

Nucleation-Limited Dewetting of Ice Films on Pt (111)

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PRL 100, 186101, May 2008

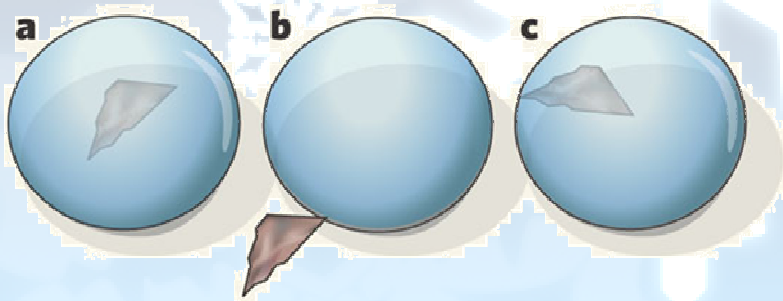
Introduction

The nucleation of ice on solid substrates is important in many natural phenomena

- ❖ Rain fall is triggered by nucleation of ice crystals on micron sized particles in clouds
- ❖ Very little information we know about early stage of ice growth at the molecular level
- ❖ To study nucleation phenomena directly on metal and semiconductor surfaces STM is the best technique
- ❖ It is difficult to image thick ice films non destructively using STM since ice is an electrical insulator
- ❖ There have been no STM observations which can track the growth of complete multilayers (first one or two layers have been already reported using STM)

Three basic questions to be answered

- ❖ How close are the growing crystals to thermal equilibrium?
- ❖ How do new layers nucleate?
- ❖ How do surface diffusion and substrate-ice interactions affect the evolution of the crystals?



- a. A nucleus immersed in the bulk drop
- b. Contact from a nucleus outside the drop.
- c. Contact from within the drop ('contact nucleation inside-out').

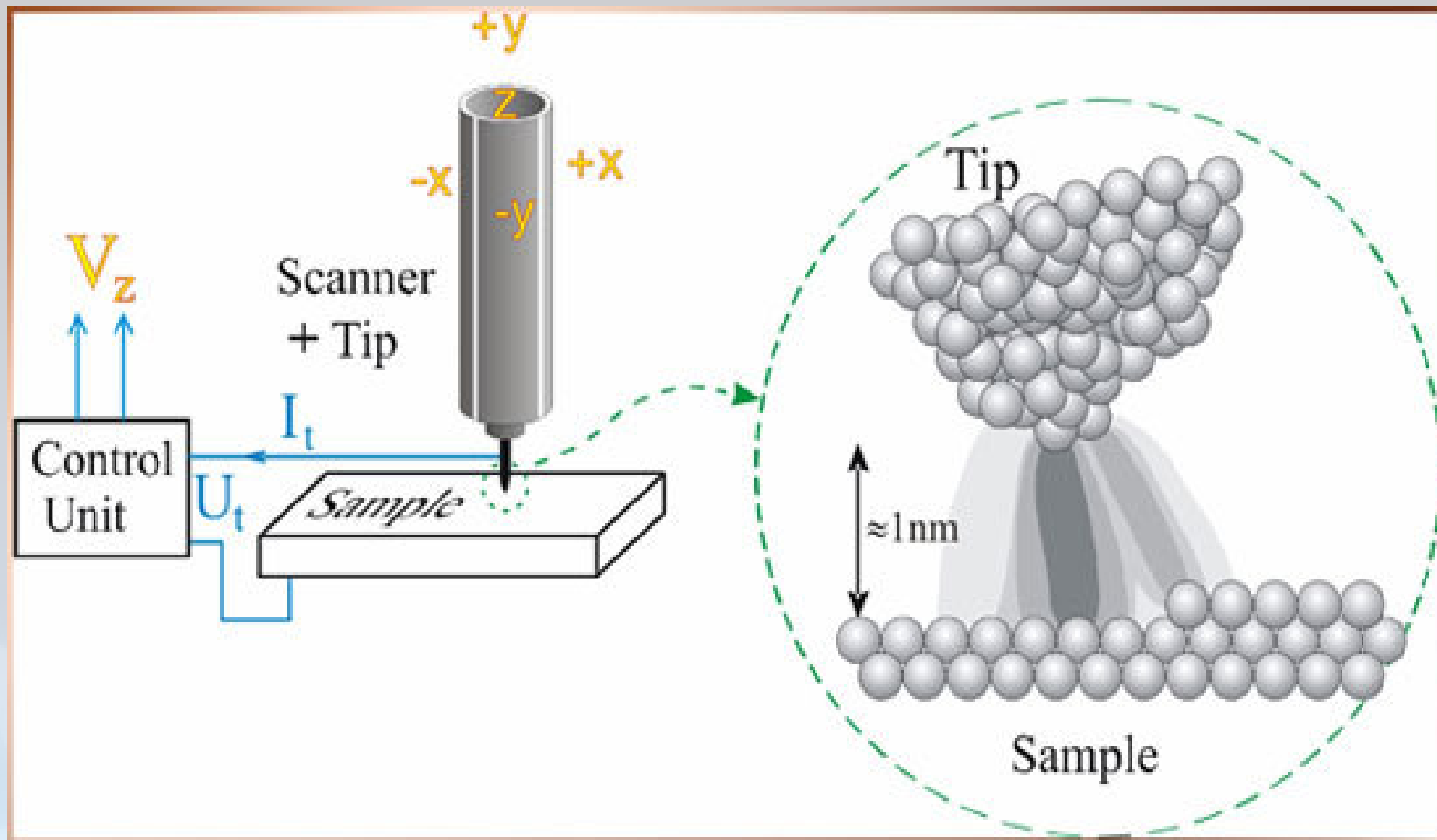
Crystallization occurs at higher temperatures in the two surface-contact situations

Three ways in which an ice nucleus may cause crystallization of a water drop

Nature **438**, 746 (2005)

Unique features of this article

- ❖ The ability to image ice film of thickness $> 3\text{nm}$ was not possible because STM relies on electrical conductivity and we know ice is a good insulator
- ❖ This is the first report of imaging thick ice films using STM by applying extremely small tunneling current and sufficiently large negative bias voltage
- ❖ With this new capability they have investigated how crystalline ice multilayers grown on Pt (111)
- ❖ Uniform thin films are often thermodynamically unstable and they tend to form 3-D crystals.
- ❖ It is very crucial to understand how the morphology of the grown films relates to their energetics and equilibrium configuration
- ❖ Ice dewets Pt surface
- ❖ Evolution of crystalline multilayer ice films formed during annealing at 140 K
- ❖ They found that 3-D ice crystals do indeed grow higher by nucleating new ice layers on their top facets even in the absence of their deposition
- ❖ The parameters that emerge from the analysis place bounds on the energetics of ice surfaces and interfaces

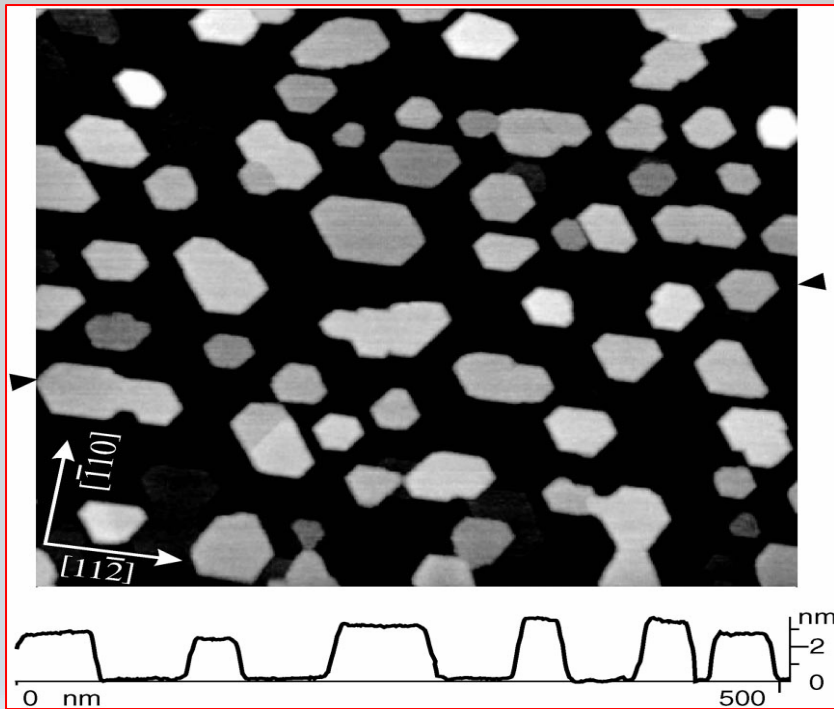


Schematic of a typical STM instrument

Sample preparation

- ❖ The ice films were grown in UHV at a rate of 0.1 nm/ min by depositing water vapor onto the platinum sample held at 140 K
- ❖ For imaging purpose which is performed ~ 120 K , a negative sample bias of $V_{\text{sample}} < -6(\pm 1)V$
- ❖ When a tunneling current is as low as ~ 0.4 Pa no sign of scanning induced surface charges were observed
- ❖ Present experiment shows reproducibility of the images at the $V_{\text{sample}} < -6(\pm 1)V$
- ❖ When $V_{\text{sample}} > -6(\pm 1)V$ the STM tip collides with the ice film and scatters material across the surface
- ❖ The threshold voltage corresponds to the energy of the first occupied states of the ice in contact with Pt.
- ❖ Hence it is possible for the applied voltage to lift the energy levels of the ice sufficiently that the electrons can tunnel through the vacuum gap from the highest occupied H₂O orbital in to empty states of the W STM tip

Surface topography of a crystalline ice-multilayer film on Pt (111)



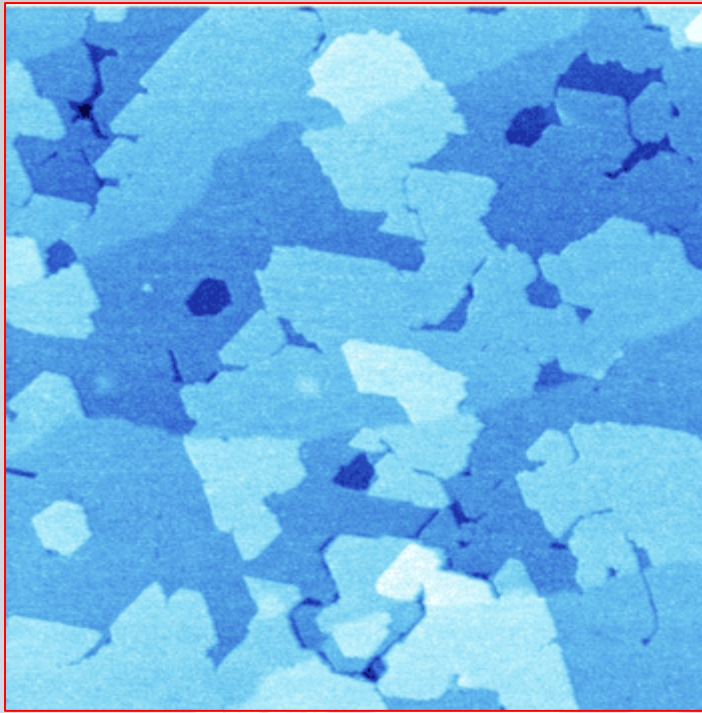
❖ 500 nm X 500 nm STM image which shows individual ~ 3 nm high ice crystals grown at 140 K

❖ The height profile displayed below the image was taken along the line connecting the two triangular markers

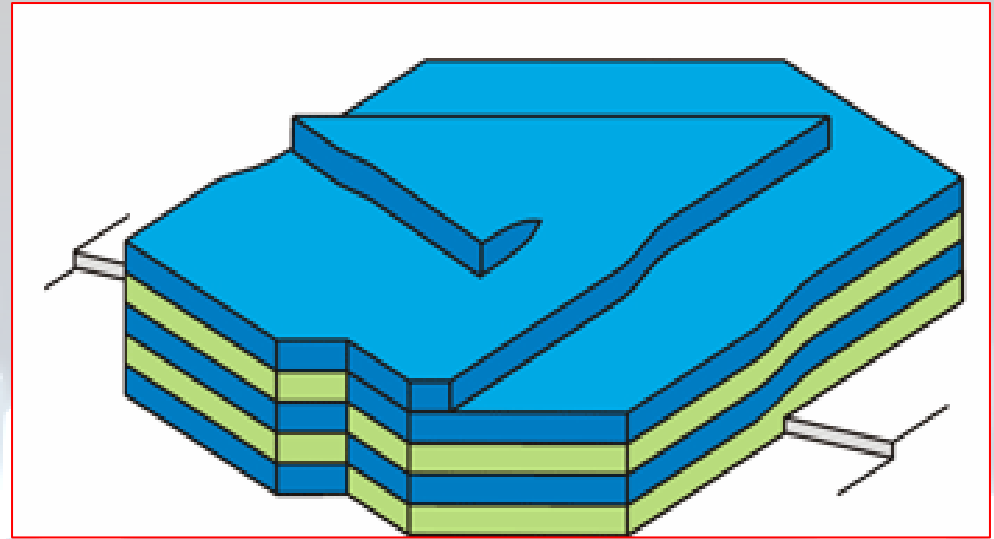
❖ The ice grown at 140 K ~ has 1 nm mean thickness and ~3 nm high crystallites embedded in a one bilayer high wetting layer

❖ The crystallites have flat top facets and exhibit straight edges along the directions of the substrate

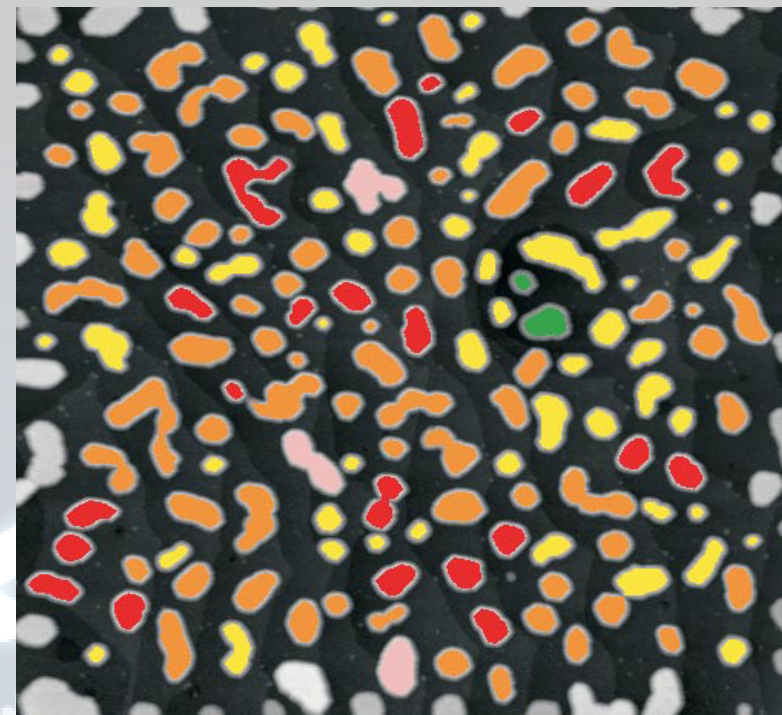
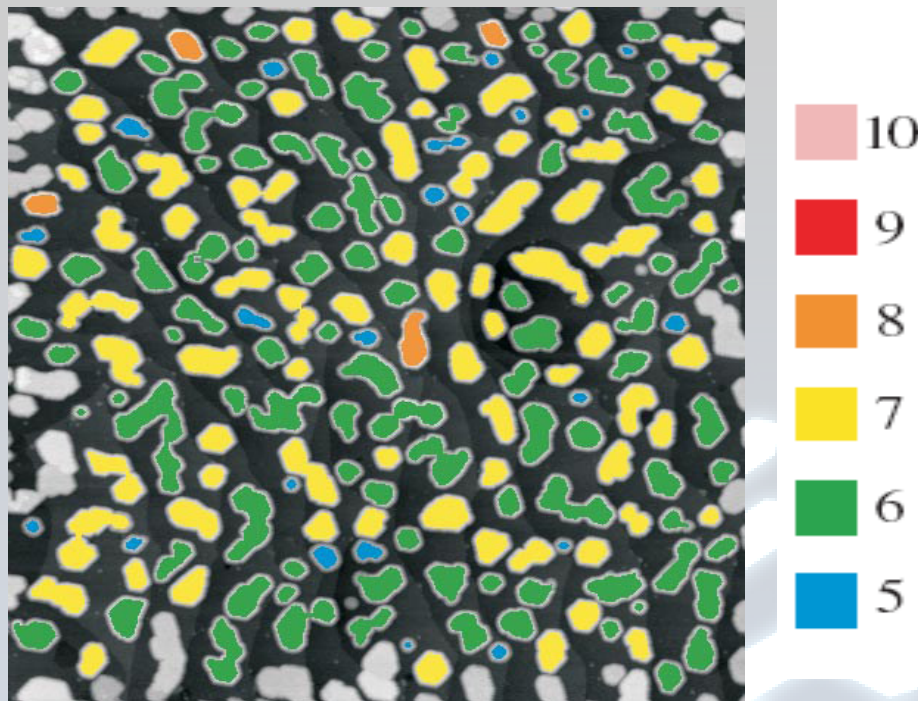
❖ The morphology of as grown films varies with thickness



Surface topography of a crystalline ice-multilayer



Schematic of a multilayer formation of ice films

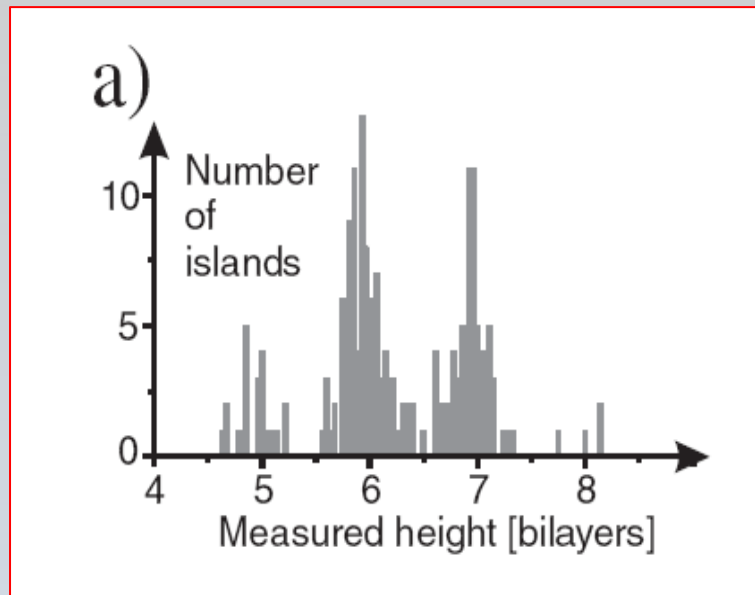


$1\mu\text{m}^2$ image of an ice film grown at 140 K with the height of each 3-D crystallite in units of bulk-ice bilayer heights colored differently

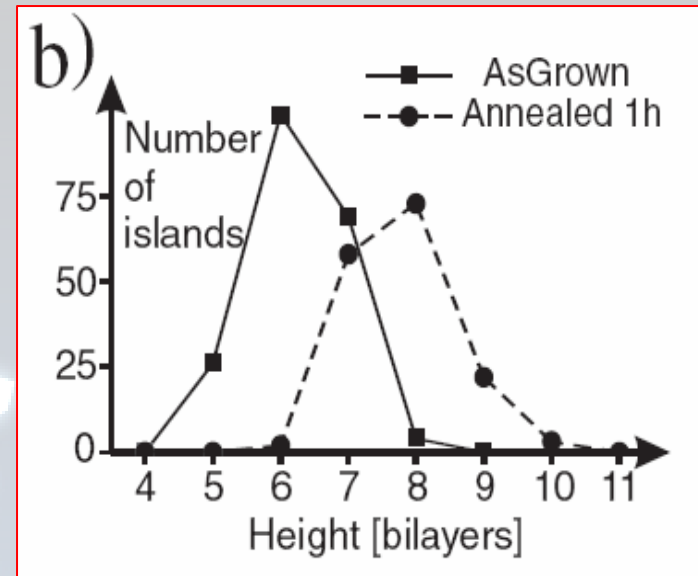
Image of the same surface region after annealing at 140 K for 1 h

- ❖ From the fig. it can be seen that the ice crystals grow thicker to expose more of the bilayer-covered Pt surface
- ❖ Fig. a) shows an image of the starting as-deposited film (1 nm mean thickness grown at 140 K)
- ❖ Heating at 140 K for 1 hr causes the crystals to grow higher as seen
- ❖ The disappearance of some very small islands may be due to sublimation

Analysis of the film evolution upon annealing

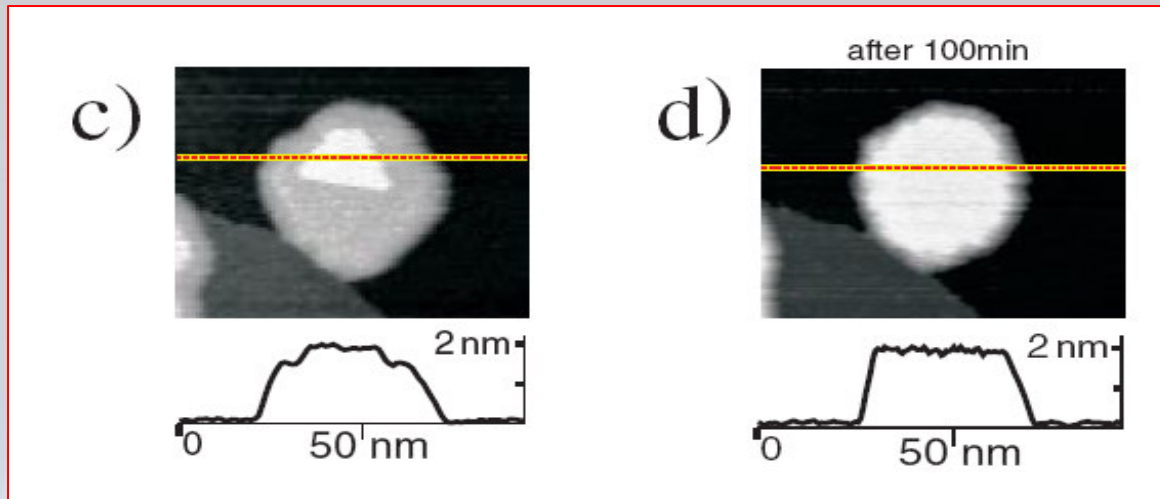


(a) Histogram of the average height of each crystallite above the wetting layer showing the discreteness in height



(b) Comparison between the height distributions of the images shown in previous figure

The formation of triangular nuclei



- ❖ When the sample voltages $|V_{\text{sample}}| < 5 \text{ V}$ several uppermost H_2O layers can be removed with the STM tip
- ❖ This creates very flat crystals for which the driving force of dewetting is extremely high
- ❖ After switching to imaging mode (increasing the sample bias to $|V_{\text{sample}}| > 5 \text{ V}$ formation of triangular nuclei was seen which readily expand until they cover the entire crystal even at 120 K

Data analysis

- ❖ The approach of Mullins and Rohrer to the dewetting case is used
- ❖ Consider the driving force (corresponding chemical potential relative to bulk ice)
- ❖ Assume the crystals are strain free and h is the height of the hexagonal prism and R is the prism length
- ❖ Assume the volume Ω per water molecule is approximately the same for the wetting layer and the crystal

$$\mu = \Omega(\gamma_b + \gamma_{\text{ice-Pt}} - \gamma_{\text{wetting}})/h + 2\Omega\gamma_p/(\sqrt{3}R). \quad (1)$$

γ_b

➤ Basal plane surface free energy per unit area

γ_p

➤ Surface free energy of the prism faces

$\gamma_{\text{ice-Pt}}$

➤ Free energy/area of the ice-Pt interface

γ_{wetting}

➤ Specific free energy of the Pt surface covered by the wetting layer

❖ The driving force μ for dewetting decreases as the crystals become higher because the change in the interfacial area per water molecule decreases as $1/h$

❖ Given the driving force the standard nucleation theory is used to calculate the rate J for nucleating triangular islands that is observed on the top of the hexagonal prisms

❖ The triangular island of side length r when subjected to μ (chemical potential) the free energy G is given by

$$G(r) = 3\beta r - \frac{\sqrt{3}}{4} \frac{h_0}{\Omega} \mu r^2$$

➤ h_0 is the height of the triangle

➤ β is the energy per length of the molecular step that bounds the nucleated layer

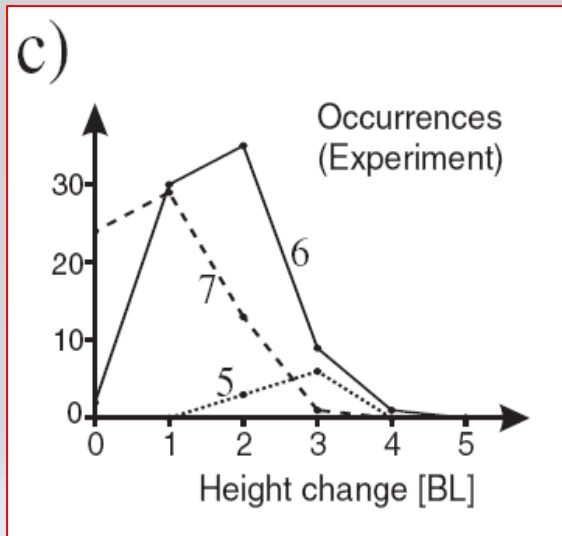
The maximum of $G(r)$ gives the critical size $r_c = 2\sqrt{3} \frac{\Omega\beta}{\mu h_0}$

This is based on the assumption that the nucleation rate is proportional to the thermal probability of creating a critical nucleus (i.e.) $J \propto \exp[-G(r_c)/kT]$

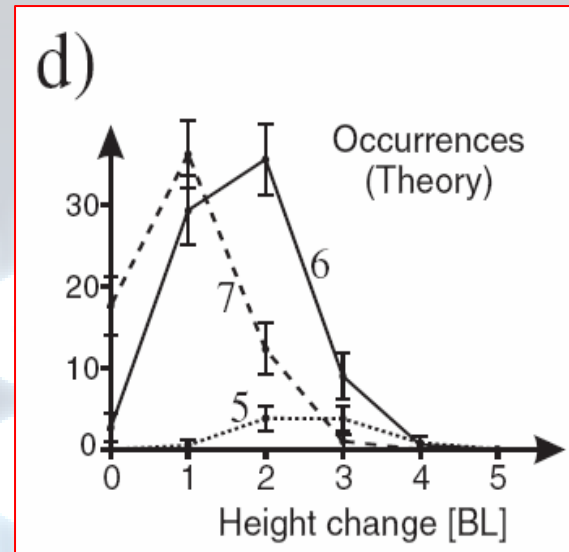
❖ The island nucleation rate J [$R \gg h$] decreases exponentially with h

$$J(h) \propto \exp\left[-\frac{1}{\gamma_b + \gamma_{\text{ice-Pt}} - \gamma_{\text{wetting}}} \frac{3\sqrt{3}\beta^2}{kT} \frac{h}{h_0} \right]. \quad (2)$$

Number of crystals of initial height h (labeled for each curve) that have changed in height by n layers



(c) Shows how often crystallites were observed to change their height by n layers during the 1 h anneal, for various starting heights



(d) Shows the numbers predicted from Eq. (2) Predicted for the crystal height changes between image a and b, along with the calculated statistical standard deviations

Now let us put $J=6$ and the right hand side of the equation 2 becomes

$$3\sqrt{3}\beta^2/[(\gamma_b + \gamma_{\text{ice-Pt}} - \gamma_{\text{wetting}})kT] \approx \ln(2.5) \approx 1 \text{ for ice at 140 K}$$

- ❖ The exponential decrease of the nucleation rate with height determines the film morphology
- ❖ For crystallites of fewer than 5 layers, nucleation is fast enough that they all grow higher than 4 layers already during the deposition
- ❖ The deposition flux will enhance the nucleation
- ❖ On the other hand, nucleation on top of crystallites more than 10 layers high becomes very slow as to be hard to observe
- ❖ These results also imply that dewetting is dominated by the rearrangement of material within crystals and not between them (i.e., not by Ostwald ripening)
- ❖ In the case of Ostwald ripening nucleation would have been proportional to the area of a crystal's top facet but independent of the crystal's height

- ❖ The energies extracted from the fitting of the nucleation data permit inferences concerning the energetics of ice steps and interfaces and their molecular structure
- ❖ They define two energies per area that measure the interactions with the substrate of 1) the wetting layer and 2) an ice crystal

$$\gamma_{\text{Pt-ice}} = \gamma_{\text{Pt}} + \gamma_b - \epsilon_{\text{Pt-ice}}$$

$$\gamma_{\text{wetting}} = \gamma_{\text{Pt}} + 2\gamma_b - \epsilon_{\text{wetting}}$$

➤ Energy decrease per unit area when the basal plane of a microscopic ice crystal is placed in contact with the substrate

$$\left(\frac{\epsilon_{\text{wetting}} - \epsilon_{\text{Pt-ice}}}{\gamma_b} \right) \left(\frac{a\gamma_b}{\beta} \right)^2 \approx \left(\frac{3\sqrt{3}a^2}{kT} \gamma_b \right), \quad (3)$$

Now put $a=0.45$ nm, the separation between equivalent O atoms at a molecular step, to make each factor in the equation dimensionless

γ_b is within a factor of 2 of 100 mJ/m²

From the bond counting arguments with a step edge energy

$$\beta = a\gamma_b/\sqrt{3}$$

Substituting β in equation 3 gives

$$\epsilon_{\text{ice-Pt}} - \epsilon_{\text{wetting}} \approx 7\gamma_b$$

- ❖ Such a large difference is not reasonable
- ❖ from the previous studies it has been proposed that in the wetting layer there are no broken hydrogen bonds pointing away from the substrate as it is seen at the surface of the truncated bulk ice

$$\epsilon_{\text{ice-Pt}} - \epsilon_{\text{wetting}} \text{ the order of } \gamma_b \text{—but not 7 times } \gamma_b$$

Thus the simple bond counting overestimates the step energies on ice by at least a factor of 3, suggesting significant relaxations or a reconstruction of the step edge

conclusion

- ❖ Ice crystals growing one molecular layer at a time can be imaged with STM
- ❖ The authors have observed and characterized the nucleation of molecular layers of ice on ice
- ❖ From the observed nucleation rates they have deduced that the step energies on ice are considerably smaller than predicted from bond counting arguments
- ❖ The difference between the bonding of the wetting layer and the bulk ice Pt interface is on the order of the ice-vacuum surface energy
- ❖ The driving force for dewetting of ice on Pt (111) is strong enough to cause nucleation of new layers, which slows down as the crystallites become higher
- ❖ Understanding dewetting-induced nucleation is crucial for predicting the stability of thin films and it has not been quantified before in any system

thanks

