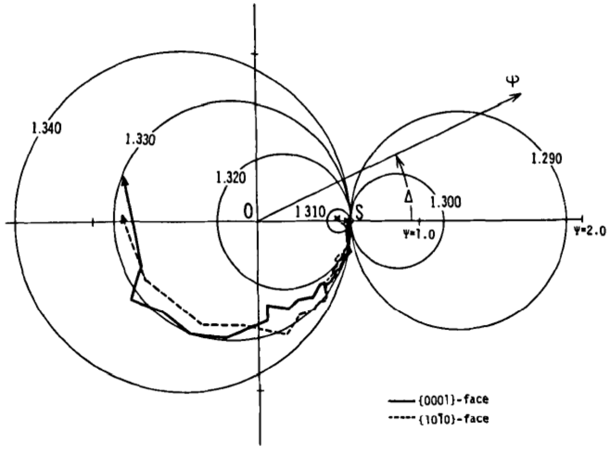
\>> 对QLL结构仍然缺少了解





核磁共振: 随着温度升高，表面的“动态分子”变多





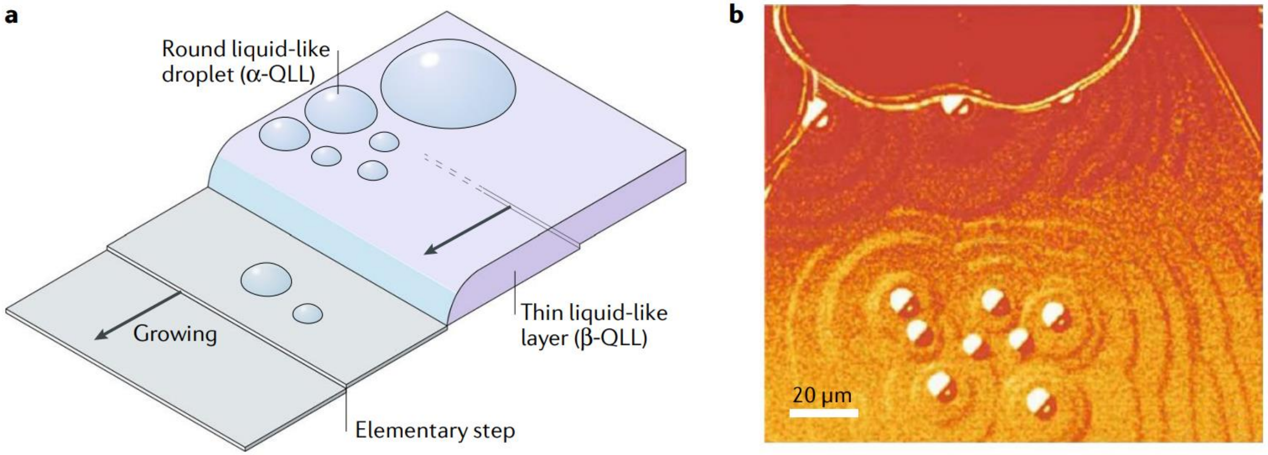
椭圆偏振: QLL的折射率~1.33, 更接近水

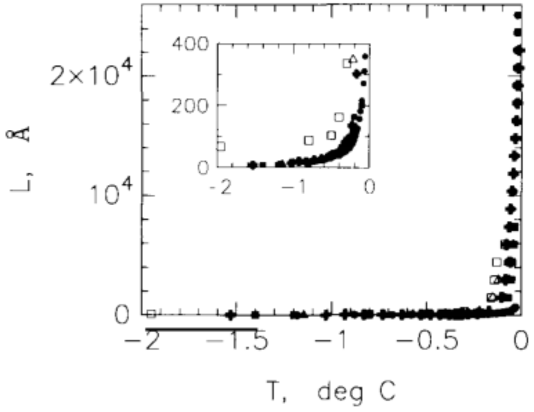
光学显微镜

- 光学显微镜 (Optical microscope)

>> 从实空间直接观察QLL形态

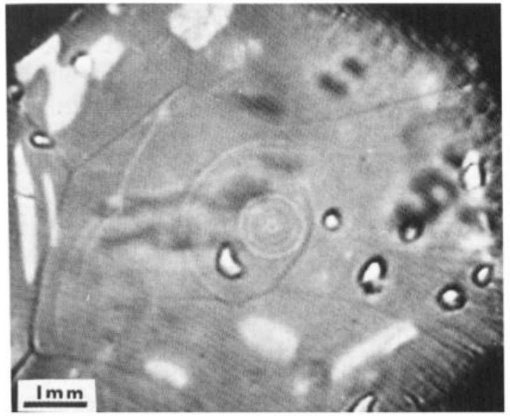
>> 观测到α-QLL和β-QLL的存在

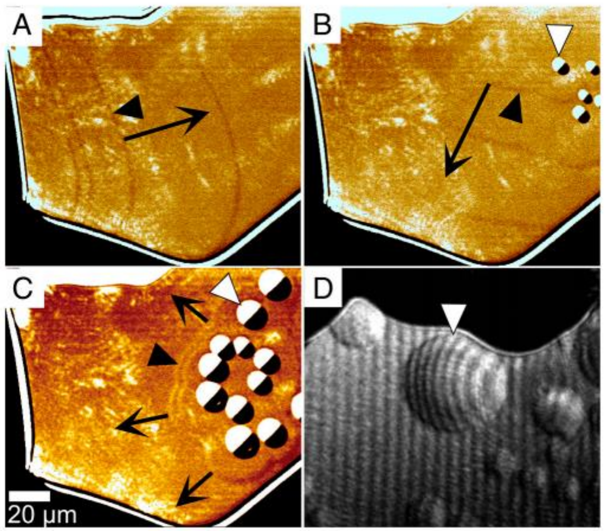


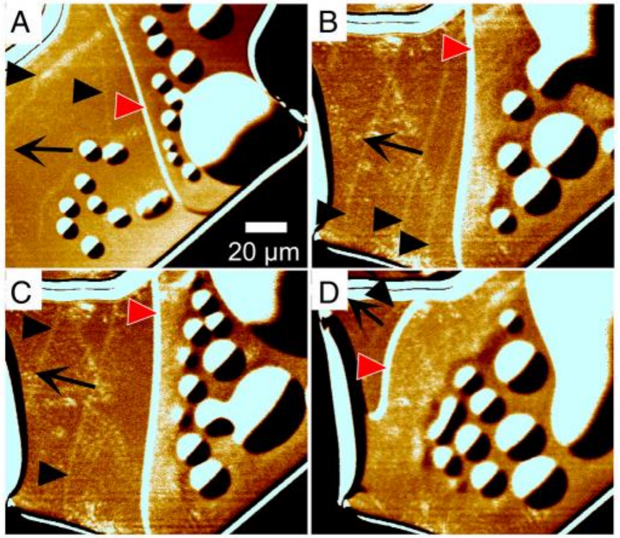


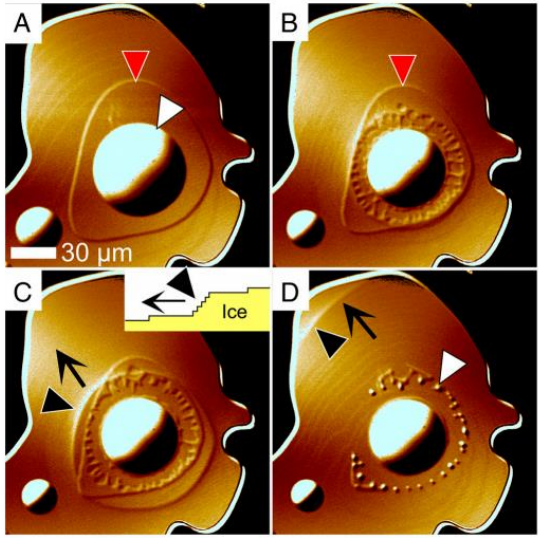
通过干涉仪
可以测量QLL的深度

α-QLL和β-QLL的直接观察, 并可测定α-QLL的大小





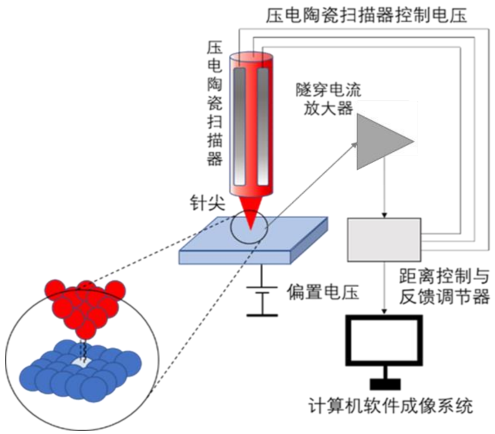


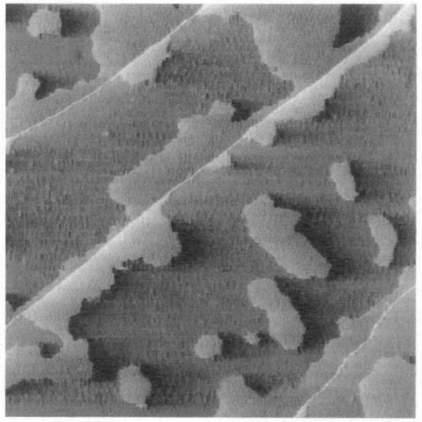


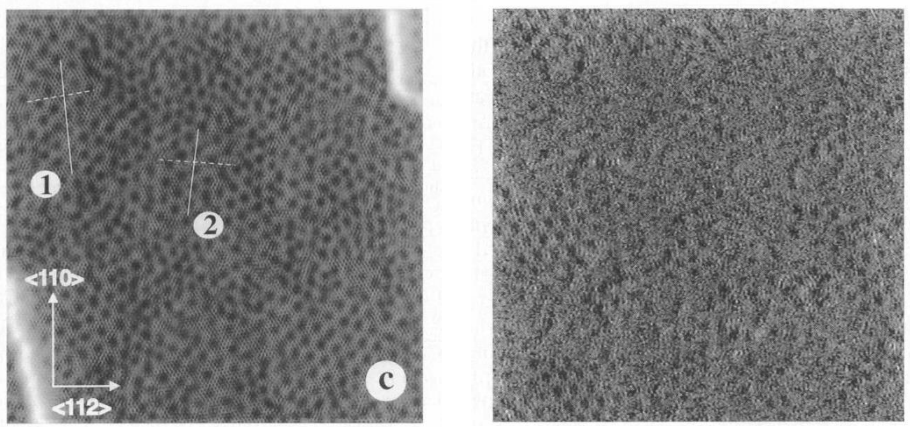
扫描隧道显微镜/原子力显微镜

- 扫描隧道显微镜（Scanning Tunneling Microscope, STM）/原子力显微镜（Atomic Force Microscope, AFM）

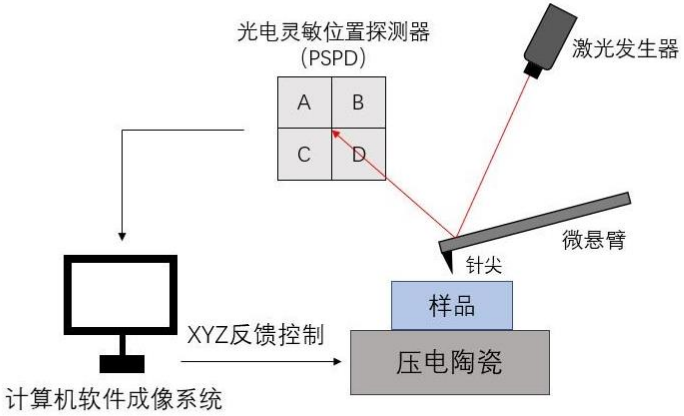
>> 更高分辨率观察结构

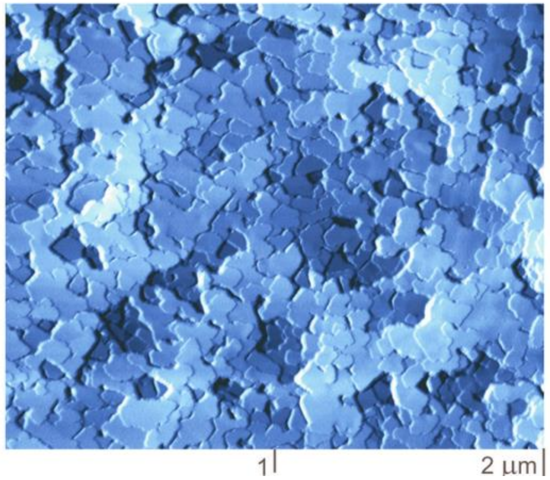






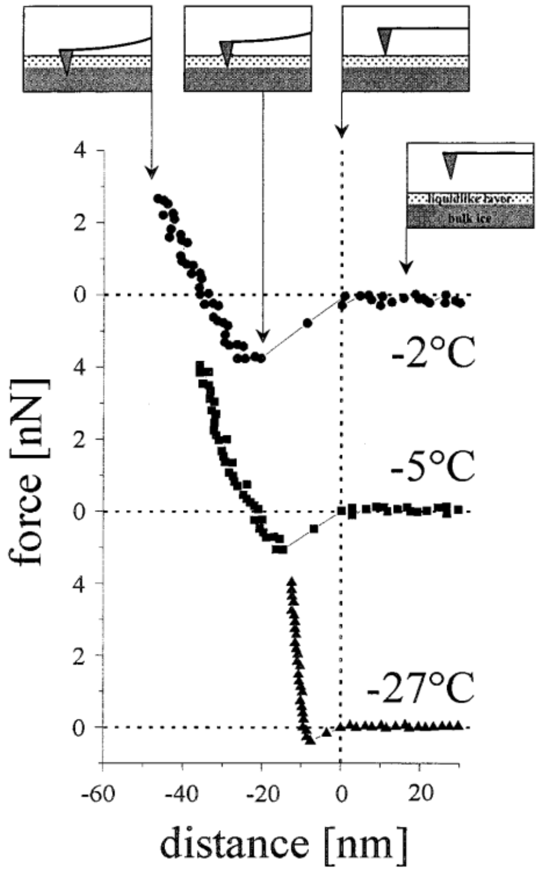
STM观察Pt(111)表面水的分布, 还可以看到晶格结构以及融化中晶格的变化





qPlus AFM看到的Pt(111)表面的冰薄膜

AFM针尖可以探入液体层可用于测定QLL深度

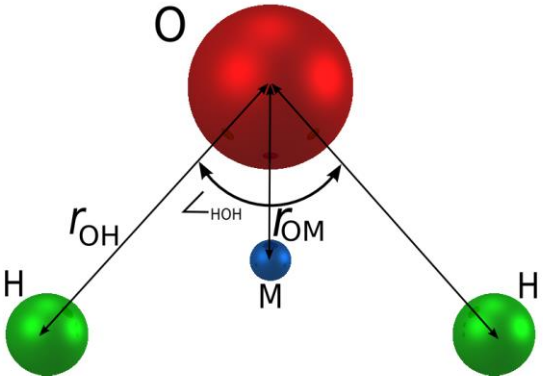


分子动力学 (Force-Field)

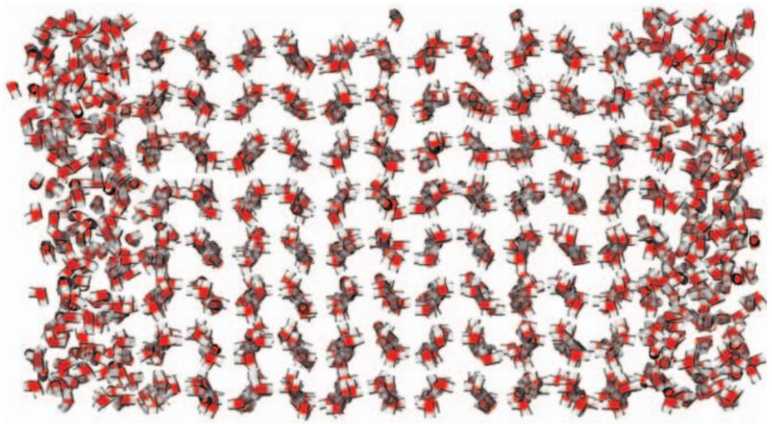
经典力场描述原子间作用

直接模拟预熔过程中原子的运动情况

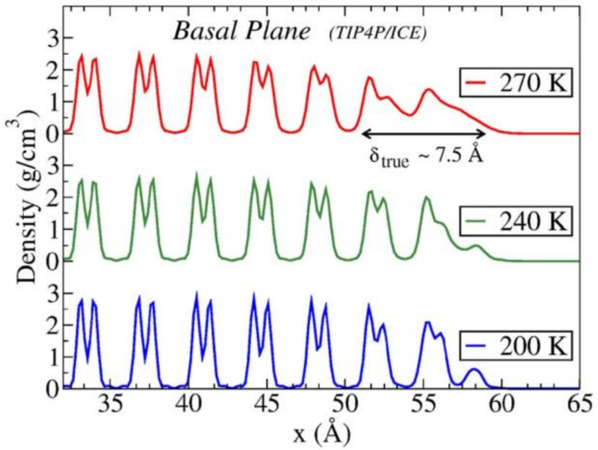
- 预熔深度与温度的模拟
- 观察预熔层的原子级结构



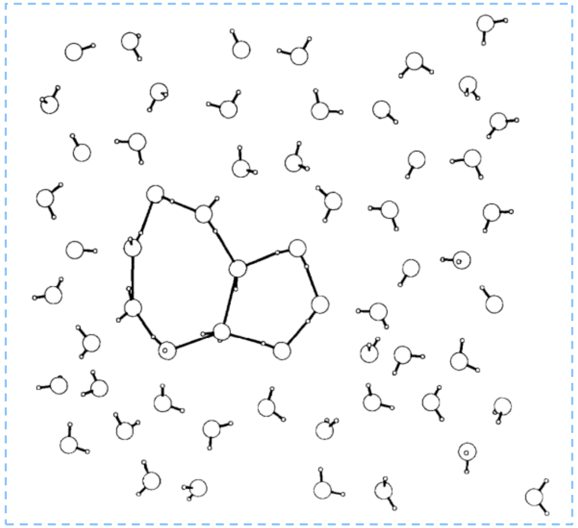
TIP4P水模型
分子动力学的常用模型之一



直接观测预熔层与体相的结构差异

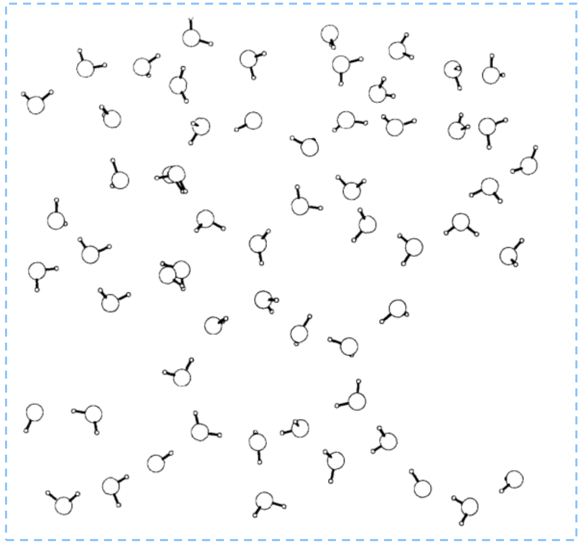


计算不同温度下的预熔层深度



低温下的表面结构
(注意六边形的排列,以及例外)

升温



熔点附近的表面结构(六边形消失)

两个问题:

- 计算速度（能做多大体系？）
- 计算精度（定量比较？）

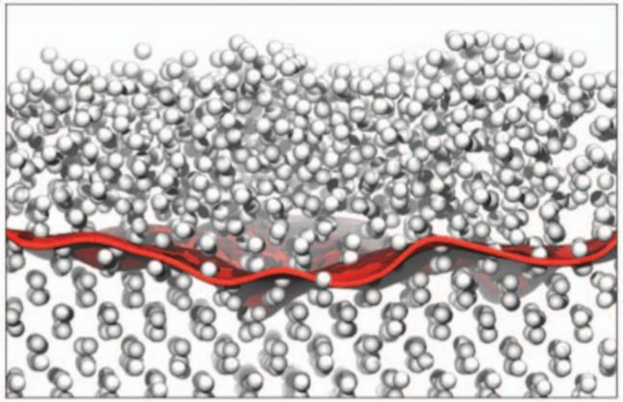
分子动力学 (Coarse-Grained)

Coarse-Grain ---- “粗晶”

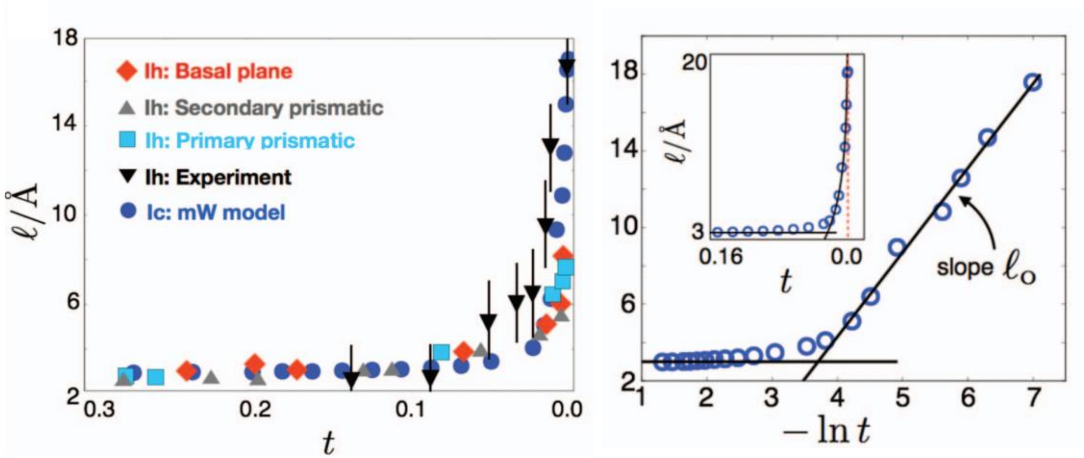
增加模拟粒度

提高计算速度和模型尺寸

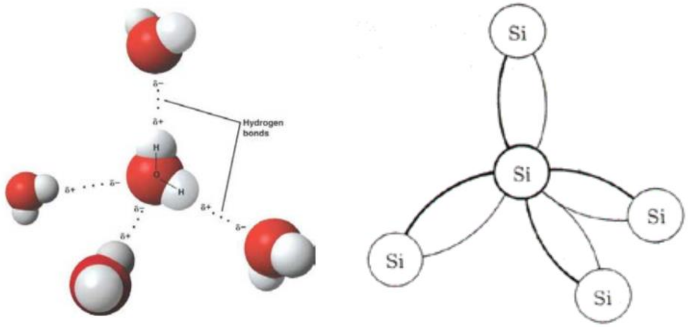
- 大规模采集数据点
- 观察“介观” 的结构特征



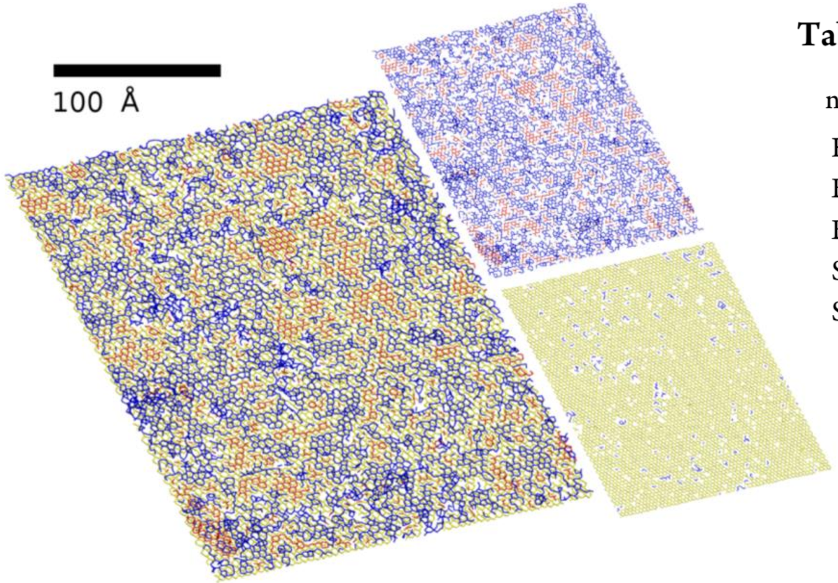
8000个分子
观察到QLL-体相界面的波动



大量数据点的采集
拟合出预熔层深度与温度的分段对数关系



mW水模型
常用的coarse-grained模型之一



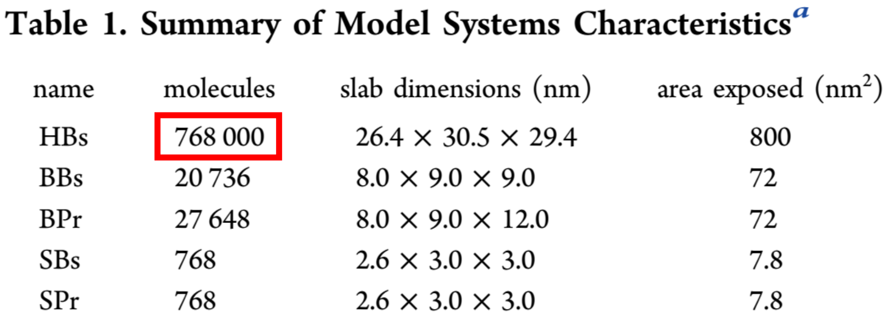


Table 1. Summary of Model Systems Characteristics[a]

name	molecules	slab dimensions (nm)	area exposed (nm^2)
HBs	768 000	26.4 × 30.5 × 29.4	800
BBs	20 736	8.0 × 9.0 × 9.0	72
BPr	27 648	8.0 × 9.0 × 12.0	72
SBs	768	2.6 × 3.0 × 3.0	7.8
SPr	768	2.6 × 3.0 × 3.0	7.8

768000个分子的大型模拟

怎么样才能实现?

第一性计算 (DFT)

基于量子力学的，更高的计算精度

- 很难模拟动力学?

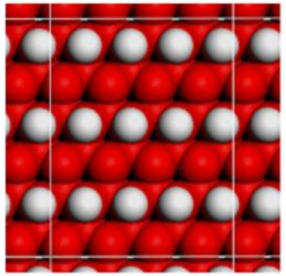
>> 静态结构的计算

>> 分析不同构型的稳定性

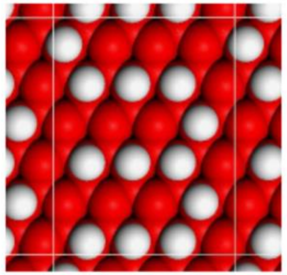
>> 得出预熔层的结构特征

>> 影响结构的物理机制

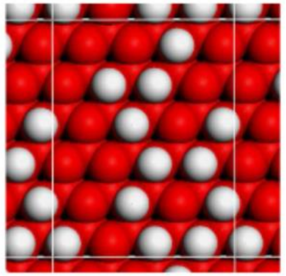
Ⅰ. C_{OH}=2. 00



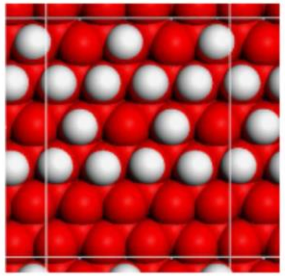
Ⅱ. C_{OH}=2. 00



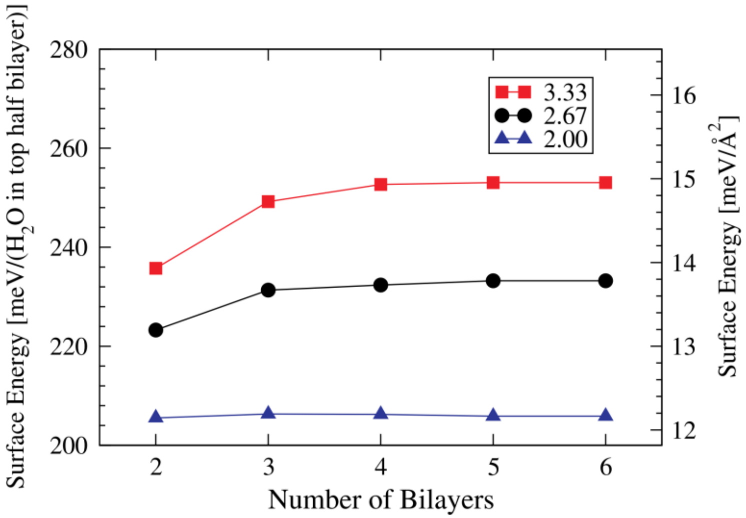
Ⅲ. C_{OH}=2. 67

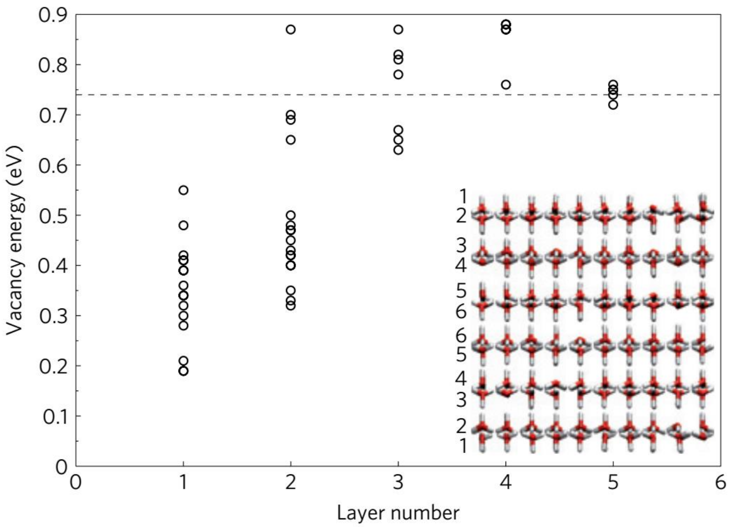


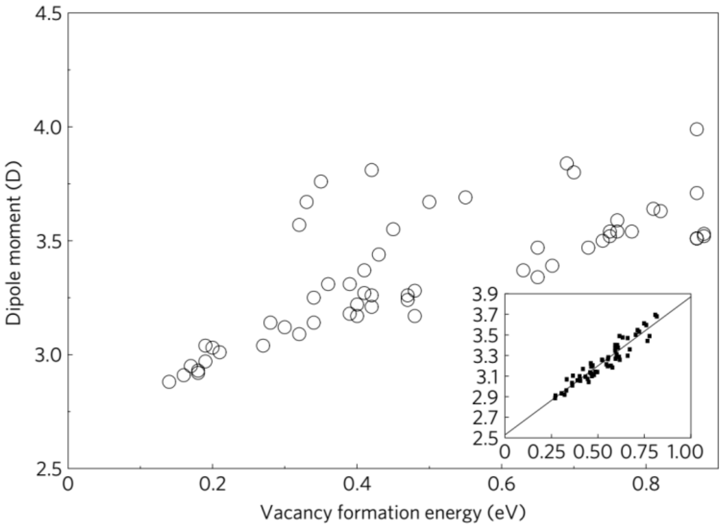
Ⅳ. C_{OH}=3. 33



表面氢原子是如何分布的
什么样的结构最稳定?





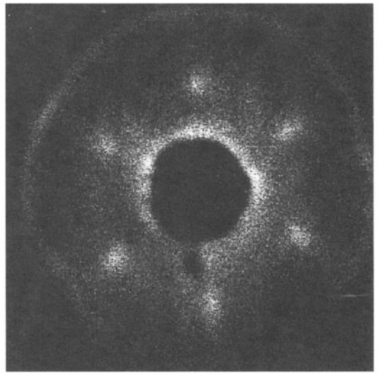


空位形成能决定了QLL的层数，但空位形成能又受到什么因素的控制?

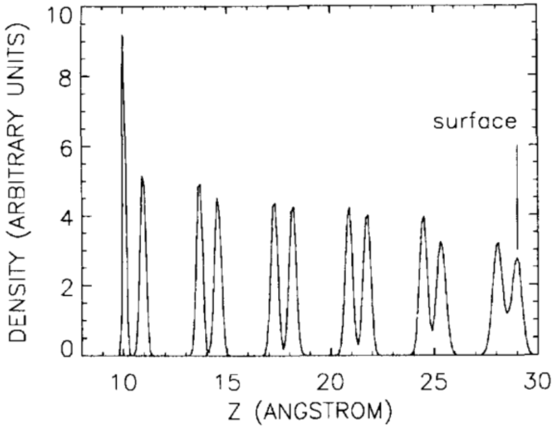
实验与计算的结合

预熔的研究很大程度上是实验与计算共同展开的，不过有时候这种共同会展现为明显的形式

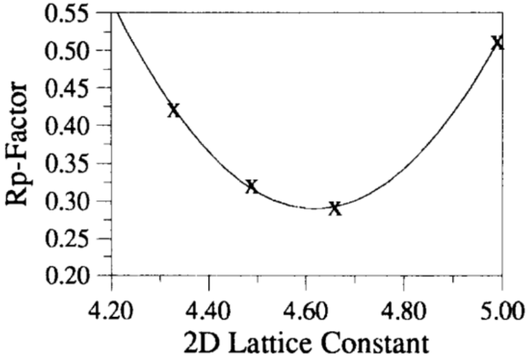
>> 计算解释实验结果



LEED
>>表面为六方晶格
>>termination是什么?



分子动力学
>>表面termination为整个bilayer

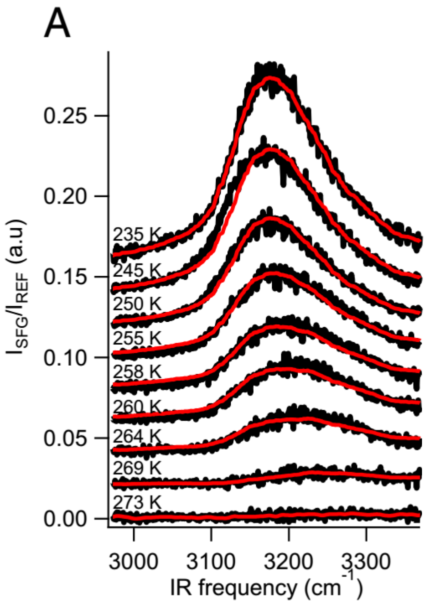


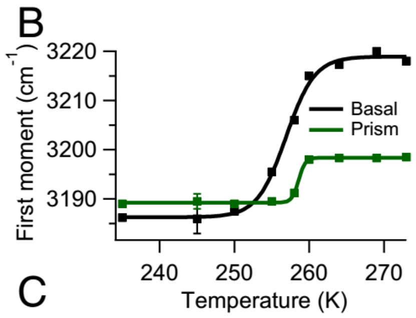
MD给出了结构特征

利用结构解释实验数据

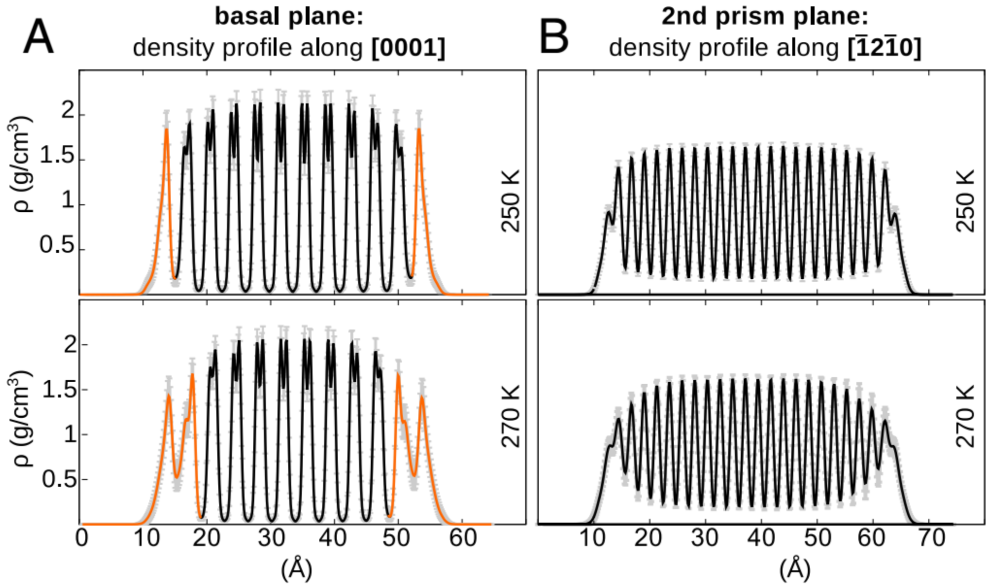
进一步分析晶格参数等物理量

>> 分析实验数据背后的物理过程





Vibrational Sum Frequency
峰位和峰值变化>>意味着什么?
不同晶面不一样>>为什么?

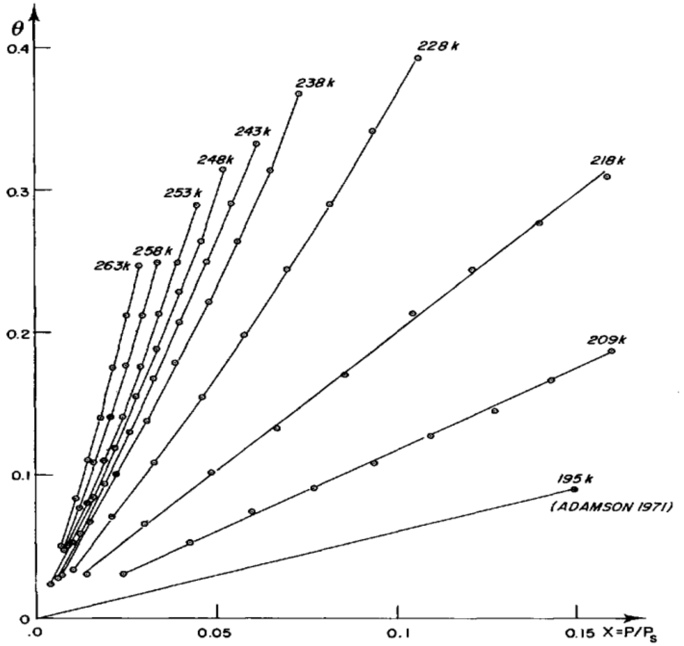


分子动力学
>>第二层bilayer的熔化
>>两个晶面的熔化方式不同

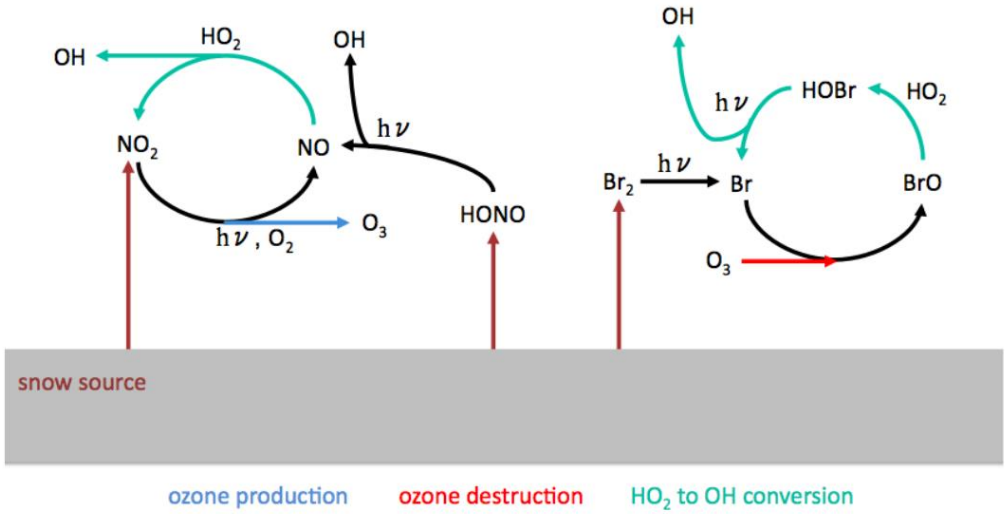
Premelting对环境的影响

举几个例子

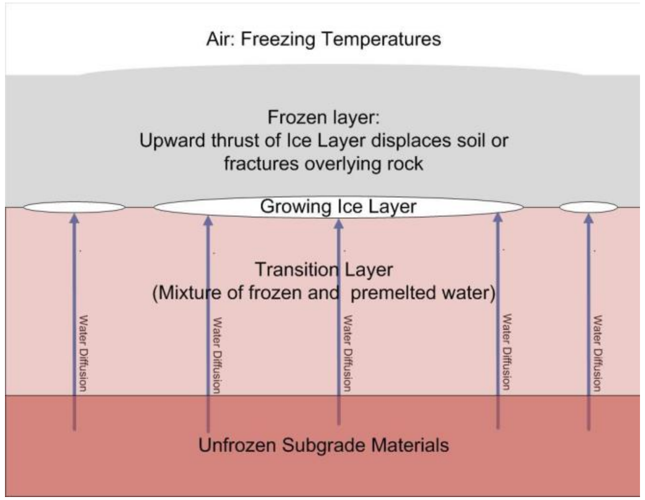
- 大气环境
- 土壤
- …



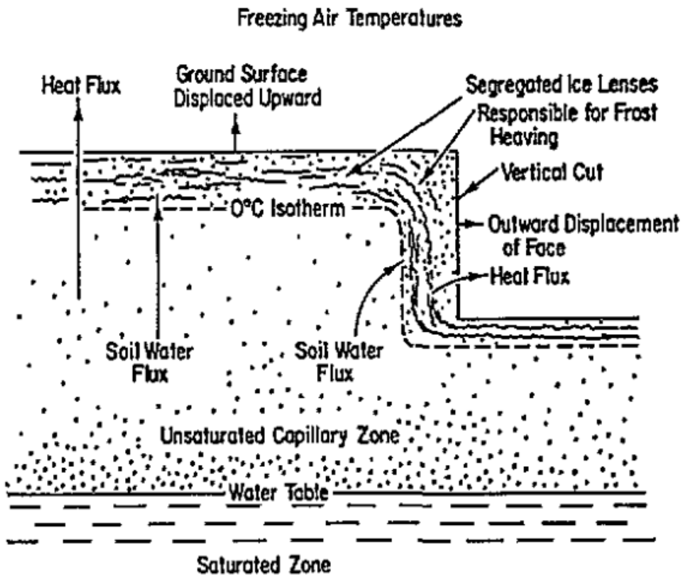
冰对CO2的吸收随温度上升,被认为是预融程度增加引起的



臭氧(O_3)的形成和破坏过程, 其中多个起重要作用的组分经由雪/冰晶的预融层释出和吸收



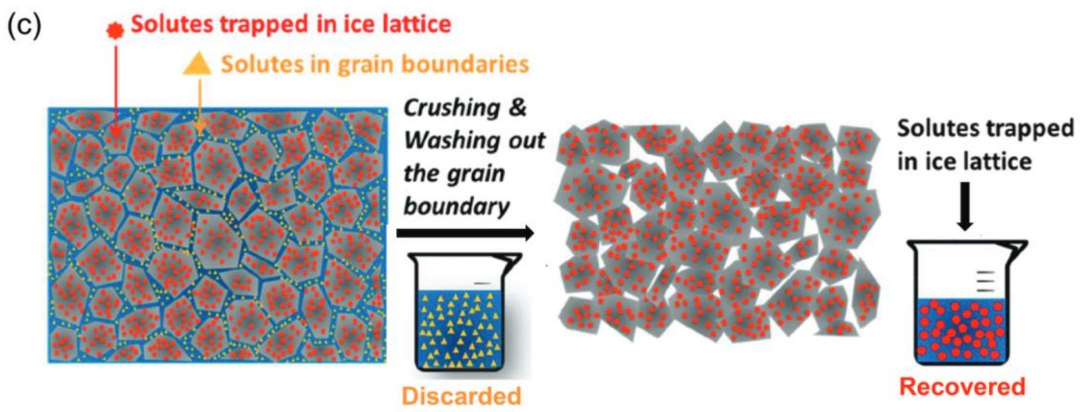
冰镜(ice lens)的形成机制与预融有关



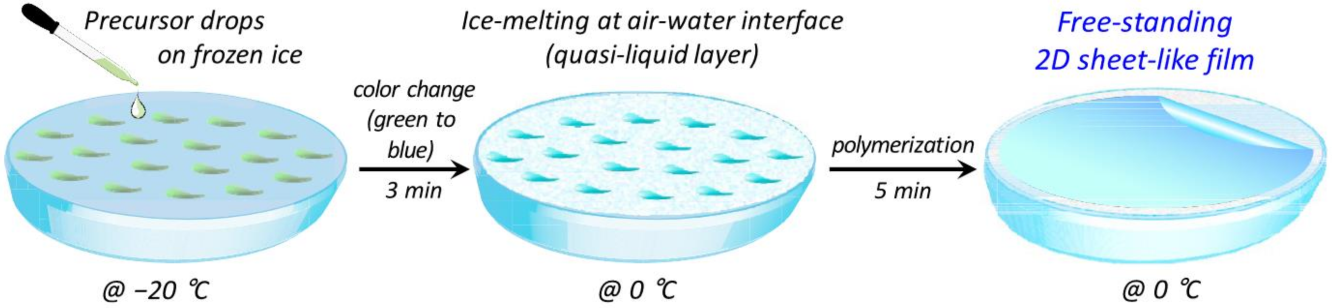
土壤冻胀(frost heave)的模型,预融层起到了重要作用

Premelting的应用

- 溶质分离：利用晶界的QLL和溶解度差异

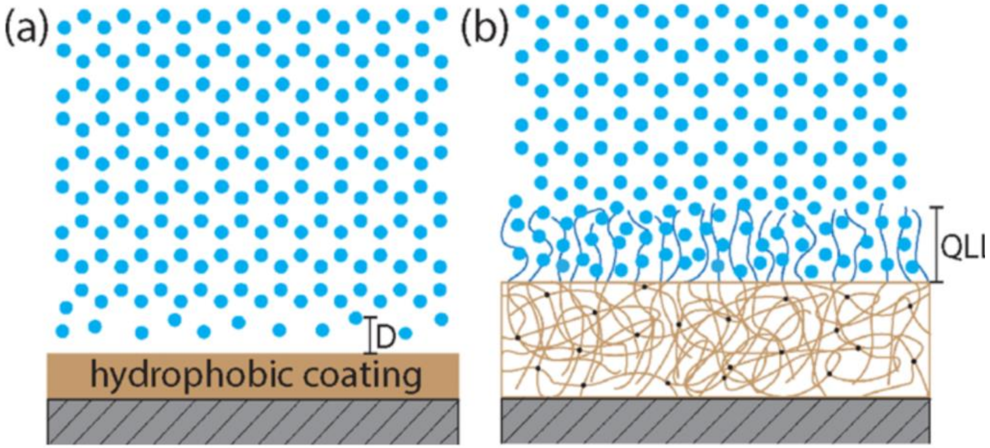


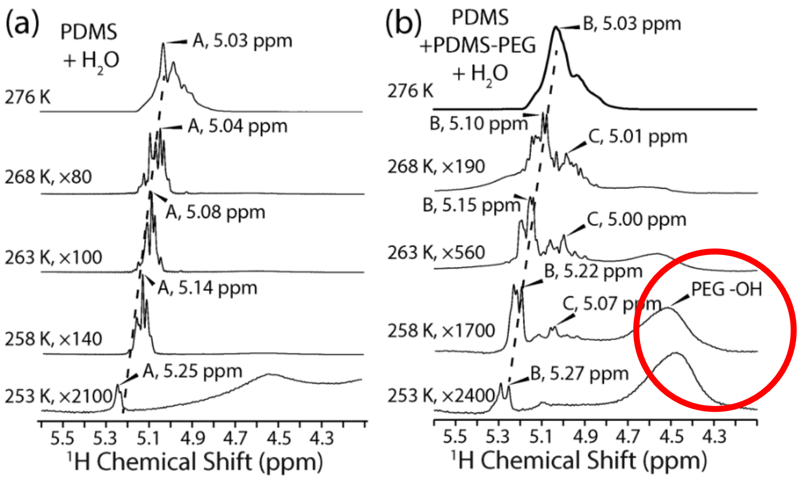
- 纳米材料的制备：反应物与QLL的作用使其在表面均匀分散，形成纳米片材料



- 防结冰涂层的设计

PDMS+PDMS-PEG涂层与冰的QLL层相互作用，降低了冰在基体表面的吸附趋势，抑制了基体的结冰





Possible Future Work

α-QLL的结构和生成条件?

- 有一些实验指出了影响α-QLL生成的一些因素，但研究并不完全、系统
- 计算可对α-QLL的结构研究起到决定性作用，但α-QLL的尺寸(数μm)使得计算不易进行

QLL深度的精确测定?

- 不同实验结论差异很大，怎么样得到有意义的结果?
- 实验与计算的差异又应该怎么理解?

imperfection对QLL的影响?

- 点缺陷/位错/溶质/环境中的杂质etc.
- 与对环境的影响/应用相关

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