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The fractal dimension of ice on the nanoscale

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ABSTRACT

Studies of supported water clusters provide a means for understanding the initial stages of heterogeneous ice nucleation in diverse areas as atmospheric chemistry and astrophysics. Despite the importance of non-perfect ice structures in these fields, research focused on crystalline ice structures. Here, we report real-space observations of fractal ice islands grown between 89 K and 119 K. The island shape changes linearly from the most fractal dimension of 5/3 to the fractal dimension close to the one of an equal-sided hexagon. The mere linear increase is assigned to a shape dependent sticking coefficient of mobile ice clusters to the fractal islands. Our study reveals the complexity involved in formation of fractal ice structures.

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1. Introduction

Our basic understanding of what makes an effective ice nucleating material to form clouds is limited. Many crystalline phases of ice are known [1]. There exist amorphous phases, metastable phases, and more than 10 stable crystalline phases. Under ambient conditions, under which snowflakes form, the equilibrium phase is a hexagonal crystalline ice phase called I_h . In this phase, each molecule has four hydrogen bonds to other water molecules leading to a regular tetrahedral arrangement. Mostly, stacking disordered ice I_{sd} , which consists of layers of metastable cubic ice I_c and hexagonal ice I_h forms in ice clouds [2]. In contrast, amorphous ice is a loose tetrahedral arrangement, which condenses at low temperature, e.g. on comets [1]. Kinetic limitations during ice formation in clouds lead to branched structures on μm dimensions, very far from a compact equilibrium structure. The exact form of snowflakes thereby reflects the history of water density and temperature during their growth. The phase and exact shape of the ice formed in clouds has an important impact on e.g. heterogeneous chemistry in the troposphere [3,4].

On the other hand, branched structures, named either fractal or dendritic, were observed in metal-on-metal growth on surfaces on the nanometer-scale. Such non-compact structures are likewise formed far from equilibrium, i.e. at high deposition rate or at low temperature [5–7]. Thereby, fractal islands are randomly branched aggregates with no preferred direction of their branches, while dendritic islands show preferred directions induced by the surface symmetry. Note that “fractal” is a terminology adapted from

mathematics for an object that can not be described by an integer, but only by a Hausdorff-Besicovitch dimension [8]. This dimension has been called fractal dimension for metal island growth on surfaces. It varies for a two-dimensional object between $D = 1$ (a line) and $D = 2$ (a filled circle) and is thus smaller than $D = 2$, the Euclidean dimension of a plane. In island growth the smallest possible value is $D = 5/3 = 1.67$ [9]. Fractal islands were observed for growth of Au on graphite [10], Au on Ru(0001) [11], Pt on Pt(111) [5], Ag on Pt(111) [12,6], and Ag on Ag(111) [13] and dendritic islands for Pt on Pt(111) [5], Ag on Ag(111) [13,14], and Ag on Pt(111) [7], but to our knowledge neither were reported for any molecular structure. Here, we grow and investigate fractal islands formed by water molecules.

2. Results

During growth of water on Ag(111) at 96 K, well-separated branched islands are formed with the branches in many different directions (Fig. 1a). The islands grow laterally with coverage (Fig. 1b) till they percolate (Fig. 1c). The arms have lengths up to $(17.2 \pm 0.2) \text{ nm}$ and varying widths between $(1.8 \pm 0.1) \text{ nm}$ and $(3.4 \pm 0.2) \text{ nm}$. Note that the STM tip broadens the branches by around 0.5–1 nm. This influences in particular very thin branches.

At higher coverages, just before coalescence, the fractal growth mechanism is perturbed by the neighboring islands. The radial growth of the fractal arms is slowed down and the islands get more asymmetric, seemingly growing into voids (Fig. 1c). This is a natural consequence of an asymmetry in existing sinks. In order to avoid artifacts in the analysis, we concentrate on lower coverages in the fractal analysis below.

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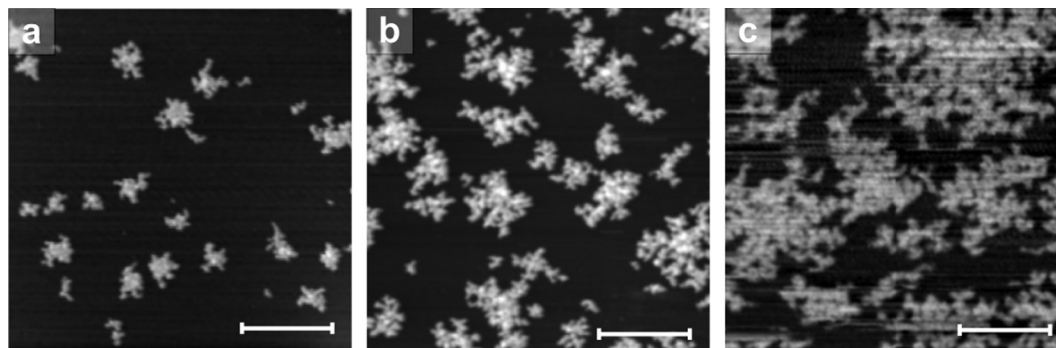


Fig. 1. Fractal growth: STM images after growth at (96 ± 3) K at coverages of (a) (0.15 ± 0.03) BL (500 mV, 29 pA, scale bar is 50 nm), (b) (0.47 ± 0.03) BL (500 mV, 20 pA, scale bar is 50 nm) and (c) (0.92 ± 0.03) BL (500 mV, 20 pA, scale bar is 25 nm).

Line-scans (Fig. 2a to c) suggest that the growth is three-dimensional but leads to a pronounced layering despite the lateral disorder. In order to determine the number of water layers of the islands, we analyze height histograms following a procedure established before [15]. Indeed, discrete maxima are found at all coverages as marked by the arrows in Fig. 2d. The smallest apparent height is (0.16 ± 0.03) nm. Further maxima are at (0.25 ± 0.03) nm, (0.33 ± 0.03) nm, and (0.41 ± 0.03) nm. Thus the islands are up to four layers high.

Such measured heights are called apparent heights, because STM underestimates real heights for insulating structures. The distinct apparent heights are attributed to tabulated geometric heights in Table 1. Further layers contribute to the apparent height by 0.08–0.09 nm, only at half the apparent height of the first layer with 0.16 nm, though the geometric heights of further layers are 20% larger than the one of the first layer. Also on Cu(111) the apparent height difference between layers of water is almost constant apart from the first layer [15]. On Cu(111), the first layer has a comparable apparent height of 0.15 nm, but the apparent height of subsequent layers are, at 0.05 nm, considerably smaller than observed here. On both surfaces, the apparent height underestimates the real heights of 0.31 nm and 0.37 nm considerably. The largest geometric height of the fractal islands investigated here is 1.42 nm and is thus underestimated by a factor of 3.5.

Having derived the height of the structures, we now characterize their lateral geometry. Island size distributions reflect the growth mechanism of islands. The island size distribution shown in Fig. 3a is reminiscent of the distributions found after simulation of growth including the mobility of small clusters [16]. Most fractal islands, around 70%, have an area of less than 200 nm^2 , though occasionally islands with areas up to 1000 nm^2 are observed at a coverage of around half a bilayer. The mean of $(229 \pm 291) \text{ nm}^2$ deviates considerably from the median, at 119 nm^2 . Both

observations are consistent with growth including the mobility of small islands [16].

Both, the arm widths and the island size distributions suggest that the fractal islands are not formed exclusively by a hit-and-stick attachment of water monomers, but by attachment of mobile clusters. To prove this point, we performed diffusivity studies, similar to the ones presented in [18,17,19]. Such studies are experimentally demanding because deposition of water on Ag(111) at the lowest possible temperature of 15 K leads already to clustering of monomers. Thus, clear conclusions could not be drawn. The reason is an exceptionally low diffusion energy of water on Ag(111) [20]. We thus investigated cluster diffusion on two related surfaces, Ag(100) and Cu(111). On these surfaces, water monomers are immobile at the deposition temperature and we are thus able to unequivocally identify the size of small clusters by following their formation from monomers. Based on these studies, we confirm our earlier attribution of disk shaped protrusions as hexamers [21]. These and slightly larger clusters are mobile on Cu(111) at 60 K and on Ag(100) at 35 K on the time scale of the measurement, which is the same time scale as the one during deposition. Both temperatures are far below the deposition temperature during fractal growth. As on Ag(111) these temperatures are expected to be even lower [20], it is confirmed that the fractal islands are formed from mobile clusters. The width of the branches, which is slightly broader than the width of hexamers [21], suggests that the mobile particles are also slightly larger than hexamers.

In order to determine, whether the structures are fractal or dendritic, we now analyze the orientation of the arms. For this aim, we determine the angle of individual arms within the islands with respect to the closed-packed surface directions, known from images with atomic resolution. The histogram of the measured angles do not reveal any preferred direction (Fig. 3b). The islands are thus classified as fractal.

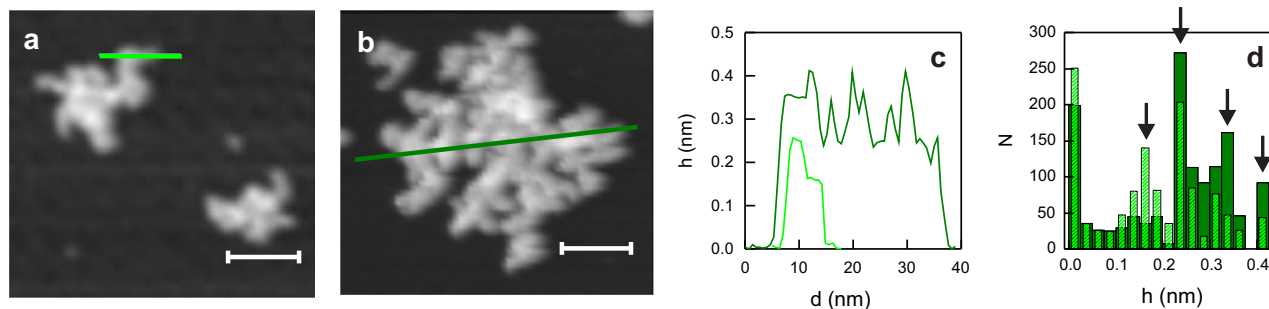


Fig. 2. Height analysis: (a,b) STM images, scale bars are 10 nm: (a) (0.15 ± 0.01) BL, 500 mV, 29 pA, (b) (0.47 ± 0.04) BL, 500 mV, 20 pA, (c) height profiles along lines as shown in STM images in same shade of green and (d) pixel histograms of heights as determined from STM images at the two different coverages in different shades of green; arrows point to maxima in histogram.

Table 1

Comparison of measured apparent heights to literature values of geometric heights from [1] and deduced number of bilayers (BL).

Apparent height (nm) ± 0.03	Geometric height (nm)	Apparent height per layer (nm)	Geometric height per layer (nm)	BL
0.16	0.31	0.16	0.31	1
0.25	0.68	0.09	0.37	2
0.33	1.05	0.08	0.37	3
0.41	1.42	0.08	0.37	4

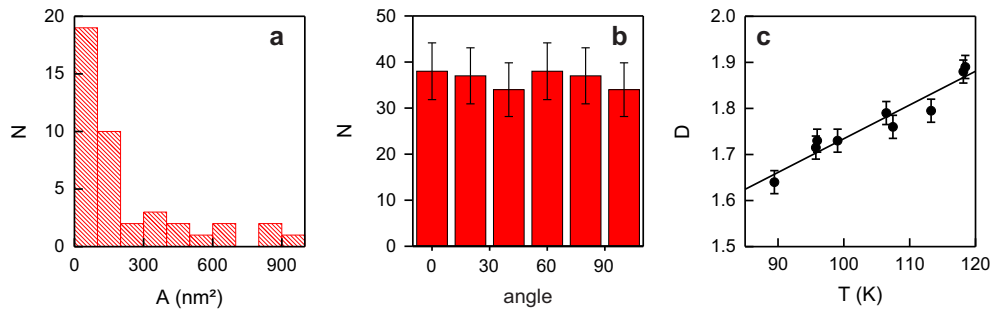


Fig. 3. Geometric characterization of fractal ice structures for a coverage of (0.47 ± 0.04) BL: (a) area histogram, (b) histogram of relative angles of island arms with statistical error bars; and (c) Fractal dimension D in dependence of growth temperature T at a deposition rate of $2.7 \cdot 10^{-4}$ BL/s at a resolution of 256 pixel by 256 pixel for an image size of 169 by 169 nm²; linear fit yields $D = (7.3 \pm 0.4) \cdot 10^{-3} 1/K \cdot T + (1.00 \pm 0.08)$.

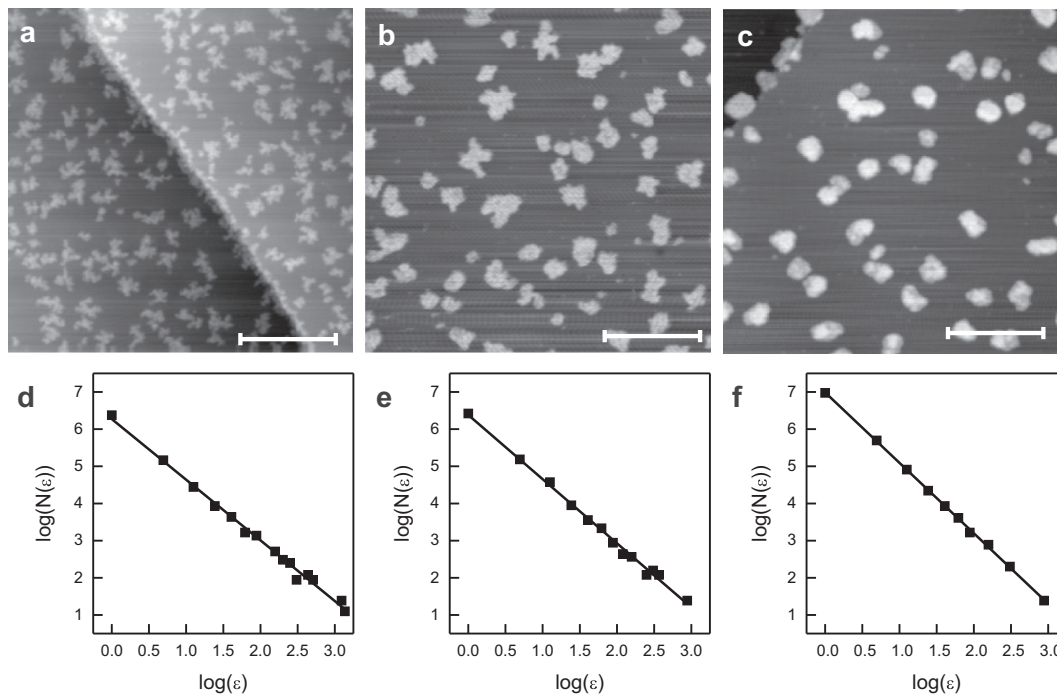


Fig. 4. Temperature dependence of fractal islands, scale bars are 50 nm: (a) 89 K, coverage: (0.39 ± 0.03) BL, 15 pA, 500 mV, (b) 98 K, coverage: (0.77 ± 0.06) BL, 37 pA, 200 mV, (c) 119 K, coverage: (0.84 ± 0.06) BL, 14 pA, 500 mV, (d) to (f) $\log(N(\epsilon))$ vs. $\log(\epsilon)$ for one island each in (a) to (c); the slopes of the fits are (d) $D = 1.63 \pm 0.03$, (e) $D = 1.72 \pm 0.03$ and (f) $D = 1.89 \pm 0.02$.

As fractal islands are kinetically limited structures, we expect their shape to depend on temperature. Indeed, the islands are more compact at higher than at lower growth temperature (Fig. 4a to c). To quantify this change in shape, the fractal dimension is determined by the box counting method (see Methods). Remember that the fractal dimension is the smaller, the more branches an island has and the larger, the more compact it is.

The fractal dimension of the islands grown at 90 K is 1.63 ± 0.03 (Fig. 4a,d). Islands grown at 98 K exhibit thicker and less branched arms (Fig. 4b) as expressed in a larger fractal dimension of

1.72 ± 0.03 (Fig. 4e). At a growth temperature of 119 K, the islands are compact without any arms (Fig. 4c) and their fractal dimension is 1.89 ± 0.03 (Fig. 4f).

In the same manner, we determined the fractal dimension for a multitude of islands grown at the same deposition rate in the temperature range of 89 K to 119 K. The average values of the fractal dimension increases linearly from approx. 1.63 at 89 K to 1.89 at 119 K with a slope of $(7.3 \pm 0.4) \cdot 10^{-3} 1/K$ (Fig. 3c). Thus, 30 Kelvin temperature difference covers the complete range of possible fractal dimensions. On the higher temperature end, the largest value is

slightly larger than the fractal dimension of 1.82 for a perfectly hexagonal island as expected to form from ice I_h . On the lower temperature end, the value is similar to the most fractal dimensions for islands growing on surfaces, at $D = 5/3 = 1.67$ [9]. The latter value was determined in Diffusion Limited Aggregation (DLA), a computer simulation framework, in which particles undergo a random walk and stick to a growing aggregate, wherever they encounter it, i.e. the sticking coefficient s of a particle to the islands is one and the diffusivity along the island border is completely suppressed. In experiment, the diffusivity is suppressed, if the energy barrier for diffusion along the island border is so high that the probability of attachment of the next particle is considerably larger than the probability for a diffusive step along the island border. This is thus the case at 89 K. With increasing temperature, the particle diffusion rate along the border of existing islands increases with respect to the arrival rate of the particles, which is fixed by the deposition rate. This leads to the observed increase in fractal dimension. At the highest observed temperature, most of the island exhibit straight edges, many with angles of 120° between them. Though these structures are not equal-sided hexagons, their fractal dimension is very close to the fractal dimension of an equal sided hexagon, which in turn would represent a piece of hexagonal ice with a short edge.

However, the mere linear temperature dependence is surprising in view of earlier results for metal-on-metal growth. For instance, the branch width was found to depend exponentially on inverse temperature for Ag/Pt(111) and Ag/Ag(111), i.e. it follows an Arrhenius behavior [13], a result also found in DLA with peripheral diffusion [22]. However, an Arrhenius plot of our data yields an unreasonably low activation energy of 3.9 meV.

A possible artifact in the temperature dependence could result from the fact that not only the shape, but also the size of the islands changes with temperature (Fig. 4a to c). Such an influence of the island size on the fractal dimension is ruled out as reason for the change in fractal dimensions in view of corresponding DLA simulations [9,23].

The same type of simulations revealed that the fractal dimension depends exponentially on sticking coefficient of the particles to the islands down to $s = 0.05$ [10]. The linear dependence could thus be understood, if the sticking coefficient, in our case of the mobile clusters, to the fractal island decreased with temperature, thereby counteracting the temperature effect. We thus discuss possible origins of a temperature dependent sticking coefficient. In atom growth, the interaction between an additional atom and an existing island is angle independent without an attachment barrier resulting in a sticking coefficient of $s = 1$. However, highly directional hydrogen bonds have to be formed in ice growth. The orientation of a water monomer on the surface with its hydrogen atoms pointing in parallel to the surface [21] is not always favorable for forming a hydrogen bond to the water island. Thus, the water molecule has to reorient for bond formation. The energy difference between different orientations is considerable, already 20 meV between a planar geometry and one with an angle of 20° between the molecular and the surface plane [24]. The reorientation thus leads to a barrier for attachment, which in turn reduces the sticking coefficient. This effect is enhanced by electrostatic repulsion, which the molecules might have to overcome before bond formation. Moreover, the attachment barrier is expected to be site selective depending on the exact orientation of the water molecules at the island's border, which determines, how much a molecule has to reorient and how large the electrostatic repulsion is. The sticking coefficient will thus be shape dependent. This implies that the observed change in shape with temperature enforces the change in sticking coefficient.

In conclusion, fractal ice islands of a fractal dimension between ≈ 1.6 , corresponding to a most fractal island, and ≈ 1.9 , correspond-

ing to a hexagon, are observed during growth of water on Ag(111) in the temperature range between 89 K and 119 K. The linear dependence of the fractal dimension with temperature suggests a temperature dependent sticking coefficient of the water clusters to the islands counteracting the exponential increase in mobility along the island border. The behavior of the molecules during island formation is thus much more involved than of atoms in metal-on-metal growth. On a more general footing, we are able to trace back the formation of specific shapes of ice islands to the temperature history as proposed for growth of fractal islands on micrometer dimensions.

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3. Methods

STM measurements are performed with a low-temperature STM under ultra-high vacuum (UHV) conditions (base pressure below $2 \cdot 10^{-10}$ mbar). The Ag(111) surface is cleaned by sputter-anneal cycles. Ne^+ -ions at a pressure of $3 \cdot 10^{-5}$ are accelerated to 1.3 keV. The ion current of 2 μA is maintained for 45–60 min in a first, and for 20–30 min in a second cleaning cycle. The sample is annealed for 30 min at 900 K in both cycles and slowly cooled back to room temperature. After this procedure, terraces are up to several 100 nm wide, some of them separated by step bundles.

D_2O of milli-Q quality and with an isotopic purity is 99.96% is purchased from Sigma-Aldrich. The fluid is filled into a glass tube that is connected to the UHV chamber via a leak valve. The water is purified by freeze-thaw cycles. Its purity is checked by means of in-situ mass spectrometry of the vapor above the fluid.

A pressure of $5 \cdot 10^{-7}$ mbar or $1 \cdot 10^{-6}$ mbar is then established in a small UHV chamber via the leak valve. This chamber is connected via a gate-through valve to the preparation chamber. Prior to opening that valve, the Ag(111) sample is turned such that its backside faces the valve. It is held above the desorption temperature of water, while the valve is opened for 2 min. By this procedure, some of the H_2O at the chamber walls is replaced by D_2O and the total amount of regular water in the rest gas is reduced.

Subsequently, the sample is cooled to the deposition temperature between (89 ± 3) and (119 ± 3) K and turned towards the tube that guides the water into the preparation chamber. After deposition the sample is cooled to the lowest possible temperature and transferred into the STM, where measurements are performed at 5 K.

The box counting method [8,25] is used to determine the fractal dimension of the islands. The same methods was used before for fractal and dendritic Ag islands [6]. In this method, a grid of varying grid size ϵ is superimposed over the object of interest and the number $N(\epsilon)$ of boxes filled by this object is counted. The fractal dimension D is calculated via

$$D = \lim_{\epsilon \rightarrow 0} \frac{\log N(\epsilon)}{\log 1/\epsilon} \quad (1)$$

A graph of $\log N(\epsilon)$ with respect to $\log 1/\epsilon$ yields a straight line with slope D . The whole procedure is automated in a Labview program.

Note that the absolute value of the fractal dimension depends somewhat on the resolution of the STM images due to their pixel nature. We thus use images of the same resolution in the analysis.

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