General Discussion

Professor Davey opened the discussion of Professor Kahr's paper: In the choice of material with which to test this hypothesis it might be important to consider the effects of mechanical properties in the generation of new dislocations. This was explored in the 1980s by Sherwood and his collaborators.[1]

1   J. N. Sherwood and T. Shripathi, *Faraday Discuss.*, 1993, **95**, 173–182.

Professor Kahr responded: We should test a full range of conceivable replicating systems. Only by investigation will we be able to sort the wheat from the chaff. The dislocation/punched-card model, in hindsight, seems like chaff, but we couldn't know this at the outset. Likewise, it was inconceivable to presuppose the mechanism of action of DNA without first developing its structure. It seems daunting to guess at the characteristics of primitive genetic systems without first playing-out some of these ideas in the laboratory. Polytypism plays a much larger role in the theory of Genetic Takeover than do dislocations. However, we began with dislocations merely because we felt that we had chemistry in hand to rigorously test this idea.

Dr Ristic said: I find this work extremely interesting. The authors managed to cast a considerable amount of light on the Cairns-Smith's 'crystals-as-genes' hypothesis. Listening to the presenter I realised that in the recent past of our research work, my colleagues and I had been somehow involved in one aspect of this intriguing problem, but with a different motivation. Our aim was to find experimental conditions at which the existing screw or mixed dislocations in a crystal seed would continue to propagate through the interface between the original seed and its re-grown part and continue to serve as active sources of growth steps. The re-growing face was observed by *in situ* laser interferometry which would enable us to see the growth hillocks at the same sites as those at the original face. In addition, X-ray topography would confirm that these hillocks originated from the same dislocations, which were propagating from the original seed to the new re-growing part of the crystal. These experiments were performed on different materials such as a brittle sodium chlorate and potash alum, and ductile sodium nitrate. In all cases the transfer of the arrangement of the growth units (ions, molecules) within a dislocation 'line' from a seed to its re-growing part would always take place under very low supersaturation. On the contrary, at moderate and high levels of supersaturation, a markedly strained interface between seed and the re-grown part would develop. In this case the original seed dislocations would end up in the strained region and cease to exist. From this region new screw or mixed type dislocations would form and act as the generators of the growth steps. Finally, it might be interesting to mention that by stretching a plate of a ductile sodium nitrate during its growth, it was possible to induce mechanical dislocations in the seed and transfer them to the re-growing part in which they would act as new sources of growth steps.

Professor Kahr answered: Is there a better choice of material? There most certainly may be. Professor Ristic already suggested several possibilities such as sodium nitrate. Moreover, I am not disputing that macroscopic inclusions can be a source of dislocations. However, we grew KAP in the presence of luminescent nanoparticles and microspheres, while also adding luminscent dyes that light-up the hillocks. If the particles cause new dislocations, then we would have expected to see bright spots at the vertices of the luminescent chevrons marking the hillocks. While the particles were easily overgrown by KAP, they were never found at the apices of the vicinal faces of the hillocks. Particles do not create dislocations in this case. When examining cleaved surfaces that have been re-grown, we observed that new hillocks formed largely on the upper terraces. Presumably material is more easily carried to the upper surfaces. But, fundamentally, what causes hillocks? What are the molecular mechanisms?

Dr Cairns-Smith commented: It is good to see this serious piece of experimental exploration on the question of how complicated information might be transferred from pre-existing structures to newly forming ones through crystal growth. The main motive for seeking efficient systems of this sort is that they might provide novel genetic materials, and hence novel physicochemical systems able to evolve through natural selection.

In 1914 Troland had suggested that some sort of crystal growth process might be part of how the genes of today's organisms pass on hereditary information to offspring,[1] and Schrödinger in the 1940s used an analogy for what he imagined our genes to be like.[2] They would turn out to be crystals of a sort but not merely repetitious like wall paper, rather they would be interestingly complicated like a tapestry. They should be "aperiodic crystals". DNA indeed turned out to be aperiodic, although more like a text than a tapestry and using some 2 million Daltons of enzymatic machinery for this "text" to be replicated by means that bear little resemblance to ordinary crystal growth processes. Particularly in connection with the origin of life on the earth we should be looking for altogether more primitive genetic materials, which is to say ones that operate without the aid of highly evolved machinery. Professor Kahr explores an experimentally sophisticated but conceptually simple version of how a 2D pattern (a "tapestry" or perhaps we should say a pile of tapestries) might replicate a particular aperiodicity. He identifies two problems which the design of any potential crystal gene must cope with. There must be occasional mutations for genetic information to evolve, but the main problem is to keep mutation rates *down* so that evolved information is preserved through repeated copying. The second point which is highlighted in this study is that crystal cleavage, an essential part of a complete replication cycle, is particularly prone to introducing new dislocations in such 2D systems.

I rather like the idea of a crystal gene based on a disordered mixed layer or polytypic material.[3] The "information" would be in the form of a particular aperiodic stacking sequence. It would be 1D, like DNA in this respect, but unlike the elaborate procedures of DNA replication we imagine this crystal gene reproduces by simple units adding only to its edges in conformity with the pre-existing stacking pattern. The result would be an extensive, perhaps branching, flat stack of uniform thickness and with the same stacking pattern displayed everywhere on its edges. Such a primitive gene would be reproducing vegetatively like a clover plant covering a field, although bits of the stack might break off from time to time to seed similar colonies elsewhere. The damage likely to be caused by such breaking off would be less serious here than for a 2D model since here the cleaved surfaces do not have to be able to re-grow. Here the process of breaking off part of the structure could leave most of the edge surfaces untouched.

1   L. Troland, *Monist*, 1914, **24**, 92–133.
2   E. Schrödinger, *What is Life?*, Cambridge University Press, 1944.
3   A. G. Cairns-Smith, *Elements*, 2005, **1**, 157–161.

Professor Kahr responded: As mentioned above, in the theories of Cairns-Smith, polytypism in layered materials plays a more prominent role than the rather off-hand proposition of dislocation propagation that we focused on. It is certainly true that our study is not a representative exploration of the mineral origins of life. We seized on the crystal-as-punched card idea only because we felt that we had the chemistries in hand to properly evaluate it in just one crystal. The stacking model surely deserves equal if not more attention. At the very least, I hope that we have shown that it is possible to design experiments that can put these ideas on a firm experimental foundation. But one study is surely not sufficient to cover the range of ideas over which Dr Cairns-Smith's imagination has travelled.

Given advances in scanning probe microscopies among other technologies, we can now test the ideas of Cairns-Smith that were not imaginable 20 or 30 years ago. Some ideas are clearly before their time. Now is the time to bring this hypothesis under the umbrella of experiment.

Dr Cairns-Smith said: Mansfield and Bailey[1] found that the unit layers of vermiform kaolinite had a kind of crazy-paving domain structure, a domain corresponding to one of three possible positions for the octahedral vacancies in the kaolinite structure, and Williams and Garey[2] found mosaic patterns in replicas of etched kaolinite surfaces. So kaolinite might provide a model for a 2D genetic material—if the same pattern is written in successive layers stacked on top of each other. Perhaps some of the newer techniques used by Professor Kahr, such as AFM, might be of help here.

1 C. F. Mansfield and S. W. Bailey, *Am. Mineral.*, 1972, **57**, 411–425.
2 D. G. Williams and C. L. Garey, *Clays Clay Miner.*, 1974, **22**, 117–125.

Professor Breu asked: Storing information and replicating it is only the first step in genetic take over. Additionally, the data need to be read out, meaning the information stored needs to be transcribed into specific chemistry. Do you have an idea how different patterns of dislocations could be transcribed into selectively different chemistry/catalytic activity?

Professor Kahr responded: We have observed that riboflavin and flavin adenine dinucleotide (FAD) can be adsorbed and overgrown by KAP. One can imagine crystals concentrating such small biomolecules and catalyzing their condensation. FAD can lead to poly-A in this way. We are not suggesting that this is how it happens. But Dr Cairns-Smith talks at length about the adsorption, concentration, and catalytic condensation of small organics by clays. We must however recognize that there may be innumerable genetic systems that precede oligonucleotides. We must resist the temptation to rush to DNA.

Dr Cairns-Smith commented: Watson and Crick were quickly able to identify DNA as a genetic material, from its structure, without having any knowledge of how the information in it might work. I think we should take a similar attitude to the origin of life in our attempts to identify truly primitive genetic materials. Of course what their messages might mean, how they might benefit the systems holding them, will be the next question, but very much the next question. The first thing to look for, the *sine qua non*, is the potential to hold and replicate information efficiently.

Professor Roberts commented: The issue of screw dislocations, particularly those generated through growth, is a surprisingly complex process being the result of the conflicting 'demands' of the real (lattice direction defects) and reciprocal (lattice growth planes) crystal lattices. The former reflect closest atom–atom (or molecules) distances between equivalent Bravais lattice sites. The latter for facetted crystals is driven by the need for slow-growing and hence close-packed crystal faces. Hence, it is often the case that crystal habit faces have a form for which the shortened lattice vector defining the screw dislocation Burgers vector does not lie along the growth normal and hence pure screw dislocation are most unlikely. There are many examples for this:

Material	Dominant crystal habit plane	Lowest area Burgers vector
Si, C (diamond)	{111}	$\frac{1}{2}\langle 110 \rangle$
Potash alum.	{111}	$\langle 100 \rangle$
KDP	{100}	$\frac{1}{2}\langle 111 \rangle$
Ammonium sulfate	{111}	$\langle 001 \rangle$
Benzophenone	{110}	$\langle 001 \rangle$

The directions of growth dislocation has been described in the seminal work of Klapper.[1] Broadly speaking, these can be defined with respect to their line (*l*), Burgers vector (*b*) and growth direction (*n*) thus

If b is parallel to n then l is parallel to n

If b is perpendicular to n then l is parallel to n

If b is not perpendicular or parallel to n then l lies between b and n

The latter case gives rise to dislocations that we often see in solution grown crystals where mixed component dislocations travel at an angle to the normal to the growth face having only a partial screw component. A related outcome is that growth spirals from such dislocation are somewhat eccentric in nature.

A related generic point is that for symmetry below cubic the growth normal is often non-parallel to the associated lattice direction. The exception to this is in the cube directions for orthogonal lattices (tetragonal and orthorhombic lattices) for $b = \langle h00 \rangle$, $\langle 0k0 \rangle$ or $\langle 00l \rangle$.

In the extreme case of a triclinic lattice then b is never parallel to n and hence pure screw dislocations can be expected. In this case b can be perpendicular to n and hence pure edge dislocations are possible. We should not close out a discussion on growth dislocation without reflecting that quite a lot of experimental evidence now exists to support the view that edge dislocations promote the growth process.

Thus, in considering the growth dislocations in crystals as templates *via* fractures in promoting genetic material, a focus on dislocations in general and not just specifically screw dislocations, might have some value.

1   H. Klapper, in *The Characterisation of Crystal Growth Defects by X-Ray Methods*, ed. B. K. Tanner and D. K. Bowen, Plenum Press, New York, 1980.

Dr Schön asked: What is the original motivation behind looking at the fractal dimension of the hillock formation/distribution? What concerns me is the fact that your distribution in Fig. 6 exhibits the fractal behavior only over one order of magnitude, which is rather short on first sight—thus it would be helpful to have a growth model that leads to fractal behavior in a "natural" fashion. Do you expect *e.g.* some diffusion limited aggregation process to be involved? Perhaps such a process could follow from the issue mentioned earlier that the axis of the screw-dislocation and the axis of the surface growth are mis-aligned? Or is it connected to your observation that there is periodical splitting of the screw-dislocation into two new dislocations?

Professor Kahr replied: We struggled with defining the kind of information a primitive crystal gene might carry. The fractal dimension seemed like a number or "score" that could be used to compare crystals grown under different conditions. However, we are dealing with random fractals that have a stochastic character, not geometric fractals that are deterministic. We are certain open to better strategies for characterizing the dispositions of all of the growth active hillocks that appear in space (xyz) and time. Since we don't know what causes the formation of new screw dislocations in KAP it is hard to presuppose what mechanisms might result in the observed correlations of their positions. There are some substantial differences between our images of hillocks and the complementary information that is available from X-ray topography. The notion of V-shaped dislocations comes from Halfpenny[1] and could explain correlations of hillock positions along the a-axis. However, movement of cores in the ac plane would blur our luminescence micrographs. This is not observed.

1   G. R. Ester and P. J. Halfpenny, *Philos. Mag. A*, 1999, **79**(3), 593–608.

Professor Roberts commented: One factor to be considered is that mixed character dislocations, as they do not have dislocation line vectors parallel to the growth normal, can tend to intersect with growth sector boundaries and 'refract' into another sector thus removing a step-creating screw component and lowering the growth rate and changing the crystal morphology. Hence, the dislocation sub-structure can effect variation in the growth process causing an oscillating crystal morphology with time.

Professor Jones said: I should like to add that some 25 or so years ago transmission electron microscopy was successfully used to identify defects in ''nanocrystals'' (although that phrase was not used at the time) and indeed was also successful in looking at stress induced phase changes and microtwinning. I believe that this is an area that we should now return to with regard to organic nanocrystals and perhaps a better understanding of the consequences of mechanical treatment of organic and similar materials.[1]

1 See W. Jones and J. M. Thomas, Applications of Electron Microscopy to Organic Solid State Chemistry, *Prog. Solid State Chem.*, 1979, **12**, 101–124.

Dr Hare communicated: The line $\log c(r) = -\alpha \log r$ does seem to provide a close fit in the central region, but is there a continuous function that will give an even closer fit over a fuller range of r values? For example, I notice that if before plotting $e^{-\alpha \ln r}$ is first multiplied by a factor $1 + \phi$ where $\phi = 1 - \exp(kr^{\alpha})$, then there is the prospect of a fit across the whole range (here, k appears to be approximately 0.4; though it could conceivably be as high as α). Could this have any physical significance?

From the outset the authors stress that their test subject, KAP, does not resemble a pre-biotic mineral. Perhaps the jury is still out on clay. Whatever further test results arise (in an "amenable" non-clay system), though, and the verdict on these, could the properties of today's clay resemble those of the pre-biotic mineral? If, for the moment, Cairns-Smith's original question remains unanswered, then could the gardener, digging through clay with a spade, even today be preparing a scaffold for the post-human era? Or do we think that, with all the false positives and mutations that there could be, little or nothing will remain of the human legacy once all our brick buildings have collapsed and weathered away? Or, setting aside clay again, might the chemist be able to choose a material better suited to transmitting (our human) information into a future age than either yesterday's clay or today's discarded hard disks?

Professor Kahr communicated in reply: The data to me seem to indicate two distinct behaviors at the small and mid-length scales. If there is a continuous function it would be a convolution of two separate functions, one that is more fractal in nature at the middle length scale and another that would be physically appropriate for the clustered region. As for the longer length scale, the outlier region, the data is distorted by limited area. For example, in an infinite crystal this outlier region should disappear and the fractal region should extend further.

Is it appropriate here to invent an arbitrary function (or so it seems to me) to fit the data? Wouldn't it be better to identify functions with a corresponding physical significance and then evaluate how well those functions match the data?

We tried to be conservative in speculating in our manuscript about past "life". We will certainly be conservative by not speculating here about future life.

Dr Hammond opened the discussion of Professor Mazzotti's paper: Could you comment on the way in which the parameters in the detailed, surface-specific growth model that has been employed to look at the growth of all the surfaces of the crystals simultaneously, should be interpreted given that, presumably, the growth mechanisms on the different crystal faces could be significantly different. Would a simpler kinetic model not fit the available experimental data equally well and be more valid for interpreting data of this kind?

Professor Mazzotti replied: The model given by eqn (19)–(22) was used to convert growth velocities of single faces published in the literature[1] to overall growth rates of the crystal that can be compared with our correlation for the overall growth rate. The growth mechanism of the single faces was identified by atomic force microscopy in another paper by the same author as being for all faces ''birth and spread''.[2] Therefore, we have decided to use the same model for the overall growth rate that we have estimated, and we have compared it only with the growth rate expression of the

BCF model. Another simple model could in principle also work, as asked by Dr Hammond, but we strongly doubt that this would bring more insight.

1. M. Kitamura, *J. Cryst. Growth*, 2000, **209**, 138.
2. M. Kitamura and K. Onuma, *J. Colloid Interface Sci.*, 2000, **224**, 311.

Professor Unwin said: I would like to follow up on the issue of mass transport. My main point is that the neglect of mass transport relies on using a Sherwood correlation (eqn (17)) to estimate mass transport coefficients. How accurate are such correlations? Moreover, under what conditions do they apply? For example, what is the concentration of particles (in terms of fractional volume, fractional mass or other) and size range of particles in solution for which the correlation can be used? A more minor point concerns the value of $D = 2 \times 10^{-9}$ m^2 s^{-1} for α-glutamic acid quoted in the paper and used in the correlation. Where does this come from? It seems rather high based on values for similar small acids.[1,2] The value of D for such acids can, of course, be measured accurately with dynamic electrochemistry methods.[3]

1   W. J. Albery, A. R. Greenwood and R. F. Kibble, *Trans. Faraday Soc.*, 1966, **63**, 360.
2   B. E. Bidstrup and C. J. Geankoplis, *J. Chem. Eng. Data*, 1963, **8**, 170.
3   See for example R. D. Martin and P. R. Unwin, *J. Electroanal. Chem.*, 1995, **397**, 325 and references therein.

Professor Mazzotti answered: Correlations of mass transfer coefficients are usually given as correlations of dimensionless numbers and are based on a large number of experimental data. In general they can be applied to many different physical systems, represented by Re and Sc numbers, as long as the characteristic dimensions, *e.g.* the characteristic length, are chosen correctly. An overview about the different correlation can be found in standard textbooks.[1,2] The accuracy for solid–liquid interfaces is typically in the range of ± 10%.[2] According to Mersmann the most severe drawback in the prediction of mass transfer coefficients is the accurate knowledge of the diffusivities.[3] In our study we have calculated the rate of diffusion controlled growth based on eqn (17) and (18) for a broad range of particle sizes and supersaturations. For a value of $D = 2 \times 10^{-9}$ m^2 s^{-1} used in this paper and also for smaller diffusivities (taken from Albery[4] and Bidstup[5]) the experimental growth rates were found to be at least one order of magnitude smaller than the diffusion limited growth rates.

1   T. K. Sherwood, R. L. Pigford and C. R. Wilke, *Mass Transfer*, McGraw-Hill, New York, 1975.
2   E. L. Cussler, *Diffusion*, Cambridge University Press, Cambridge, 2nd edn, 1997
3   A. Mersmann, *Crystallization Technology Handbook*, Marcel Dekker Inc., New York, 2nd edn, 2001.
4   W. J. Albery, A. R. Greenwood and R. F. Kibble, *Trans. Faraday Soc.*, 1966, **63**, 360.
5   B. E. Bidstrup and C. J. Geankoplis, *J. Chem. Eng. Data*, 1963, **8**, 170.

Dr Vonk addressed Professor Mazzotti and Professor Unwin: Industrial experience with similar components like α-gluacid shows that mass transfer is usually much faster than surface integration.

Professor Mazzotti answered: Whether or not the growth of a substance is surface integration or mass transfer controlled depends very much on the substance and on the operating conditions. However, we have also found that for other small organic compounds the growth process is indeed integration controlled.

Professor Hyne asked: The data presented in Fig. 12 should permit an Arrhenius type plot of crystal growth rate *vs.* temperature to be constructed and the equivalent of enthalpies and entropies of activation for the growth process to be extracted (also by eqn (9)). Do such additional "pseudothermodynamic" parameters provide useful information about the crystallization process or is it comprised of too many discreet steps to be associated with any one?

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Professor Mazzotti replied: The growth rate expression that we have used describes a two step process: formation of nuclei on the surface and spreading of the layer at the kink sites of these nuclei. Hence, the growth rate expression given by eqn (9) comprises of a nucleation and a surface diffusion term. The parameter C in eqn (9) is related to surface nucleation and depends on the surface tension between the crystal and the solution. The parameter B in eqn (9) is related to surface diffusion and depends on the activation energy between two neighboring equilibrium points.[1] This is how the parameters in the growth rate equation should be interpreted. In general, an Arrhenius type plot is drawn to estimate the parameters in an Arrhenius type equation. In this case the growth rate expression is more complex than that, and the parameters are estimated as described in the paper hence there is no need for an Arrhenius plot.

1 A. Mersmann, *Crystallization Technology Handbook*, Marcel Dekker Inc., New York, 2nd edn, 2001.

Professor Addadi opened the discussion of Dr Rieger's paper:

(1) In the amorphous calcium carbonate phases observed in biological environment, the stable amorphous calcium carbonate (ACC) phases are hydrated with composition $CaCO_3 \cdot H_2O$, while the transient ACC phases are anhydrous. What do you think is the role of water in your system?

(2) The Asprich proteins also stabilize ACC. They are composed of 50–70% carboxylate-containing amino acids, which makes them more acidic than polyacrylate, but they are much more efficient than polyacrylate in ACC induction and stabilization. Do you have any explanation for this effect?

(3) You suggest that the stabilization is due to coverage of the particles by the polymer. Do you know that as a fact or is this a suggestion? What would prevent nucleation inside the particle bulk if the polymer is coating the particle only? How do you envisage the stabilization mechanism?

Dr Rieger replied:

(1) Since we do not have sufficient information about the evolution of the water content in the amorphous precursor structures I refrain from speculating about any molecular processes. The simple phenomenological explanation relies on referring to Ostwald's rule of stages stating that "an unstable system does not necessarily transforms directly into the most stable state, but into one which most closely resembles its own",[1] where it is sometimes implied that this resemblance refers to the local structure of the original and the forming phase.

(2) In some instances it has been reported that aspartic acid-rich polymers exhibit nucleating and dispersing efficiencies which differ from those of polyacrylic acid. To my knowledge there is yet no convincing (molecular) explanation for this finding.

(3) Presently we have only indirect evidence for the hypothesis that the polymer is forming a shell around the $CaCO_3$ particle: we observe that a critical amount of polymer is necessary in order to stabilize the metastable precursor particles. When working in the under-critical concentration range we can tune the duration of the metastable state by varying the amount of polymer added. It may be assumed that part of the polymer is located within the precursor particles, thus preventing nucleation. Again, we do not have any direct proof.

1 J. W. Mullin, *Crystallization*, Butterworth-Heinemann, Oxford, 1997, p. 201.

Professor Breu asked: What is the role of ACC? Is it a precursor that is transformed *via* a solid–solid reaction into crystalline forms? Or is it just a buffer system that fixes Ca^{2+} and CO_3^{2-} concentrations to a level that speeds up nucleation and/or growth of one or the other polymorph?

Dr Rieger answered: Both cases seem to occur: in an earlier study we observed by means of X-ray microscopy *in situ* how the amorphous calcium carbonate precursor particles dissolve completely while material recrystallizes at a different spot (the "buffer" mechanism),[1] whereas in other cases micron-sized vaterite spheres seem to be assembled from precursor particles which must have undergone a solid-state transformation, Fig. 5 of our paper). The degree of supersaturation and the mode of mixing seem to be the decisive parameters to switch between the two modes in the case of calcium carbonate.

1 J. Rieger, J. Thieme and C. Schmidt, *Langmuir*, 2000, **16**, 8300.

Professor Unwin said: Dr Rieger's paper contains significant new data which may clearly have major implications for the way in which we describe crystal growth from solution. The experiments in which emulsion structures are observed at short times are deliberately at high concentration to induce significant precipitation. Have any experiments been carried out at lower concentrations of Ca^{2+} and CO_3^{2-}, similar to those that are typically encountered in studies of seeded growth or growth at single crystals? It would be interesting to know the nominal threshold saturation ratio needed to produce the emulsion structures found in this study.

Dr Rieger replied: We did not vary the educt concentrations because we focused our interest on the role of additives on the formation of calcium carbonate under conditions which resemble applications using very hard water. Concerning the proposed supersaturation threshold between the formation of precursor structures and classical nucleation and growth we recommend a recently published article by Meldrum *et al.*[1] where it is postulated that the transition between ion-by-ion growth as compared to aggregation of nanoscopic building blocks is continuous.

1 A. N. Kulak, P. Iddon, Y. Li, S. P. Armes, H. Cölfen, O. Paris, R. M. Wilson and F. C. Meldrum, *J. Am. Chem. Soc.*, 2007, **129**, 3729.

Professor Davey asked:
(1) In the case of the amorphous calcium carbonate system, does the dispersion behave in a similar way to other colloidal dispersions? Can it be stabilized by simple surfactants?
(2) Do the dispersed particles have to aggregate before vaterite can form?
(3) Do other systems show this behaviour?

Dr Rieger replied:
(1) Once the spherical particles are formed from the inorganic emulsion structure they can be considered as colloidal particles. Surfactants might be suitable to stabilize these particles against aggregation but I assume that they do not provide a dense enough shell to stabilize the precursor particles against dissolution.
(2) We still were not able to clarify this point, the problem being that it is very difficult to sample enough of the precursor nanoparticles for XRD right before they aggregate to form the micron-sized vaterite spheres.
(3) There are a number of systems where colloidal particles are formed from nano-sized precursor particles; this field was pioneered by Prof. Matijevic and Prof. Sugimoto. Some references are given in our review on p. 4337.

1 D. Horn and J. Rieger, *Angew. Chem., Int. Ed.*, 2001, **40**, 4330.

Professor Kahr addressed Professor Davey and Dr Rieger: Likewise, Peter Vekilov has observed disordered aggregates of a variety of proteins that form prior to crystallization.[1]

1 O. Gliko, W. Pan, P. Satsonis, N. Neumaier, O. Galkin, S. Weinkauf and P. G. Vekilov, *J. Phys. Chem. B*, 2007, **111**(12), 3106–3114.

Professor Addadi addressed Professor Davey: In answer to your question: Are there other known cases of hydrated amorphous precursor phases before crystallization? Yes, there are: Calcium phosphate is a classical case, following a cascade of phase transformations from amorphous calcium phosphate to octacalcium phosphate, which is hydrated and crystalline, to apatite. Other known cases are for iron oxides and iron oxides hydroxides (ferrihydrite).

Dr Rieger said: I would like to point out that we observed similar precursor phases as discussed here for the case of calcium carbonate when investigating the precipitation of quinacridone (an organic red pigment) and boehmite (aluminium oxide hydroxide), though we could not obtain any quantitative information on the water content of these initial phase-separated structures.[1]

1 H. Haberkorn, D. Franke, Th. Frechen, W. Goesele and J. Rieger, *J. Colloid Interface Sci.*, 2003, **259**, 112.

Professor Roberts addressed Professor Addadi: Do we know why we get this sequence of hydrated complexes and amorphous precursors which seem to be prevalent for a number of mineral and organic systems? What is the current state of our fundamental understanding and are these effects generic in your view?

Professor Addadi replied: We do believe that the existence of amorphous precursor phases in the pathway to crystallization of many biogenic minerals may be much more widespread than what was believed until now. The existence of various forms of amorphous calcium carbonate (ACC) precursors to calcite has been proven in several sea urchin skeletal parts (larval spicules, adult spines and teeth) as well as in sponge spicules.[1] Mathias Epple's work[2] and Ingrid Weiss' work[3] have demonstrated ACC precursors to the formation of aragonite in larval mollusc shells. Other biogenic amorphous precursor phases include, among others, amorphous calcium phosphate as a precursor to apatite and ferrihydrite as a precursor to magnetite in chiton teeth.[4]

1 I. Sethmann, R. Hinrichs, G. Worheide and A. Putnis, *J. Inorg. Biochem.*, 2006, **100**, 88.
2 J. C. Marxen, W. Becker, D. Finke, B. Hasse and M. Epple, *J. Mollus. Stud.*, 2003, **69**, 113.
3 I. M. Weiss, N. Tuross, L. Addadi and S. Weiner, *J. Exp. Zool.*, 2002, **293**, 478.
4 H. A. Lowenstein and S. Weiner, *On Biomineralization*, Oxford University Press, New York, 1989.

Professor Addadi then addressed Dr Rieger and Professor Roberts: If I remember correctly, the first suggestion of a liquid amorphous calcium carbonate phase was from Aksay and Groves back in 1998.[1] They followed formation of calcite under monolayers of carboxylated porphyrins. They observed that an amorphous film is formed first, which subsequently crystallized.

1 G. Xu, N. Yao, I. A. Aksay and J. T. Groves, *J. Am. Chem. Soc.*, 1998, **120**, 11977.

Dr Rieger replied: In their 1998 paper Aksay and Groves indeed describe the "phase transformation from an initially deposited amorphous phase to crystalline calcite during the film formation". Their approach differs from ours insofar as they initiate the solid state formation at "a porphyrin template/subphase interface" in water—in all cases in the presence of polyacrylic acid. In our experiments we investigated the precipitation in the bulk system without any interfering interfaces; furthermore we also observed the formation of amorphous calcium carbonate in the absence of any additive.

Professor Roberts responded: This is most interesting but how can one be sure that the phase is truly amorphous and not just nanocrystalline. For example, a crystalline cluster of say 50 molecules of $CaCO_3$ would not be easy to identify *via* X-ray diffraction methods. In principle X-ray absorption spectroscopy (see *e.g.* ref. 1) can

be used but for $CaCO_3$ this is not trivial given the weakly scattering second coordination shell Ca–Ca interactions, the absence of which would be needed to clearly quantify the amorphous state.

1   K. J. Roberts, *Mol. Cryst. Liq. Cryst.*, 1994, **248**, 207–242

Professor Harding addressed Dr Rieger: In your paper you mention some MD simulations performed on polycarbonates interacting with calcium ions in solution. Could you please expand on what these simulations found about the binding of polycarbonates?

Dr Rieger responded: We studied the binding of Ca ions to polycarboxylates both by means of MD simulations as well as by attenuated total reflectance Fourier transform infrared dialysis spectroscopy, *c.f.* ref. 31 and 32 in our paper. This complementary approach gave consistent results: an ionic chelating complex evolves either to a unidentate complex, which can form a pseudobridge by coordinating a water molecule, or a pseudobridge with a sodium ion. The process leads to a chelating bidentate product, the yield of this step may be not complete. Within this general scheme an influence of the degree of polymerization has been observed. Concerning the MD simulations it must be stressed that it is mandatory to include the water molecules and the local chemistry of the oligomer/polymer in the simulation in order to obtain meaningful results. It is by no means sufficient to rely on considerations of charge density of the polymer, ionic strength, *etc.*

Professor Davey commented: In the context of the initial phase separation of inorganic materials it is important not to confuse this with liquid–liquid separation seen in protein solutions. The latter is due to a liquid–liquid miscibility gap that lies hidden beneath the solubility curve.

Dr Rieger answered: Professor Davey is of course right and we thank him for this clarification. At the same time we would like to stress that still virtually nothing is known about the process of initial phase separation in inorganic systems during precipitation. The complexity arises from the influence of several timescales: meso- and micromixing, diffusion, the reacting ions, phase formation, phase restructuring, and expulsion of water from the initially formed phase. As a further complication it must be recognized that the local viscosity of the system changes during solid state formation. The latter point renders any quantitative consideration very difficult since it affects all the above points.

Professor Heyes said: It has been known for about 15 years that for quenched fluid systems, if the attractive interaction between the particles is short-ranged compared to their diameter, the crystallisation phase separation occurs first through an amorphous phase, which is consistent with your experiments. The fluid–fluid separation which occurs first is metastable with respect to and within the solid-vapour coexistence. This behaviour could be "tuned" by changing the ionic strength of the solution. Have you investigated the effects of ionic strength change on the morphology of the initial $CaCO_3$ precipitate?

Dr Rieger replied: At the present state of knowledge I would not compare the phase behaviour of dispersions made from colloidal particles/proteins with ions dissolved in water. Nevertheless, it would be interesting to know more about the influence of ionic strength on the precipitation. But due to the ion specificity of the calcium carbonate precipitation this endeavour would open another large parameter field (apart from concentration of educts, temperature, mode of mixing, type and concentration of additive, *etc.*) which we did not attempt to tackle.

I agree that it might be interesting to change the interaction between the precipitating ion by varying the ionic strength in order to compare with phase separation mechanisms known from protein crystallization. The problem is that, once we change one parameter of the system the precipitation behaviour of the whole system is affected. To make things worse, sometimes step-like changes occur upon continuous variations of parameters like ionic strength, temperature, etc. This differentiates the precipitation of ions ($Ca^{++}_1 CO_3^{--}$) from the crystallization of proteins. The latter system can be discussed in terms of colloidal hard sphere systems with short-range interaction whereas the former evades such an approach.

Professor Heyes then asked: Have you measured the viscosity of the polyelectrolyte $CaCO_3$ nanoparticle aggregates? The intrinsic viscosity, for example, would give you some idea of the rigidity of the aggregates formed. You could use for example the Mark–Houwink equation (see, *e.g.*, ref. 1). The intrinsic viscosity characterises the dilute solution behaviour, which could be particularly appropriate here.

1 K. Kamide and T. Dobashi, *Physical Chemistry of Polymer Solutions*, Elsevier, Amsterdam, 2000.

Dr Rieger answered: Due to the difficult handling of the precipitating systems and the rather short timescales involved we did not attempt to measure the evolution of the viscosity though these data might indeed yield valuable information if available.

Professor Hodnett asked: Did you measure the solubility of calcium in equilibrium with the amorphous calcium carbonate? How does this value compare with the starting concentration (0.01 M) and the equilibrium concentration for calcite?

Dr Rieger replied: The data can be derived in a first order approximation from Fig. 11 in our paper. If we extrapolate the activity of free calcium ions to a polymer concentration of zero we arrive at a value of roughly 70 ppm, which corresponds to 1.75 mM, compared to 5mM l^{-1} Ca ions at the start of the precipitation (0.01 M l^{-1} educt solutions are mixed in equal volumes).

Dr Lewtas asked: The stability of very small particles in the presence of polymers depends upon the absolute size and the relative size compared to the polymer. How does the proposed mechanism vary with changes in polymer MW and also polymer MWD?

Do you see a change from dispersion to bridging/flocculation? If so, at what MW? Is there a relationship? MWD should also have an effect— do you have any data?

Is there a transition from stabilization/dispersion to nucleation with the rasing of polymer MW?

Dr Rieger responded: To a certain extent the known rules of colloid science apply here, *i.e.* higher molar mass polymers tend to flocculate, among other effects. The situation is complicated by the fact that polyacrylic acid strongly interacts with both the calcium ions in solution and the calcium carbonate in the form of dispersed solid particles. Neither in our case where we precipitate calcium carbonate in the presence of polyacrylic acid nor in the classical field of dispersing hardly soluble salts, such as calcium carbonate, is there a complete understanding of how the different effects affect each other.

Professor Mazzotti asked: With reference to Fig. 9, are these images of the same spot in the precipitator? If yes, how can you rule out the effect of concentration gradients?

With regard to the effect of supersaturation, which is not considered in the manuscript, can one assume supersaturation levels that are consistent with the phenomenological picture that has been presented?

Dr Rieger answered: The five micrographs shown in Fig. 9 are indeed taken at the same spot of the sample; related experiments were performed in order to ensure that

the result is not impaired by radiation damage of the sample in the X-ray microscope. It is safe to assume that there are concentration gradients in the sample, but at the same time we assume that variations of the gradients due to the different geometries (bulk *vs* 10 μm thick layer) will not affect the outcome of the experiments qualitatively. In some cases we observed that the timescale of morphological transformations was stretched in the latter case. With the educt concentrations used our system falls into the class of precipitation–crystallization reactions where it is known that classical crystallization theory only applies to a limited extent. A typical example for the complication encountered is the occurrence of several intermediate steps preceding the final crystallization.

Dr Hare communicated: One unanswered question was why growth was observed at right angles to the expected direction. In the absence of other suggestions—and purely "off the wall"—might one line of enquiry be to ask whether there is *any* growth in the expected direction? If there were, but it were slow, then could it be that to achieve the stablest outcome, the bulk of the crystal needs "to go around" the obstacle of the slow-growing crystal already growing, *i.e.*, must the bulk of it begin by setting off in the perpendicular direction? Might this also be consistent with a "two paths" mechanism (in which the first has a low followed by a high activation-energy barrier, while the second has one of medium height)? Could it really be, perhaps, that the *inanimate* ensemble is adopting an animal-like strategy?

Professor Catlow opened the discussion of Professor Watanabe's paper: First let me congratulate you on the quality of the data you have obtained in these experiments. Could you discuss in more detail the coordination numbers obtained from simulation and experiment? Fig. 4 indicates an apparent discrepancy, while the $S(Q)$ data indicates good agreement between theory and experiment. Could you also give more details as to how the coordination numbers change with temperature?

Professor Watanabe replied: Our conclusion from experiments and simulations is that there is no change in the temperature range from 1200–1800 K. It is too difficult to discuss more details regarding coordination number change, because the coordination number obtained by both experiments and simulation is an averaged value from moving atoms. Thus the number contains large errors. In future, we must develop the technique to obtain precise atom coordinates from one shot pictures of moving atoms.

Professor Roberts said: It is interesting to note the observation of 6-fold coordination in liquid Si related to 4-fold tetrahedral short-range correlating and an average of 2 for the second shell. The first 3 shells in the radial distribution function from the bulk crystal Si structure should be 4, 12 and 6. Hence, this implies the fraction of second shell co-ordination (2/12) which may be indicative of diffusional motion between the Si tetrahedra. Its important to note that crystal size plays a role and that when small (<1 μm) the radial distribution function will be reduced by surface effects, *i.e.* allowing for the effects of undercoordinated surface atoms, and that the calculated coordination numbers need to be corrected for this to allow for this effect.

Professor Watanabe answered: We did not consider the effect of surface on the radial distribution function. It is very difficult to consider the surface effect on the radial distribution function by conventional experimental and analysis techniques.

Professor Catlow asked: Could you give more details of the 6 coordinated structures? What is the detailed geometry of the coordination shell?

Professor Watanabe replied: From the one shot picture of MD simulations, we identify tetrahedral coordination of atoms. We think that the 6 coordinated structure is not important to short-range structure of liquid Si. Our ideas about

the short-range structure of l-Si are that tetrahedral coordination is important to the short-range structure of l-Si. Since the tetrahedral coordinated atoms are moving in the liquid, the average nearest neighbor coordination number was 6. Thus, we think that the rigid 6 coordinated structure would not exist in liquid Si.

Dr Schön said: You model the liquid state using *ab initio* MD for a 64-atom supercell. While this is already quite a challenge, I am concerned about the typical effects of a rather small simulation cell (we have encountered such effects ourselves, too) such as a considerably elevated melting temperature or an overly strong prevalence of solid-like local coordinations. This is of particular concern, since you are discussing the issue of changes in the local coordination number and the jump in the density upon melting. Did you check for or notice such effects? You might perhaps be seeing some transition states from a four-fold to a six-fold coordinated state that exhibit local ordering with 4 + 1- or 4 + 2-coordinations. Studies of the energy landscape of *e.g.* alkali halides have shown that there are many local minima with comparable energies that correspond to crystalline configurations with 4-, 5- or 6-fold coordinations.[1] Similar analogous configurations might appear during the simulations at high temperatures in the Si-system.

Quite generally, what criterion do you use to recognize that you are dealing with a liquid-like state? Do you observe a rapid increase of the diffusion constant near the melting point?

1   J. C. Schön and M. Jansen, *Comput. Mater. Sci.*, 1995, **4**, 43.

Professor Watanabe replied: In our simulation, we start from crystalline state to liquid state with temperature increasing. In this sequence, we clearly observed an energy jump at melting temperature, thus we can identify the transition from the crystalline to liquid state. In the cooling cycle from high temperature liquid state, we did not observe any drastic change at the melting temperature. Thus, we can achieve a supercooling state from the high temperature liquid state. In these conditions, a rapid increase in the diffusion constant was not observed at the melting temperature.

Dr Murray asked: Could the magnetic field influence the freezing process?

Professor Watanabe replied: No.

Professor Roberts commented: The key issue relates to how magnetic levitation might affect nucleation. If the material is diamagnetic then the effects should be quite small or the field should just effect dipolar rotation (Larmor effect) and providing the field is small, which it is, then such effects should be small. The main utility of the levitation technique reflects the effect that the sample size is small and the "container'' is removed thus providing little opportunity for heterogeneous nucleation and hence providing an opportunity to study a purely homogeneous process.

Dr Hughes addressed Professor Roberts and Professor Watanabe: Examples exist in the literature where the effect of a magnetic field on crystallization has been to orient the crystals but not to affect the polymorphism. The particular example I have in mind is a study on α-glycine by M. Sueda *et al.*.[1]

1   M. Sueda, A. Katsuki, Y. Fujiwara and Y. Tanimoto, *Sci. Tech. Adv. Mater.*, **7**, 2006, 380–384.

Professor Watanabe replied: I did not know of Sueda's paper. However, the effect of magnetic field on the Si crystallization is different from the glycine. In the case of Si, magnetic fields suppress melt flow by the Lorentz force. Therefore, the Si crystal growth behavior is unchanged from that in the case with no magnetic field.

Professor Roberts responded: Yes, this is a good point and indeed several commercial devices have been produced, *e.g.* for anti-water scaling applications, in which claims are made concerning the effect of magnetic fields in suppressing scale-forming crystallisation processes. The science basis for such action remains, though, quite weak and there is much still to be done in order to understands such "effects". To my knowledge, there have been no substantial work concerning the effect of magnetic field on polymorph formation and its control.

Dr Ristic asked: A static magnetic field of 6 T generated by a superconductive magnet appears to be very strong compared to the maximum strength of the magnetic field that can be achieved by a conventional electromagnet ($\approx$ 1 T). Have you observed any influence on the crystallisation of silicon at 6 T?

Professor Watanabe responded: Magnetic fields of 6 T cannot be generated by a normal electromagnet. Magnetic fields can suppress the Si melt flow by the Lorentz force. We have not observed any difference in the crystal growth behavior.

Professor Heyes asked:
(1) Classical MD simulations with a small number of particles (*e.g.* 64) readily show crystallisation. The periodic boundary conditions promote crystallisation. Your simulations do not show this (*e.g.* no density change at the experimental melting temperature). Is this difference a consequence of the first principles method or some other reason?
(2) SiO_2 and H_2O manifest density maxima above the normal melting temperature. The tentative density maximum for Si suggests a density maximum below the normal melting temperature. Do you have any ideas why there should be this qualitative difference?

Professor Watanabe answered:
(1) Many classical MD simulations showed supercooling liquid state (see, *e.g.*, ref. 1), the same as our results. Therefore, the supercooled state does not depend on simulation technique.
(2) For the case of l-Si, the reason for the temperature of maximum density existing below the melting temperature would be the balance of thermal energy and binding energy. The balance of thermal energy and binding energy may decide the maximum density temperature. This is just my impression, in future we must clarify the reason for the difference by qualitative analysis.

1   C. A. Angell, S. Borick and M. Grabow, *J. Non-Cryst. Solids*, 1996, **205–207**, 463.

Dr Hammond said: It would, I think, be interesting to extract information about the motion of silicon atoms in the molten state from the FPMD simulations that you have performed. Have you calculated time correlation functions to describe this motion?

Professor Watanabe replied: Yes, we can obtain a time correlation function from the MD results. Please see the previous paper evaluating diffusivity of liquid Si under high pressure conditions.[1]

1   T. Morishita, *Phys. Rev. E*, 2005, **72**, 021201.

Professor Catlow asked: Are you able to calculate the Si diffusion coefficient in your MD simulations? If so, what values do you obtain?

Professor Watanabe answered: Yes, we can obtain a diffusion constant from our MD results. Our diffusion coefficient is of the same order as normal liquid metals (10^{-4} cm^2 s^{-1}).

Dr Wakisaka opened the discussion of Dr Michaelides' paper: Are there any differences in the following cases: (i) water clusters in the gas phase have a soft-landing on the Cu surface; (ii) monomeric H_2O adsorb onto the Cu surface?

Dr Michaelides replied: As far as I am aware the experiments which could provide an answer to this question have not been performed.

Dr Murray asked: Real atmospheric particles have defects and faults. Have you looked at the clustering of H_2O molecules on defects on surfaces?

Dr Michaelides answered: No, not yet.

Professor Unwin asked: My question is related to the previous one. The STM image presented in the overview of this paper appeared to show extensive decoration of steps with entities that did not look like water clusters, as well as the water clusters of interest which were distributed at various locations on the terraces. Are the steps preferential binding sites for water on such surfaces and have you tried to model the adsorption of water at steps?

Dr Michaelides responded: We have not looked into this issue in any great detail. It's an interesting question and one we would like to address. Knowledge of molecular adsorption (including water adsorption) on other metal surfaces would lead one to expect that binding at the step sites will be greater than on the terraces and that whatever the barrier for water dissociation on the terraces is, it is likely to be lower than on the steps.[1–3] Here we have simply focused on attempting to understand the structures of the clusters on the terraces. In the future we would like to turn our attention to the steps, although it's worth pointing out that to examine clusters such as the hexamer adsorbed at a step site will be computationally challenging because a very large simulation cell will be required.

1 M. Morgenstern, T. Michely, and G. Comsa, *Phys. Rev. Lett.*. 1996, **77**, 703.
2 A. Michaelides, A. Alavi, and D.A. King, *Phys. Rev. B*, 2004, **69**, 205411.
3 A. Michaelides, Z.-P. Liu, C. J. Zhang, A. Alavi, D. A. King and P. Hu, *J. Am. Chem. Soc.*, 2003, **125**, 3704.

Professor Bensch asked: Do you obtain different results if the nucleation of H_2O occurs on different orientations of the Cu surface?

Dr Michaelides answered: The structure of the substrate does indeed play an important role. On Cu(110), for example, one dimensional chains, which differ greatly from the structures observed on Cu(111), have been observed in similar low-temperature STM experiments[1] to those performed by K. Morgenstern and discussed in my paper.[2] Further, by altering the surface structure one will also alter its reactivity and make it more likely that the water molecules will dissociate. Some discussion along these lines can be found in ref. 3. Likewise the chemical nature of the substrate[4,5] and the presence of co-adsorbates play important roles in the structures which form.[6]

1 T. Yamada, S. Tamamori, H. Okuyama, and T. Aruga, *Phys. Rev. Lett.*, 2006, **96**, 036105.
2 A. Michaelides and K. Morgenstern, *Nat. Mater.*, 2007, DOI: 10.1038/nmat1940.
3 A. Michaelides, *Appl. Phys. A*, 2006, **85**, 415.
4 J. Cerda, A. Michaelides, M.-L. Bocquet, P. J. Feibelman, T. Mitsui, M. Rose, E. Fomine and M. Salmeron, *Phys. Rev. Lett.*, 2004, **93**, 116101.
5 A. Michaelides, A. Alavi, and D. A. King, *J. Am. Chem. Soc.*, 2003, **125**, 2746.
6 A. Michaelides and P. Hu, *J. Chem. Phys.*, 2001, **114**, 513.

Dr Schön said: I want to follow up on the earlier discussion on the accuracy of the calculations, both in the gas phase and on the surface. I would agree that DFT is not sufficient for catching the subtle effects of the gas phase energies of the water

oligomers. Probably post-Hartree–Fock methods such as coupled cluster calculations are necessary. Have you looked at such calculations?

Concerning the oligomers on the surface, such accuracy is probably difficult to reach (perhaps MP2 level is possible). Have you checked how your results vary with the use of different kinds of pseudo-potentials or functionals, in order to get some feeling regarding the robustness of your results? Regarding Fig. 4, why is there an apparent convergence of the two quantities plotted at about $n = 9$? Is a convergence expected to follow from the definition of these quantities? (The shape of the $n = 9$ cluster in the gas phase is surely quite different from the one on the surface?)

Dr Michaelides replied: The gas phase energies of the water oligomers and how well different DFT functionals do at describing their relative energies is still an open question. In particular for the gas phase water hexamer in which there are at least 4 isomers (cage, book, prism, cyclic) all within a few meV per H_2O of each other. We are currently looking into this issue and using MP2 at the complete basis set limit to generate our reference data; a paper by Santra, Michaelides, and Scheffler is currently being prepared on this topic. For the adsorbed hexamers our DFT PBE calculations find a preference for the cyclic hexamer. Since this is also what is observed in experiment it gives us some confidence that DFT is accurate enough to reliably treat these systems. Also, in a few previous publications we found "good" agreement between DFT GGA calculations and experiment: specifically, by good I mean that DFT GGA calculations correctly predict the correct binding site for water monomer adsorption on several metal surfaces[1] and the correct intermediate in the water formation reaction on Pt.[2,3] However, for the specific issue of the buckling predicted by DFT for the adsorbed hexamer on Cu(111) we checked our DFT results against MP2. The MP2 calculations were all-electron and performed on small Cu clusters. Some of these results are reported in Table 2, where it can be seen that the all-electron MP2 calculations and the pseudopotential DFT calculations agree that there is a strong preference for the H_2O hexamer to buckle when adsorbed. Also in this table are results with two other DFT functionals ("RPBE" and the hybrid "PBE0" functional) and in a forthcoming paper results with B3LYP as well as additional tests on the numerical accuracy of our results will be reported.[4] I think the "convergence" of the gas phase and adsorbed phase cluster energies is just a coincidence.

1 A. Michaelides, V. A. Ranea, P. L. de Andres and D. A. King, *Phys. Rev. Lett.*, 2003, **90**, 216102.
2 A. Michaelides and P. Hu, *J. Chem. Phys.*, 2001, **114**, 513.
3 A. Michaelides and P. Hu, *J. Am. Chem. Soc.*, 2001, **128**, 4235.
4 A. Michaelides and K. Morgenstern, *Nat. Mater.*, 2007, DOI: 10.1038/nmat1940.

Professor Catlow asked: Have you been able to calculate activation energies for water migration on the copper surface?

Dr Michaelides answered: Yes and no. A reasonable estimate of the diffusion barrier for a molecule across a surface can be obtained by comparing the binding energy of the molecule at the most stable and next-most stable adsorption sites. On Cu(111) and many other metal surfaces we have made such estimates.[1] If you look in ref. 1, for example, you will find such an estimate for the diffusion barrier on Cu(111) (and several other metals) giving a value of 0.05 eV. However, when we looked at this issue in detail for water diffusion on Al(100)[2] in which we explicitly mapped out the potential energy surface between the most stable and next-most stable adsorption sites we found that the actual diffusion barriers were a little bit larger (10-100 meV) than the binding energy difference and that the diffusion barriers depended quite strongly on the orientation of the water molecule. For Cu(111) we have not performed such a complete scan of the potential energy surface as we did for Al(100). Also, I note that when water clusters diffuse much more complex and interesting mechanisms are predicted.[3,4]

1 A. Michaelides, V. A. Ranea, P. L. de Andres and D. A. King, *Phys. Rev. Lett.*, 2003, **90**, 216102.
2 A. Michaelides, V. A. Ranea, P. L. de Andres and D. A. King, *Phys. Rev. B*, 2004, **69**, 075409.
3 V. A. Ranea, A. Michaelides, R. Ramirez, J. A. Verges, P. L. de Andres and D. A. King, *Phys. Rev. Lett.*, 2004, **92**, 136104.
4 A. Michaelides, *Appl. Phys. A*, 2006, **85**, 415.

Professor Kahr asked: Your trimer is chiral as are some of the other clusters. Recently there have been extensive investigations into enantioselective processes of high index metal surfaces such as the Cu (643). This surface is naturally chiral.[1] Do you think that you can calculate enantiomer discriminating energies of chiral clusters on these surfaces?

1 A. J. Gellman, J. D. Horvath, *J. Am. Chem. Soc.*, 2002, **124**, 2384.

Dr Michaelides replied: This is a very interesting issue and something we plan to look into. It is certainly possible to compute water cluster, in particular chiral hexamer, adsorption on these intrinsically chiral surfaces.

Professor Roberts asked: It is interesting to note the rather beautiful water hexameric structures on Cu surfaces. Is there any evidence for these in other structures provided for bulk 3D X-ray/neutron crystallographic structures? It would be interesting to search, *e.g.*, the CCDC to see if such structures have been found, *e.g.* in the crystallography of organic hydrates.

Dr Michaelides replied: Water hexamers are not uncommon; regular hexagonal and cubic ice are built out of them. As for the presence of water hexamers and the finer details of their structures in organic hydrates and other bulk hydrates I cannot comment. I agree, however, that it would be interesting and worthwhile to check the CCDC for evidence of water hexamers in other environments.

Professor Vlieg asked: Can you perform calculations with similar accuracy on surfaces of salt?

Dr Michaelides replied: Yes. See, for example, ref. 1 or 2.

1 B. Li, A. Michaelides, and M. Scheffler, *Phys. Rev. Lett.*, 2006, **97**, 046802.
2 Y. Yang, S. Meng, and E.G. Wang, *Phys. Rev. B*, 2006, **74**, 245409.

Dr Hare communicated: Given the characterisation of the adsorbed hexamer as a weak "triple-dimer" structure, would it be worthwhile to study the tetramer specifically as a double dimer (neglecting both trimer and pentamer), not necessarily seeking low-energy configurations but with a view to exploring possible paths from single to triple dimer?

Given the adsorption-energy minimum at or near $n = 6$ (Fig. 4), do the hexamer's electron-density isosurfaces (Fig. 6) suggest a symmetry for the crystal nucleus? Once a hexamer has formed, could this survive throughout bulk growth into the ice crystals we see with hexagonal shape, such as in a snowflake? If we are seeking a model for the crystal growth of ice, do we need look at values beyond $n = 6$, or, might it be possible to study aggregation of the hexamer, allowing it to buckle and unbuckle? To understand the melting of ice, do we need to establish an activation-energy surface for its nucleation and growth over a range of values from small to extremely large $6n$?

Dr Michaelides communicated in reply: Addressing each question in turn: (i) This is an interesting suggestion but not something we have looked at. My feeling, however, is that the most likely growth mechanisms of these clusters is by the sequential addition of individual water molecules and not necessarily through the grouping of dimers. Probably the main reason I favour a mechanism of sequential water addition is the nice set of experiments by Salmeron and co-workers[1] in which they saw adsorbed clusters (on Pd(111)) grow one molecule at a time with STM.

(ii) Yes, the hexamer structures do survive in the bulk; cyclic water hexamers are often called the "smallest piece of ice" since they are the building blocks of ice Ih. In a closely related study to this one on Pd(111) we saw that the local hexameric structure and hydrogen bonding pattern within an individual adsorbed hexamer directly impacted upon the mesoscopic (2D) ice structures which formed on this surface.[2,3] (iii) I fear that these systems are so complex and that the relative energies between different water clusters with different numbers of molecules and even clusters with the same number of molecules but with different structures are so small (meV per water) that a clear picture of aggregation will require knowledge of many more clusters than just the cyclic hexamer. (iv) I don't know.

1   T. Mitsui, M. K. Rose, E. Fomin, D. F. Ogletree, and M. Salmeron, *Science*, 2002, **297**, 1850.
2   J. Cerda, A. Michaelides, M.-L. Bocquet, P. J. Feibelman, T. Mitsui, M. Rose, E. Fomin, and M. Salmeron, *Phys. Rev. Lett.*, 2004, **93**, 116101.
3   A. Michaelides, *Appl. Phys. A*, 2006, **85**, 415.

Dr Hughes opened the discussion of Dr Wakisaka's paper: The method discussed in the paper can only observe charged clusters with odd numbers of ions and cannot see neutral clusters with even numbers of ions. Nonetheless, a model for crystallization is proposed which ignores neutral clusters. Hence, I wanted to know if the energies of the neutral clusters had been calculated, along with those of the charged ones, in order to determine how common such species might be.

Dr Wakisaka responded: By means of mass spectrometry, the charged clusters with odd numbers of ions can be observed, but the neutral clusters with even numbers of ions cannot be observed. Therefore, we cannot compare the stability of clusters with charged and neutral clusters experimentally. Diefenbach and Martin calculated the stability of these clusters in the gas phase.[1] The calculation suggests that the neutral clusters are more stable than the charged clusters. However, in the liquid phase, the charged clusters may become more stable due to the solvation. Fig. 5 of our paper (model of crystallization) shows just an example. We do not exclude the neutral clusters from the crystallization processes.

1   J. Diefenbach and T. P. Martin, *J. Chem. Phys.*, 1985, **83**, 2238.

Professor Vlieg said: For larger NaCl crystals, two morphologies are known to occur: {100} which is charge neutral, and {111}, which is polar and should be charged. However, inside a liquid, the {111} morphology turns out to be stabilized through an electrochemical double layer. We have evidence from surface X-ray diffraction for this.[1] Thus: how does this compare to your results? And would you not expect neutral species to be at least as stable?

In an STM experiment combined with DFT calculations[2] it was found that a three layer NaCl crystal, Na–Cl–Na, is in fact charge neutral because the Na atoms were found to have only charge 1/2, making the system stable through a different charge transfer than normal.

1   N. Radenović, D. Kaminski, W. J. P. van Enckevort, W. S. Graswinckel, I. Shah, M. in 't Veld, R. Algra and E. Vlieg, *J. Chem. Phys.*, 2006, **124**, 164706.
2   W. Hebenstreit, M. Schmid, J. Redinger, R. Podloucky and P. Varga, *Phys. Rev. Lett.*, 2000, **85**, 5376.

Dr Wakisaka replied: In our mass spectrometry, liquid droplets charged by the excess cations or anions are generated by the electrospray method. The charged clusters are formed through the fragmentation of these charged liquid droplets. Since the electrospray is a kind of electrochemical process, our results should have some correlation with your study. As for the neutral clusters, we do not exclude them from the crystallization processes.

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Dr Michaelides addressed Professor Vlieg: With regard to your point about the double layer at salt surfaces, I note that very recently dynamic scanning force microscopy and Kelvin probe force microscopy revealed that a double layer exists even on the (001) surface of alkali halide surfaces such as NaCl(001) due to the presence of divalent impurity ions in the bulk which causes the surface to carry a net negative charge.[1]

1   C. Barth and C. R. Henry, *Phys. Rev. Lett.*, 2007, **98**, 136804.

Professor Kahr opened a general discussion, addressing Dr Michaelides: Richard Saykally has for many years studied small water clusters in the gas phase by rotational-vibrational spectroscopy.[1] How do your clusters on metal surfaces compare with what has been observed in the gas phase? It appears that, for example, your trimer and Saykally's trimer are diastereomers.

1   N. Pugliano and R. J. Saykally, *Science*, 1992, **257**, 1937.

Dr Michaelides responded: Referring to Fig. 2 in the paper, with our current DFT set-up, we are able to predict the correct ground-state for the gas phase trimer. This is the (chiral) cyclic trimer observed by Saykally to which you refer.[1] Upon adsorption on Cu(111) we predict that two other isomers [(a) and (b) in Fig. 2] become more stable than the cyclic structure. The analysis of the electronic structures in section 4.2 provides some explanation for why this is the case. I think the low energy adsorbed trimers predicted here are probably best described as constitutional isomers of the cyclic trimer since it is the connectivity of the water molecules that differs between the structures.

In general, our calculations predict that upon adsorption the relative energetic ordering of different isomers of a given $n\mathrm{H_2O}$ molecule cluster are liable to change from the gas phase and that the internal O–O bond distances of a $\mathrm{H_2O}$ cluster can be different when in the gas phase and when adsorbed. Notably, for the $\mathrm{H_2O}$ dimer we find that, both here on Cu(111) and on Pd(111),[2] the O–O distance decreases by about 0.2 Å upon adsorption.

1   N. Pugliano and R. J. Saykally, *Science*, 1992, **257**, 1937; F. N. Keutsch, J. D. Cruzan and R.J. Saykally, *Chem. Rev.*, 2003, **103**, 2533.
2   V. A. Ranea, A. Michaelides, R. Ramirez, J. A. Verges, P. L. de Andres and D. A. King, *Phys. Rev. Lett.*, 2004, **92**, 136104.

Dr Schön addressed Dr Wakisaka: The magic numbers in your MS measurements indicate that there are very likely clusters in the gas phase which correspond to blocks from the rock-salt structure. Our *ab initio* calculations on bulk crystalline modifications of alkali halides have shown that there is a very strong competition between, in particular, the wurtzite and the rock-salt modification in essentially all systems.[1] Thus it would be interesting to know whether other classes of clusters are present besides rock-salt based ones. Would some of the other (non-magic) peaks correspond to blocks taken from the wurtzite structure?

The $3 \times 3 \times 3$ clusters with $+$ and $-$ charge are suggested to match *via* one of their 3×3 faces. Since these clusters are most likely quite distorted in the gas phase, might their union look more like a dumb-bell, a fully merged approximately "spherical" block, or do you expect them to form a $3 \times 3 \times 6$ block as your picture suggests?

How do these clusters come into existence in the first place during the electrospray process? Do you first form individual atoms in the gas phase which then react, or does the process produce larger clusters from the solution right away? What is the influence of the solvent on the process?

1   Z. Cancarevic, PhD Thesis, Universität Stuttgart, 2006.

Dr Wakisaka replied: In our experiment, clusters are formed through fragmentation of liquid droplets generated by the electrospray. When the alkali halides in the liquid droplets are concentrated *via* evaporation of the solvent molecules from the liquid droplets during the flight in the vacuum chamber, the salt clusters are formed efficiently. The concentration and electric field effects suggest this mechanism for the cluster formation. The clusters formed in the liquid phase are isolated in the vacuum chamber. Therefore, the cluster formation was dependent on the solvent. The salt clusters were more efficiently formed from methanol than from water. Fig. 5 suggests a possible mechanism for cluster growth in the liquid phase.

Dr Hare communicated: Given a suitable choice of salt solution, would it also be feasible to study, for a given concentration, the effect of a chemical reagent, possibly as a function of time? Even as long ago as *Faraday Discussions* 61, on Precipitation, there was interest in cluster formation. With aluminium salt solutions in mind, and models of octahedra (in which the Al^{3+} cation is surrounded by 6 ligands), I remarked to P. de Bruyn that the ultimate crystal form in bulk *could perhaps* be determined as early as the event of the 3rd cation attaching itself to a dimer in solution (whether in a straight line, or at a $60°$ angle). I recall Peter de Bruyn agreeing that "this would be a beautiful experiment", but I never could devise one. Now I am wondering if Akihiro (Dr Wakisaka) has come very close to doing so? Suppose that next he were to choose $AlCl_3$, instead of KCl; is the mass spectrum sensitive enough to identify, and distinguish between, clusters that might contain the hypothetical cyclic complex $Al_6(OH)_{12}(OH_2)_{12}^{6+}$ or linear series like $Al_n(OH)_{2(n-1)}(OH_2)_{2(n+2)}^{(n+2)+}$? What then might be the effect of introducing the smallest aliquots of KOH into the solution (and could the $K^+(KCl)_x$ contribution now be subtracted out in some way) ? Over time, could we anticipate small n values superseded by large ones, for example?

A bigger question, I suppose, might be whether the salt solution (or indeed, melt) is really nothing more than "a crystal waiting to happen" (*i.e.*, comprises a pre-determined set of nuclei of given geometry), or whether the reagent—or impurity, or other field or perturbation—must first radically alter the structure of the solution (or melt) to induce its own characteristic nucleus.

Dr Wakisaka communicated in reply: This suggestion and comment are very important. I am going to observe clusters from an aqueous $AlCl_3$ solution. We are thinking that there is a relationship between the cluster structure in the solution and the crystallization. At the cluster level, ions and molecules cannot be mixed homogeneously in the solution. Since the clusters in the liquid phase are determined by the balance of interactions in the solution, these structures are sometimes different from these in the gas phase. The balance of interactions in the condensed phase controls the clustering, nucleation and crystallization. The important point is to know what kind of balance of interactions is working in the solution.