



Structure Matters – Direct In-situ Observation of Cluster Nucleation at Atomic Scale in a Liquid Phase

Trond R. Henninen,* Debora Keller, and Rolf Erni*[a]

Abstract: The formation of almost all solid crystalline materials starts with a nucleation reaction, where a handful of atoms come together to form the initial crystal seed, which then grows to a larger crystal. Thus, understanding and controlling nucleation is essential for the synthesis and manufacturing of most material systems, especially nanomaterials. Despite this, little is known from direct experimental observations about the initial steps of nucleation, the formation of sub-nanometer sized clusters. Here, we directly study the atomic nucleation reactions of such sub-nm clusters of Pt in-situ in a liquid phase. We do this by inducing nucleation in suspended nanofilms and supported nanodroplets of an ionic liquid (1-butyl-3-methyl imidazolium chloride, 5–50 nm thickness), which is observed at atomic resolution by scanning transmission electron microscopy. We can observe Pt atoms to nucleate into few-atom clusters, which coalesce and grow into cluster agglomerates or nanoparticles, or redissolve. When comparing nucleation in nanofilms and carbon-supported nanodroplets, nucleation is rarely observed in nanofilms, while easily observable at high nucleation rate in nanodroplets. This is due to the presence of the pre-existing liquid-solid interface, resulting in heterogeneous nucleation in the nanodroplets while there is only homogeneous nucleation in the nanofilms. Ultimately, our results show that the nucleation pathways of nanoparticles are not just determined by the local chemical environment, but are also influenced by size and structure of the initially formed clusters.

Nucleation reactions play a fundamental role in a vast variety of natural processes, such as the formation of snow and ice,^[1] and nautilus shells.^[2] Furthermore, engineering nucleation is essential for a vast amount of industrial processes, for example drug manufacturing^[3] and metallurgy. When metals solidify from a melt and form a grained microstructure, the grain formation starts with a liquid-to-solid nucleation reaction, and thus the

density of nuclei determines the size of the grains after solidification.^[4] Furthermore, solid-state nucleation determines the formation of precipitate particles that are essential in engineering the mechanical properties of alloys.^[5,6] In particular, for the synthesis of nanoparticles, nucleation is instead initiated by precursor molecules reacting in a liquid solvent (e.g. water or ethanol). Such synthesis is currently not based on a bottom-up understanding of nucleation and growth, but is instead based on intuition and trial-and-error. The reason for this is that theoretical models, such as the Classical Nucleation Theory (CNT), can only qualitatively model nucleation-type phase transitions, but fail at modelling observable quantities such as nucleation rates.^[4,7–9] Therefore, the knowledge obtained from direct experimental observation of atomic-scale nucleation reactions would enable the development of more robust fundamental modelling of nucleation theory, improved possibilities for a better-controlled synthesis of existing nanomaterials, and new possibilities for the rational bottom-up design of novel nanomaterials.

In CNT it is assumed that approximately spherical metastable nuclei continuously form and dissolve (Figure 1c). While the surface free energy (ΔG_{surf}) increases with size (R^2), the volume free energy (ΔG_{vol}) reduces with size (R^3). This results in an energy barrier (ΔG_{crit}) that has to be overcome to form a stable nanoparticle, whereas clusters smaller than the critical size (R_{crit}) are expected to be unstable and thus dissolve. Notably, CNT predicts that there is a lower energy barrier for heterogeneous nucleation (ΔG_{het}) on a pre-existing liquid-solid interface, than for homogeneous nucleation without an interface (ΔG_{homo}).^[10] For many materials, such as Pt or Au, the size of the smallest stable nanoparticles is about 1–1.5 nm (or ca 50–100 atoms), but even smaller particles can be stabilized at higher temperatures or by adding molecules interacting with the surface of the clusters.^[11–13] More recent nucleation modelling considers the dynamics of discrete atoms in cluster formation, by using Molecular Dynamics and Density Functional Theory calculations.^[8,14] Such simulations can generate a large variety of hypothetical clusters and suggest many conflicting growth pathways.^[15–19] However, there is little experimental data that tests these predicted clusters or growth pathways. Some experimental data comes from indirect observations in cluster beam experiments (in vacuum),^[20–23] or ligand-stabilized chemically synthesized clusters.^[24–27] Though, these approaches can only provide limited information about the structure and properties of certain clusters, and cannot directly observe the nucleation process in-situ.

In more recent years, advances in aberration-corrected scanning transmission electron microscopy (STEM) have enabled the atomically resolved study of sub-nm sized atomic

[a] T. R. Henninen, Dr. D. Keller, Dr. R. Erni
Electron Microscopy Center, Empa, Swiss Federal Laboratories for Materials
Science and Technology
8600 Dübendorf (Switzerland)
E-mail: trond.henninen@empa.ch
rolf.erni@empa.ch

Supporting information for this article is available on the WWW under
<https://doi.org/10.1002/cnma.202000503>

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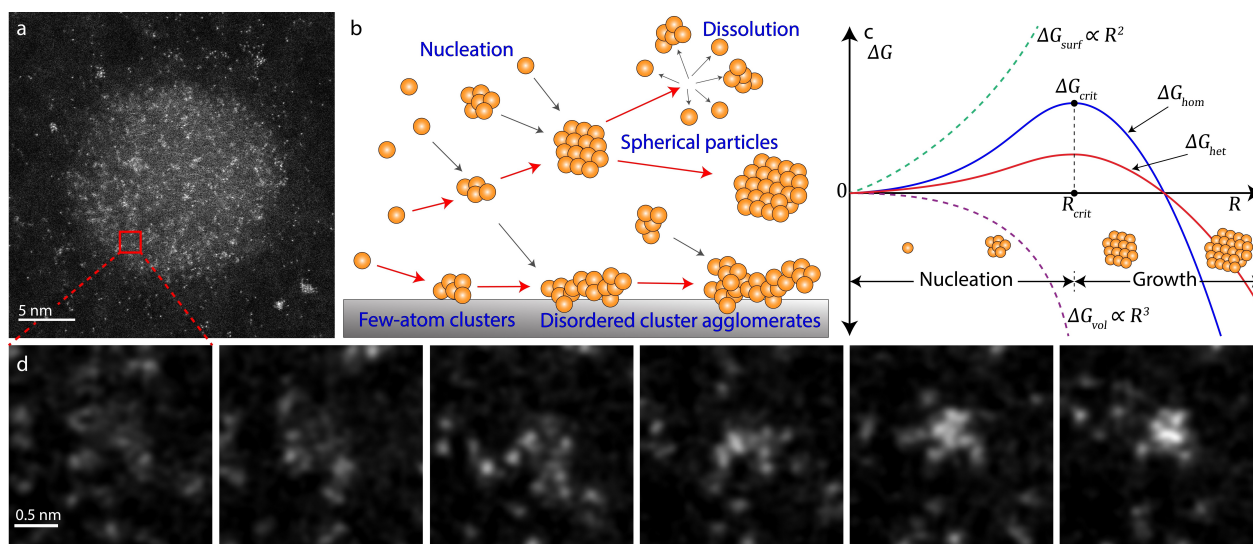


Figure 1. a: An example of a ca 20 nm sized nanodroplet of ionic liquid, enriched with Pt, wetting a carbon surface. b: Summary of the initial nucleation reactions observed in this work. 1st a few atoms nucleate to form a few-atom cluster. 2nd one or more few-atom clusters coalesce and/or grow into mainly disordered cluster agglomerates on the liquid-carbon interface or occasionally spherical nanoparticles on the interface or in liquid (both upwards of ca 1 nm in size). 3rd many of the nanoparticles (and the unstable few-atom clusters) are observed to redissolve into the liquid, but this is not observed to happen to the more stable cluster agglomerates. c: Free energy (ΔG) diagram of a nucleating cluster according to CNT. d: Step-by-step experimental observation of a ca 8–9 atom Pt cluster nucleating from individual atoms dispersed in the nanodroplet.

clusters, including counting atoms, interpreting 3D structures and the atomic dynamics of the clusters.^[12,25,28–30] These kinds of studies have proven to be more challenging to do in-situ in a liquid environment. Modern liquid cell holders, where the liquid is separated from the vacuum by electron transparent membranes (tens of nm thick), have enabled the study of growth mechanisms of few-nm sized particles.^[31–33] However, these previous studies only show growth processes once the initial particles have formed, and have been unable to directly trigger and observe the atomic mechanisms of *how* the initial sub-nm sized cluster forms, which then grows into a nanoparticle. The limit here has been that very thin samples (liquid + film < 50 nm) are required for obtaining reliable atomic resolution images, for which liquid cell holders are unsuitable due to the bulging of the membranes in vacuum and the thickness of these membranes. To surpass this, and achieve atomic resolution in liquid, there are currently two approaches, either wrapping the liquid in graphene,^[34–36] or using vacuum compatible ionic liquids.^[37–39] In our work, we have focused on the latter approach of using ionic liquids as a liquid phase to directly observe the initial step of nucleation, the formation of sub-nm sized clusters, in-situ at the atomic scale. We can form two different nucleation systems from the ionic liquids, thin enough to see nucleation at the atomic scale. In the first system, i.e. nanofilms suspended in the holes in the amorphous carbon (C)-film (Figure S1e), there is no liquid-solid interface, so any observed nucleation is a homogeneous nucleation reaction. In the second system, i.e. nanodroplets on the C-film support (Figure 1a), the presence of a pre-existing liquid-solid interface makes the vast majority of nucleation events happen as heterogeneous nucleation on the liquid-solid interface.

Homogeneous nucleation in suspended liquid thin films:

Suspended films of ionic liquids are formed across pre-existing holes in the amorphous carbon membrane (ca 15–20 nm) on Protochips Fusion heating chips, whose temperature can be controlled by resistive heating in the microscope. Within a hole in the C-film, there is typically a consistent liquid thickness, varying within a factor of two, yet in the thinnest films of tens of nm, there are often variations in the local concentration of Pt by multiple orders of magnitude. We have observed nucleation only in a few areas 10–100 nm in size with a locally high concentration of monoatomic Pt, yet with few pre-existing nanoparticles. Such areas were identified at low magnification by a brighter contrast compared to their surroundings. Two instances of nucleation are shown in Movie S1, and frames from this movie are shown and explained in Figure 2. So far, only 4 such nucleation events have been observed, all recorded as the ionic liquid was heated to 120 °C, above its melting temperature of 80 °C, causing an observable increase in the mobility of the Pt species. Considering that the Pt was dispersed as neutral atoms, and not as a reactive precursor, the nucleation was made possible largely due to heating-induced high mobility and the locally high concentration of atoms. The actual nucleation reaction is then triggered by the locally reactive environment caused by the electron-beam irradiation.

Heterogeneous nucleation reactions in nanodroplets:

Nanodroplets on the amorphous carbon film with typical diameters below 100 nm can often be seen forming along the edge of larger microdroplets after a short bake-out of the membranes that is needed to remove residual hydrocarbon contaminants. These nanodroplets form due to the phenomenon known as the Coffee-ring effect.^[40] As the heating causes a significant amount of ionic liquid to evaporate from the edge of

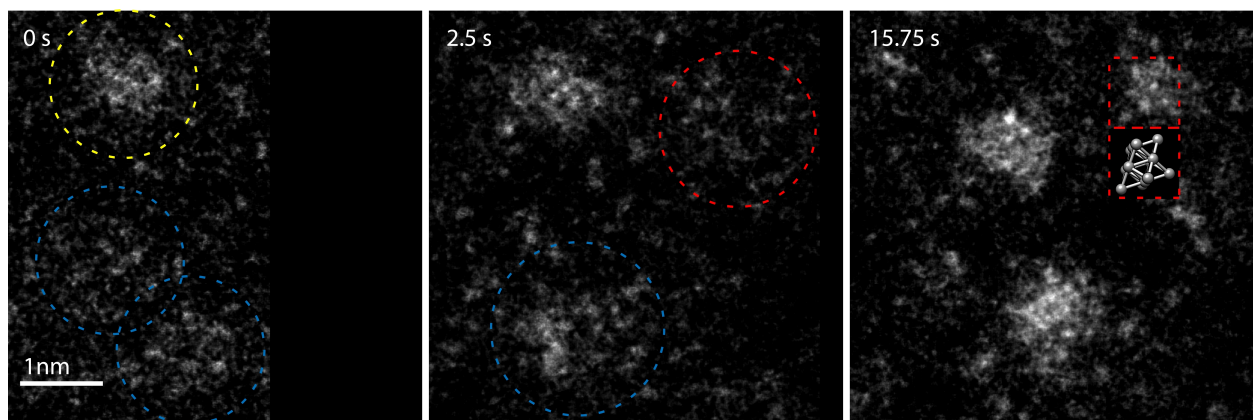


Figure 2. Images from Movie S1 showing two Pt clusters nucleating in a suspended ionic liquid film at 120 °C. The black bar on the right in the first image is because the whole area was not initially within the field of view. **0 s** – Initially, in the top there is a pre-existing cluster of ca 30 atoms marked yellow (Y). At the bottom there are two volumes marked in blue (B), with a high local concentration of dispersed Pt atoms, both estimated to hold at least 20 atoms. **2.5 s** – In B, atoms from both volumes have formed a nucleus at an estimated size of 10–15 atoms. Another high-density volume of ca 20 atoms is marked red (R). **15.75 s** – B has now grown to ca 30–40 atoms in size. Meanwhile, R stabilizes at an estimated size of ca 10–15 atoms, briefly showing a close-packed structure, and starts growing into a larger cluster. In the insert, for comparison, is the model of a 13-atom fcc cuboid.

the larger nanodroplets, this leads to a flow of liquid to the edge, and an accumulation of metal species (see Figures S1 f–g). Due to being enriched by the flow of liquid towards the edge, these newly formed nanodroplets typically have a very high concentration of mono- and few-atomic Pt species, yet have very few to none of the larger nanoparticles. The highest concentrations of monoatomic Pt we have found so far, have only been seen in such droplets enriched by the Coffee-ring effect. These nanodroplets are thus highly suitable as nano-reactors for inducing nucleation in a controlled manner.

In the current data of movies of nanodroplets ranging ca 20–100 nm in diameter, we can start to understand some aspects of the nucleation process from direct observations. Recording at an acquisition speed of 1 frame per second, we observe that the vast majority of the nucleation reactions appears to happen as the Pt atoms become adsorbed onto the amorphous carbon/ionic liquid interface (determined by the reduced mobility of Pt), as is expected from CNT. During nucleation, the metal atoms stick to the interface, and thus move with a low enough mobility that many individual atoms can be tracked. The heterogeneous nucleation reaction we observe appears as a highly dynamic state, particularly reflected in the smallest few-atom clusters which appear chaotic and disordered with a lack of consistent and interpretable structures. An example of a typical such dynamic nucleation is given in Figure 3a (Movie S2), showing a few-atom cluster nucleating near the edge of a small nanodroplet. Despite this disorder, certain trends are apparent. There is no clear and sharp nucleation threshold at a specific number of atoms, as clusters can be found of all sizes down to two atoms. However, evidence of a nucleation barrier indeed manifests as these smallest few-atom clusters are more unstable and likelier than the larger clusters to dissolve back into the liquid.

After the few-atom clusters have nucleated, as the clusters grow and coalesce, there are two types of species forming from

ca 1 nm in size and upwards. Firstly, disordered cluster agglomerates, and secondly, spherical nanoparticles, where the agglomerates have formed vastly more often than the particles. An example of the formation of such a cluster agglomerate is shown in Figure 3b. These agglomerates appear similar to the recently reported “cluster clouds”,^[33] and form due to the very high nucleation rate of few-atom clusters in our experiments, where multiple clusters often nucleate less than 1 nm apart, coalescing shortly thereafter. Though, we cannot conclude whether this is in fact the same phenomenon, as it is difficult to compare given the limited resolution and lack of quantitative contrast in this previously reported case.^[33] Other clusters are still mobile enough that they coalesce into the agglomerates from a distance of several nm. We believe the high nucleation rate in our experiments are largely a result of three factors: 1) the typically very high concentration of Pt in these nanodroplets, 2) the reactive environment caused by the electron irradiation, and 3) a further increase in concentration due to e-beam charging repelling a significant amount of liquid from the droplet during a nucleation experiment. For further clarification of the e-beam effect on the liquid, see Figure S3. The disordered structure of these agglomerates is likely due to a strong interaction with the C-surface of the liquid-solid interface, as sub-nm clusters on a C-surface (without liquid) near room temperature tend to be disordered and largely 2-dimensional, like a liquid wetting the surface.^[12,28,30] Furthermore, the e-beam is also known to suppress crystallinity of small clusters.^[12] Even when observed over a long period of up to 15 min, these agglomerates densify very slowly, and show a low degree of crystallinity.

Occasionally, the few-atom clusters can be seen to grow or coalesce into spherical nanoparticles upwards of 1 nm in size. These are distinguished from agglomerates as the more spherical 3D shape of the particles gives a much brighter signal for the same size as the more 2D-like agglomerates. Compared

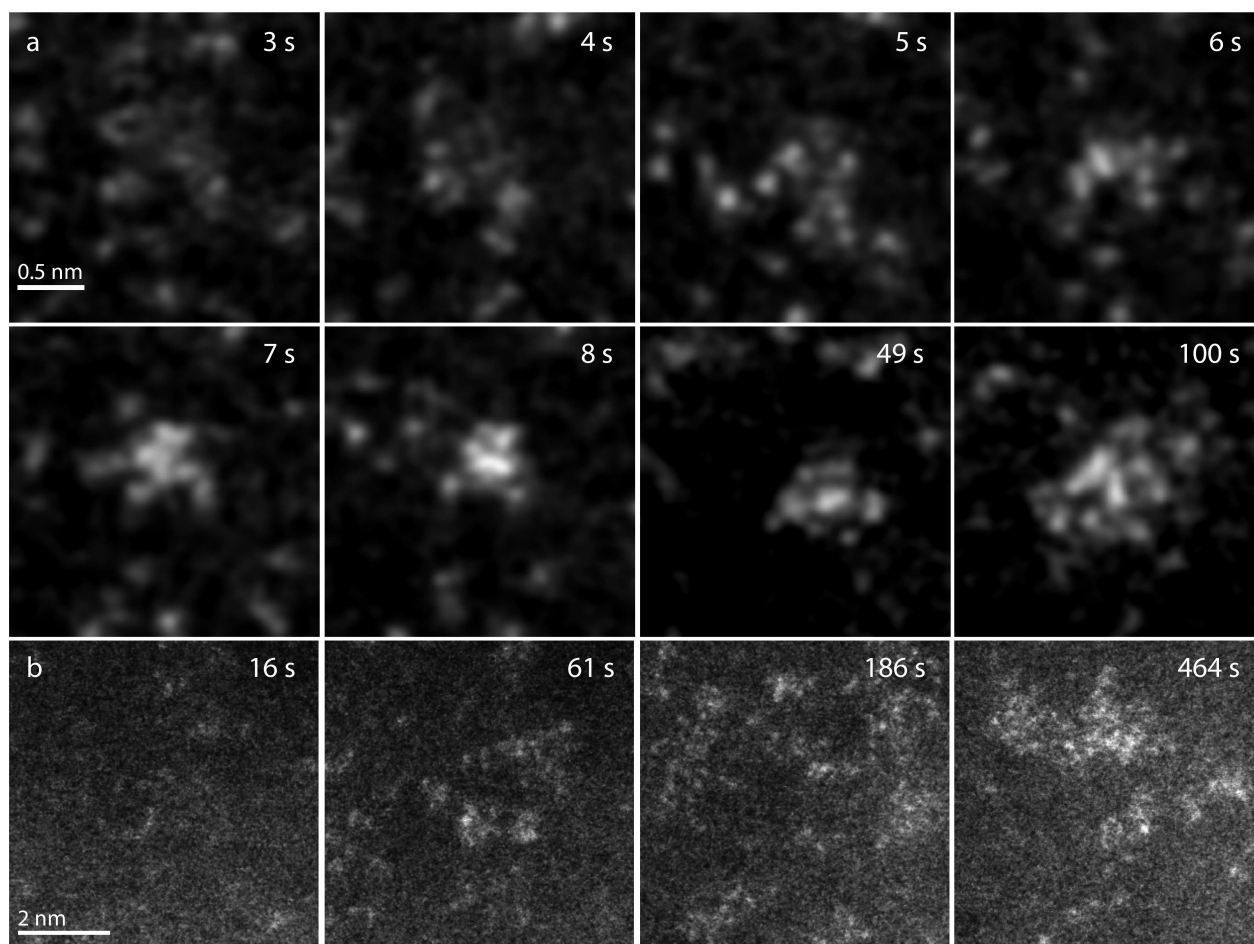


Figure 3. Experimental STEM images showing nucleation reactions in nanodroplets. **a:** An example of a few-atom cluster nucleating from Pt atoms dispersed in a thin layer of liquid close to the edge of a nanodroplet (Movie S2). From 3 to 6 s – The atoms are gradually forming a loosely connected cluster of 8–9 atoms. 7 to 8 s – The cluster densifies into a higher connected, more close-packed cluster. After nucleating many atoms attach onto or detach from this cluster, which gradually grows in size towards the end of the movie. In this period, the cluster briefly shows multiple unstable structures, for example at 49 s – a 12–13 atom icosahedral cluster, and at 100 s – a 16–18 atom cluster with a close-packed core (likely hcp or fcc cuboctahedral). For more details of these two structures, see Figure 5. **b:** Typical formation of disordered agglomerates from multiple few-atomic clusters (Movie S3). 16 s – First a few atoms attach onto the liquid-solid interface. 61 s – The high nucleation rate causes a high density of few-atomic clusters to nucleate. 186 s – Many clusters connect together forming a disordered agglomerate. 464 s – The agglomerate slowly grows and densifies.

to the agglomerates, the spherical particles form only rarely, and appear unstable, with a vast majority dissolving shortly after forming. This leads to the above mentioned, highly dynamic nucleation environment where metastable particles are continuously forming and dissolving. Examples of such are shown in Figure 4 (from Movie S4). Where the agglomerates appear to interact strongly with the interface, the spherical particles interact less with the interface, and can be seen to more dynamically move along it. The fact that this nucleation system has such a strong trend towards agglomerates forming instead of spherical particles, and that the particles tend to dissolve, makes us assume that it is energetically favourable for the Pt clusters to interact more closely with the interface instead of the liquid. As the spherical particles detach from the interface shortly after forming and then start moving in the liquid, it becomes more energetically favourable for the Pt to dissolve and reform as new clusters on the interface.

Evidence of crystallinity in newly nucleated sub-nm clusters: Despite the high degree of disorder in the sub-nm clusters that nucleate, there is evidence of crystallinity in the smallest few-atom clusters already immediately after nucleation. Many clusters can be identified to briefly adopt highly symmetric and close-packed structures. Some examples can be seen in Figure 5. CNT models clusters below the nucleation threshold as stochastic fluctuations, and although we observe clusters forming and dissolving, such a simple stochastic model is insufficient. Rather, there appear to be many competing nucleation pathways, where various structured clusters appear already at the few-atomic scale. The potential stability of such clusters is supported by density functional theory simulations.^[15–19] However, there is yet no clear evidence of any long-term stable structures among these sub-nm clusters, as higher time resolution and/or slower dynamics is needed to study these in greater detail. Furthermore, clusters in the estimated size range of ca 8–13 atoms are often seen to rapidly

snap into a denser and more close-packed configuration, from a loosely connected configuration, such as what happens at 6–8 s for the cluster in Figure 3a. This clearly indicates that there is a size dependence of the nucleation process in the sub-20 atoms range.

Overall, our results stand in contrast to the recently reported two-step nucleation mechanism, where first amorphous sub-nm clusters form, which then crystallizes.^[41] We rather observe a high degree of crystallinity very early in the nucleation process, such as in figure 3, though this cluster is more disordered until 8 s. However, these sub-nm clusters rapidly change structure, e.g. between 8, 49 and 100 s in figure 3, and generally so frequently that we cannot reliably track these structural changes at 1 fps frame rate. This provokes a question into what can really be considered an amorphous sub-nm cluster; are reported amorphous clusters truly disordered, or more like an ensemble of many rapidly changing metastable structures, like a quasimolten particle?

Conclusions

In this work, we demonstrate a simple and general method of inducing nucleation reactions of heavy metal clusters and nanoparticles in ionic liquid. This is the first time (to our knowledge) that solid-phase nucleation has been directly observed at atomic resolution in a liquid phase. The observed nucleation reactions represent highly dynamical states where clusters form and dissolve, exchange and transfer atoms, and only a few of them eventually overcome the nucleation barrier. Although the results show nucleation of Pt, no part of this method is specific to Pt, and therefore nucleation reactions can likely be studied for many other materials, by similarly dispersing atoms or precursor molecules into ionic liquids.

In this system, the nucleation is possible because of a sufficiently high concentration of highly mobile atoms, and is triggered by the electron beam irradiation. Such nucleation reactions can be induced in both suspended nanofilms and supported nanodroplets, both with typical thicknesses of ca 5–50 nm. In the suspended nanofilms, nucleation is rare and hard to reproduce, as the absence of a pre-existing liquid-solid interface results in homogeneous nucleation imposing a higher energy barrier.

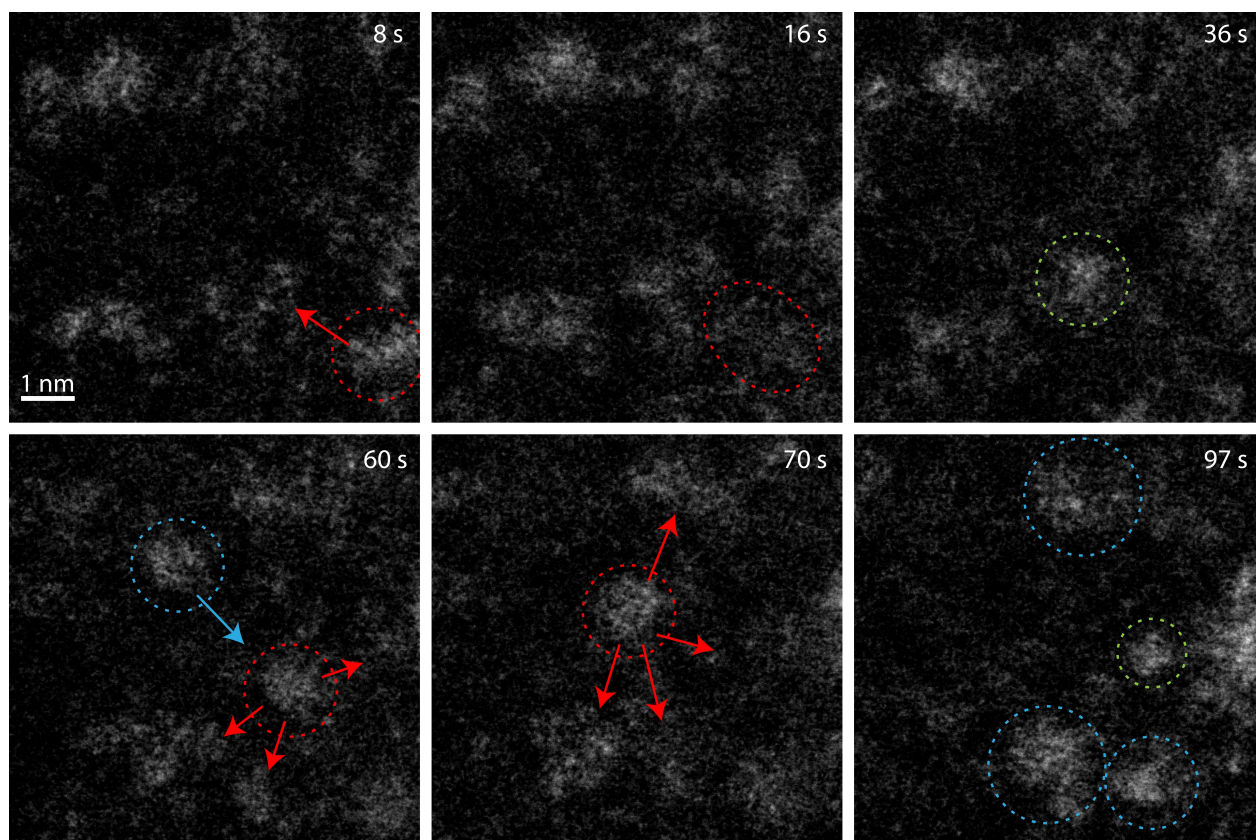


Figure 4. Nucleation and dissolution cycles of ~1 nm spherical clusters near the centre of a nanodroplet (ca 20–40 nm liquid thickness). Clusters marked in red are dissolving, green are newly nucleated clusters, while blue are persisting clusters (from Movie S4). 8 to 16 s – The cluster in the bottom right dissolved, and many of its atoms can be seen moving to an area with multiple smaller few-atom clusters. 36 s – The addition of more atoms have caused the multiple small clusters to nucleate into a single new ~1 nm cluster. 60 s – The new cluster starts dissolving, with atoms spreading to nearby clusters. A second cluster (marked in blue) migrates towards the first cluster. 70 s – The second cluster also starts dissolving, with atoms spreading to neighbouring clusters. 97 s – Atoms from the two last dissolving clusters have caused another new cluster to nucleate, and nearby clusters to grow significantly.

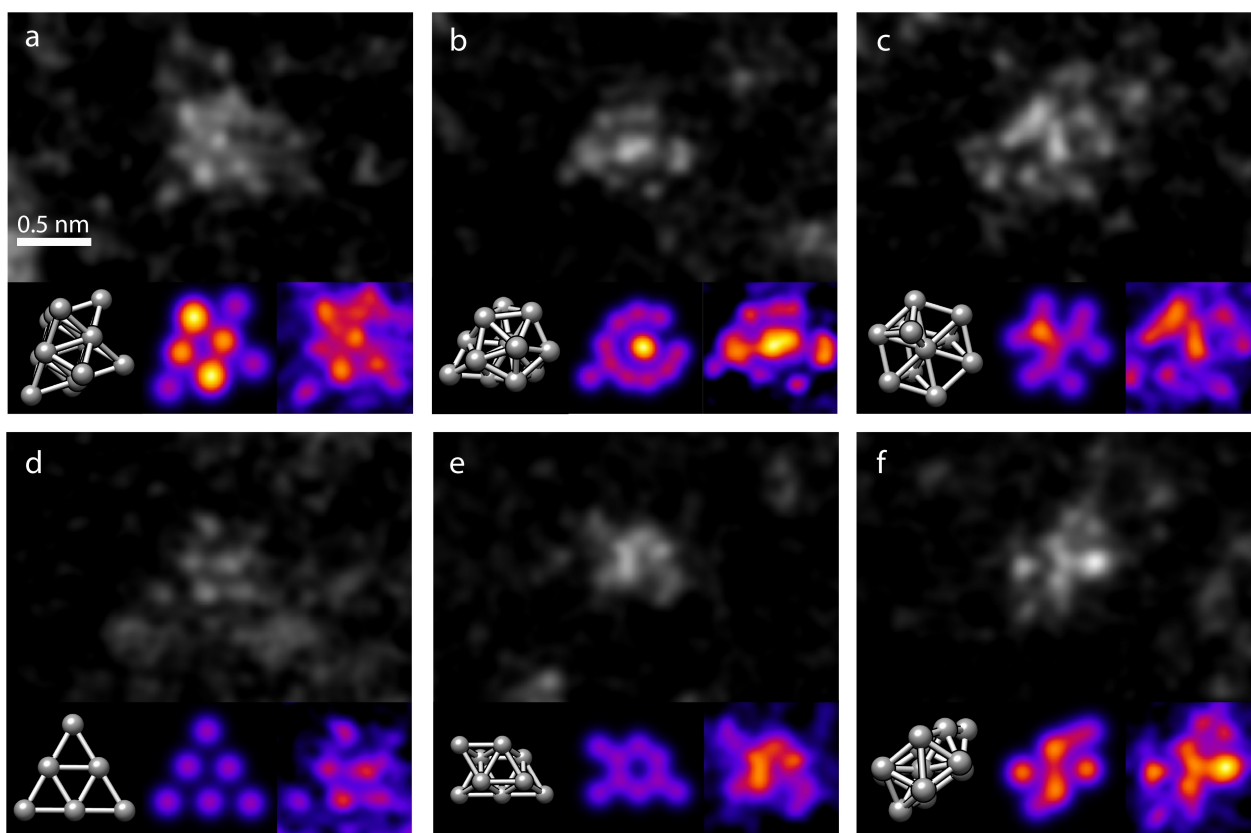


Figure 5. Examples of close-packed structures briefly appearing in newly nucleated few-atom clusters. Above are the processed experimental images and inset below is from left to right, respectively, proposed atomic models, false-coloured simulated images from the atomic models, and false-coloured experimental images for comparison. **a:** The ca 10–15 atom cluster from Figure 2c, which shortly after nucleating showed an fcc-like close-packed structure. For comparison, is the model of a 13-atom fcc cuboid. **b:** The cluster in Figure 3a, which around 49 s has 12–13 atoms and shows multiple frames with strong similarities to icosahedral structures. For comparison, is a model of 13-atom icosahedron with 1 atom displaced. **c:** The cluster in Figure 3a at 99 s, which with ca 16–18 atoms showed a close-packed core. This was likely structured as either hcp or fcc cuboctahedral, where a 11-atom hcp model is shown as comparison. **d:** A likely 6-atom triangle, which dissolved immediately after nucleating. **e:** A 9–11 atom cluster which showed multiple close-packed structures. For comparison, is a 9-atom close-packed model. **f:** An 11–13 atom cluster which showed three icosahedral structures. For comparison is a 12-atom icosahedral model.

In contrast, in the carbon-supported nanodroplets, nucleation is easily and reproducibly induced, due to the interface causing largely heterogeneous nucleation, with a lower energy barrier, and because the droplets accumulate (by the Coffee-ring effect) a very high concentration of dispersed Pt atoms without forming numerous pre-existing particles. There are three types of species forming from the nucleation reactions. Initially, small few-atomic clusters nucleate, which typically quickly start growing, but they can also linger as few-atomic clusters. These smallest clusters are highly dynamic and unstable, yet brief close-packed structures can occasionally be identified. Nevertheless, there is no clear evidence of any stable or preferred structure, yet we believe that novel analysis algorithms can track in detail how these nuclei form atom-by-atom. As the clusters grow and coalesce, they form either disordered cluster agglomerates or spherical nanoparticles. The few-atomic clusters and nanoparticles frequently redissolve shortly after forming, which is as expected from CNT. However, the disordered cluster agglomerates are stabilized by interaction with the liquid-solid interface at the carbon surface.

Overall, our experiments show the importance of modelling nucleation processes not just from the local chemical environment, but also to consider the current size and structure of clusters as they nucleate. Furthermore, as larger nanoparticles form with a multitude of different structures, their nucleation pathways likely depend on the structures appearing already at the initial step of few-atom clusters forming.

Author Contributions

T.R.H and R.E conceived the research work. T.R.H and D.K conducted the experiments, and T.R.H did the data analysis. The manuscript was written by T.R.H and all authors contributed to it. Authors declare no competing interests.

Acknowledgements

The project is funded by the European Research Council (ERC) under the EU's Horizon 2020 research and innovation program (Grant Agreement No. 681312).

Conflict of Interest

The authors declare no conflict of interest.

Keywords: nucleation · atomic cluster · ionic liquid · platinum · transmission electron microscopy

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Manuscript received: September 29, 2020

Revised manuscript received: November 2, 2020

Accepted manuscript online: November 6, 2020

Version of record online: November 19, 2020