Faraday Discussions

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DISCUSSIONS

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Nanoalloy structures and catalysis part 2: general discussion†

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Riccardo Ferrando opened a general discussion of one of the papers by Damien Alloyeau: In many systems, the approach to equilibrium of the cluster shape is faster than that of chemical ordering, since the latter may require diffusion processes in the inner part of the cluster. This is already observed in binary nanoalloys,[1] and it is likely to apply even more in multi-component systems because of the increased complexity of their energy landscape. How is this problem tackled in experiments? A further comment: if multi-component systems are produced out of equilibrium, the equilibrium phase diagram may not be the best reference.

1 D. Nelli, M. Cerbelaud, R. Ferrando and C. Minnai, *Nanoscale Adv.*, 2021, **3**, 836–846.

Damien Alloyeau answered: In the present study (**https://doi.org/10.1039/d2fd00118g**), no chemical ordering was observed in the high entropy nanoalloys (HENA). Therefore we could not study the ordering kinetics. Here, we used two bottom up fabrication methods, therefore you're right, the final shape and structure of HENA depends on both thermodynamic and kinetic effects. Further works are necessary to distinguish both effects.

Éric Marceau asked: Is it known if the small, homogeneous nanoparticles, and larger, core–shell particles presented in the paper exhibit different physical or chemical properties?

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Damien Alloyeau responded: So far, we have only studied the effects of size and composition on the structural properties of high entropy nanoalloys. Nevertheless, given the close link between the structure and the properties of nanoalloys (*i.e.*, mechanical, catalytic… properties), we can expect that the size, the conformation and the defect density will influence the physico–chemical behavior of these complex nanostructures.

Marcelo M. Mariscal said: Are you able to measure by means of TEM the strain on the HENA? Is it possible to observe vacancies, stacking faults or twins? That could be very interesting to future studies on the mechanical properties of these HENA.

Damien Alloyeau replied: You are right! It is essential to study the atomic structure of high entropy alloy (HEA) nanoparticles to understand their mechanical properties. Using HRTEM, we have already identified many types of defects within our nanostructures, including, stacking faults, twin planes, dislocations and vacancies. As shown by Professor Yacaman (**https://doi.org/10.1039/d2fd00137c**), we can use GPA to measure the strain in nanoalloys, but we did not do it so far.

Ewald Janssens remarked: If one makes alloys with five metals, there must be a billion possible metal combinations. Likely the choice will be guided by the properties of the metals in their pure form, but the behavior of alloys cannot be predicted entirely on the basis of the behavior of the corresponding pure materials. What strategy will you follow to choose the combination of metals for a particular application?

Damien Alloyeau answered: Obviously, it depends on what you want to do with your nanostructures, but in general it is important to take into account the cost and availability of the selected metals when designing your high entropy nanoalloys. For example, discovering a "cocktail effect" that would boost the efficiency of noble-metal-free nano-catalysts could be very valuable.

Riccardo Farris commented: How important is the most favourable close packing of the chosen metals for the formation of a high entropy alloy?

Damien Alloyeau responded: In the present study, we have selected five face centred cubic (FCC) metals in order to favor the formation of FCC high entropy nanoalloys. However, it is worth noting that high entropy alloys can form FCC, body centred cubic (BCC) or hexagonal close packing (HCP) phases depending on their composition and formation processes. It is therefore very likely that high-entropy nano-alloys can be made with other structures.

Jette K. Mathiesen asked: When gold is added, a high degree of twinning is observed. As a conclusion, you thus relate the presence of twinning to be induced by the presence of gold. However, when looking at the nanoparticle sizes, the twinned nanoparticles are significantly smaller than the twin-free nanoparticles. How do you distinguish the effects of composition (*i.e.*, presence of gold) and size on the degree of twinning?

Damien Alloyeau responded: Experimentally, we noted that adding gold in the nanoalloys induces the formation of multi-twinned nanoparticles. As the twin formation energy is low in gold, we assume that gold brings this structural feature to the nanoalloys. Nevertheless, you're right, there may also be an interplay between size and composition effects in the twinning processes. Further experimental or theoretical works are needed to unravel this mystery.

Jette K. Mathiesen commented: In high-entropy theory it is believed that the presence of more elements promotes a higher degree of mixing due to an increased configurational entropy term. From the experimental electron microscopy data, it is observed that the elemental distribution is inhomogeneous, when more elements are introduced. Have you considered other effects besides entropy, such as enthalpy, that might dictate the mixing/segregation behavior observed? And from a general perspective, when do you believe we can call these multimetallic nanoparticles high-entropy alloys?

Damien Alloyeau answered: It is worth noting that in all samples the great majority of HEA nanoparticles are close to the equiatomic composition. Only the biggest nanoparticles slightly deviate from the equiatomic composition which could explain why they present a core–shell configuration. This result can be interpreted by the decrease in the mixing entropy term that is then not high enough to stabilise the FCC solid solution. Nevertheless, it is known in bulk HEA that the entropy-driven stabilization of a solid solution in HEA is an incomplete interpretation, since other composition-dependent parameters can also affect the crystal phase of HEA, including the variation of the enthalpy of mixing, the size difference of atoms or the electronic affinity between elements. Deeper theoretical and experimental investigations are necessary to evaluate the respective impact of those parameters on the phase diagram of high entropy nanoalloys. Changing the name of high entropy alloys to multi-metallic alloys is a debated issue in the literature. The original name has more impact and captures the history of this field of research, while the second name is perhaps a more scientifically accurate description. I think both names can be used depending on the context.

Georg Daniel Förster asked: How important is configurational entropy for the stabilization of high-entropy nanoalloys? Since you presented 4- and 5-element particles, do you have evidence that it is easier to stabilize the latter, in particular at higher temperatures?

Damien Alloyeau responded: In the present study, all the samples were fabricated at the same temperature (600 °C by pulsed laser deposition and 280 °C in solution) and in each sample the great majority of nanoparticles are FCC. Our results also suggest that the stabilization of the FCC phase depends strongly on the composition of nanoparticles, which highlight the role of the entropy of mixing. Nevertheless, given the complexity of the energy landscape of multimetallic nanoparticles, other parameters can be at play such as the variation of the enthalpy of mixing, the size difference of atoms and the electronic affinity between elements. Deeper experimental and theoretical investigations are necessary to fully understand the nanophase diagram of HEA nanoparticles.

Pascale Andreazza commented: The interest of the high entropy alloys is their high degree of mixing in a disordered chemical atom arrangement. Already for binary nanoalloys, you explained that the mobility of atoms in the substrate (diffusion coefficient) is highly dependent on the nature of atoms and is enhanced at high substrate temperature. As your deposition technique pulsed laser deposition (PLD) is performed at 600 °C, it is certainly expected that the nanoparticles obtained with the deposition of high number of atom types (5 elements) will have a high distribution of composition (chemical heterogeneity) in the assembly of particles on the substrate. Have you controlled and observed this behaviour? Have you an idea of the consequence of this variation of composition on a possible segregation, especially when we know that AuCo and AuNi are immiscible?

Damien Alloyeau answered: As described in our paper, in all the samples prepared by chemical or physical routes, the great majority of nanoalloys are close to the equiatomic composition. Nevertheless, EDX nano-analyses have shown that large nanoparticles slightly deviate from the equiatomic composition. Given that this effect due to the different mobility of metals during Ostwald ripening was also observed in many bimetallic nanoparticles, we assume that our results can be explained by this inhomogeneous Ostwald ripening. The great majority of HEA nanoparticles have FCC structures. Phase segregation is only observed in the largest nanoparticles. Therefore, one can easily assume that the deviation from equiatomic composition that results in a decrease of the mixing entropy in large nanoparticles, favors the formation of a core–shell structure. Nevertheless, theoretical works are necessary to confirm this hypothesis.

Mona Treguer-Delapierre said: With the synthetic approach adopted, can you control the shape of the multimetallic nanoparticles? Are any shapes possible?

Damien Alloyeau responded: PLD synthesis allows controlling the size of nanoalloys but there is always a shape dispersity due to defect formation and also because the nanoparticles don't have the time to reach thermodynamic equilibrium during the synthesis. Shape control can be improve if we perform epitaxial growth on crystalline substrate.

Our wet chemical protocol provide a much better control over the shape of nanoparticles because the faceting processes are driven by the ligand during nanoparticle formation in solution. So far, we only worked on the synthesis of isotropic nanoparticles but the strategies used in colloidal chemistry to form anisotropic nanoparticles can be applied to high entropy nanoalloys.

Trang Nguyen asked: What are the advantages of having multiple metallic alloys (5 or more elements) compared to bimetallic alloys in specific applications such as electrocatalysis? How do you control the composition of the alloy? (In other words: how to find the optimum loading of each element in the alloy?)

Damien Alloyeau answered: The potential of high entropy nanoalloys for applications in catalysis has already been reported in some publications (see ref. 1 for example). We can assume that the increase in defect density and lattice distortions observed when complexing the composition of nanoalloys may play a role in these promising catalytic properties. Moreover "the cocktail effect" could allow designing very efficient nanocatalysts containing no (or less) expensive and rare noble metals. Exploring the vast compositional space of HEA nanoparticles is obviously a tremendous task, but the knowledge and know-how acquired on bimetallic nanoalloys can help target the right composition.

[1] P. Xie, Y. Yao, Z. Huang, Z. Liu, J. Zhang, T. Li, G. Wang, R. Shahbazian-Yassar, L. Hu and C. Wang, *Nat. Commun.*, 2019, **10**, 4011.

Jonathan Quinson commented: You stress the potential role of Ostwald ripening in the formation of the high entropy alloys. I am wondering if you investigated this hypothesis further by, for instance, annealing the samples further (*e.g.* PLD samples) and/or assessing the effect of longer/shorter synthesis time (maybe more for the chemical method). Alternatively: treating the nanoparticles prepared by PLD in the solvent used for chemical synthesis?

Damien Alloyeau answered: Thank you for these suggestions. Of course, further studies are needed to confirm the role of Ostwald ripening in the formation of high entropy nanoalloys. Nevertheless, the size dependent composition observed here after the synthesis were also observed in many bimetallic nanosystems (CoPt, AuPd, AuCu…) and are clearly attributed to the different mobility of metals during Ostwald ripening. It remains essential to study this issue in detail in order to gain control over the size and composition of high entropy nanoalloys, especially if we want to form larger nanoparticles with homogenous structures.

Micha Polak commented: Are the core–shell structures, which were obtained for the large NPs, affected by the mixing/demixing tendencies of the binaries?

Damien Alloyeau answered: It is difficult to evaluate how the phase diagram of binary alloys affect the phase diagram of HEA nanoparticles. The HENA under study was selected because all individual elements crystallize into a FCC structure at the nanoscale and most sub-binary systems tend to mix in a FCC or a chemically ordered solid solution.

Fuyi Chen communicated: What is the difference between the HENA obtained by the physical and chemical routes?

Damien Alloyeau communicated in reply: HENA obtained by chemical and physical routes have many common structural properties. Nevertheless, HENA obtained by a chemical method are functionalized while HENA obtained by PLD are ligand-free. This could explain that the size dependent composition of nanoparticles formed under vacuum and in liquid are different because surface ligands affect the mobility of metals.

Yufei Zhang opened a general discussion of the paper by Alexis Front: It is very interesting to see the crystalline core with liquid skin, I want to know if this phenomenon only occurs on PtAg alloy nanoparticles with specific compositions, sizes and elements, or if similar can be observed for other metals or particles with smaller size such as gas phase clusters, thank you very much!

Alexis Front replied: We have shown here (**https://doi.org/10.1039/d2fd00116k**) that the surface pre-melting phenomenon is enhanced in bimetallic nanoalloys as soon as the element with the lower melting temperature segregates to the surface.

Vincenzo Amendola asked: Thank you for your interesting talk.

It is known that d-orbitals of gold have a larger “spatial extension” than in silver and this leads to the higher stability of some alloys like Au–Zn.[1,2] It has also been hypothesized that this is the reason for observing better miscibility between Au and Fe [3] or Co [4] compared to Ag–Fe [5] and Ag–Co.[6] Can you explain the reason for the choice of silver *vs.* gold and what effect is this switch expected to have on the melting properties of the nanoalloy and its overall stability?

1 O. Alsalmi, M. Sanati, R. C. Albers, T. Lookman and A. Saxena, *Phys. Rev. Mater.*, 2018, **2**, 113601.
2 V. Coviello, D. Forrer and V. Amendola, *ChemPhysChem*, 2022, **23**, e202200136.
3 D. T. L. Alexander, D. Forrer, E. Rossi, E. Lidorikis, S. Agnoli, G. D. Bernasconi, J. Butet, O. J. F. Martin and V. Amendola, *Nano Lett.*, 2019, **19**, 5754.
4 A. Guadagnini, S. Agnoli, D. Badocco, P. Pastore, R. Pilot, R. Ravelle-Chapuis, M. B. F. Raap and V. Amendola, *ChemPhysChem*, 2021, **22**, 6.
5 V. Amendola, S. Scaramuzza, S. Agnoli, G. Granozzi, M. Meneghetti, G. Campo, V. Bonanni, F. Pineider, C. Sangregorio, P. Ghigna, S. Fiameni, L. Nodari, S. Polizzi, P. Riello, S. Fiameni and L. Nodari, *Nano Res.*, 2015, **8**, 4007.
6 A. Guadagnini, S. Agnoli, D. Badocco, P. Pastore, D. Coral, M. B. Fernàndez van Raap, D. Forrer and V. Amendola, *J. Colloid Interface Sci.*, 2021, **585**, 267.

Alexis Front replied: In this case, we have chosen the Ag–Pt system because they are two elements with two very different melting temperatures. However, in this work, we seek to characterize the solid–liquid transition of a bimetallic system with elements having two very different melting points. Gold also has a low melting temperature compared to platinum and the Au–Pt system can also be interesting to study in this context. However, all systems are different and one cannot be predictive without the help of simulation or experiments. Indeed, the conclusions on the liquid–solid transition will strongly depend on the alloying properties of the system *i.e.* core–shell, phase separation, Janus structure, …

Regarding our choice of a d-band model, we perform Monte Carlo simulations in the canonical ensemble using a specific N-body potential derived from the second moment approximation (SMA) of the tight-binding (TB) scheme. This is particularly well suited to model structural properties of transition metals where the cohesion is mainly governed by the d-electron band. It has been successfully used to study the thermodynamic properties of bulk alloys, surface alloys or bimetallic nanoparticles by numerous groups across the world.

Florent Calvo said: Your results on the melting of Ag_3Pt particles suggest two precursors to melting, namely core alloying and surface melting. Are there thermal signatures of these precursors, that would be associated with changes in appropriate properties (heat capacity or other physical fluctuations)?

Alexis Front answered: There is only one precursor to the melting: the pre-melted surface. The surface and sub-surface atomic position are disordered (broad peaks on Fig. 6 at 1200–1250 K in our article, **https://doi.org/10.1039/d2fd00116k**), whereas peaks in the core (even if the core is chemically disordered) do not present broadening as compared to the crystalline structure. This is why the atomic density of atoms as a function of distance from the center, is a good signature to melting and we can distinguish the core from the surface–subsurface. We could have also calculated the heat capacity to characterize the melting transition but it would have been associated with the whole nanoparticle, without distinguishing the core and the shell. However, it is an excellent idea! I will compute the heat capacity as soon as possible.

Riccardo Ferrando remarked: For gold–platinum, the equilibrium shape at sufficiently low temperatures and a non-extreme composition is Pt@Au. The Au shell will melt at a lower temperature than the Pt core. In (AgPt)@Ag the Ag shell is very thin, so that its melting may produce very small features in the caloric curve.

Hakim Amara added: Concerning the mechanism observed on the nanoscale, it is not so surprising because it is finally what one observes for an infinite surface, *i.e.* a mechanism in two steps: pre-wetting of the surface and then a diffusion towards the bulk.

Moreover, the idea of studying another system like Au–Pt is not necessarily interesting in this case. Indeed, different groups have shown that from CoW nanoparticles, it was possible to grow tubes with a defined structure. However, this system is rather difficult to model, hence the idea of looking at Ag–Pt nanoparticles where the elements have two very different melting points.

Emmanuel Cottancin asked: In your model is it possible to take into account the possible evaporation of silver?

Alexis Front answered: In this work, the energetic model is based on a semi-empirical many-body potential derived from the density of states of the d-band metals approximated to its second moment (width of the d-band) in the tight-binding framework. From it, there is no real difficulty in studying Ag evaporation from our model. Indeed, it is mainly developed to reproduce the energy properties of a compact system (such as FCC, BCC …). It is also suitable for dealing with disordered liquid-like systems without any difficulty. For evaporation, during simulations at very high temperature, one can clearly see atoms detaching, corresponding to evaporation.

Damien Alloyeau remarked: It is well known that segregation effects in nanoparticles are influenced by the environment. In particular, nanocatalysts used for the growth of carbon nanotubes are used under gaseous media. Can your simulations take into account the effects of gas molecules? What would be your strategy for such developments?

Alexis Front responded: Our simulations can not take into account the effects of gas molecules. Actually there is no model able to do this except *ab initio* molecular dynamics (*cf.* talk of Hazar Guesmi, **https://doi.org/10.1039/d2fd00130f**). I would like to develop a tight-binding model (at least 3 elements: two metals + gas) where charge transfer will be explicitly treated (needed in the case of O_2). This model will be implemented in a Monte Carlo code to investigate equilibrium structures.

Catherine Amiens remarked: The catalysts used for the growth of CNTs are generally supported. So can you take into account the interaction with the support? This might be the reason why the shape of the NPs is maintained at higher temperature than expected.

Alexis Front replied: Yes, the substrate delays the melting since it decreases the free surface and modifies the radius of curvature of the particle (slightly "flattened" shape *i.e.* larger radius of curvature, compared to an isotropic shape). Simulations of pure Pd nanoclusters on MgO(100) have shown this delay of melting linked to the support.[1] However, the support should not modify the mechanism observed in two states: pre-melting of the surface then melting of the core.

1 C. Mottet and J. Goniakowski, *Surf. Sci.*, 2004, **443**, 566–568.

Pinkie Ntola communicated: Has this alloy been used with a support? Which support would you choose for these and why?

Alexis Front communicated in reply: No, it was not the purpose of this numerical study. Experimentally, Ag–Pt nanoalloys have been synthesized on an amorphous carbon grid.[1]

1 J. Pirart, A. Front, D. Rapetti, C. Andreazza-Vignolle, P. Andreazza, C. Mottet and R. Ferrando, *Nat. Commun.*, 2019, **10**, 1982.

Emmanuel Cottancin commented: The results obtained in the Ag_3Pt system are actually essentially the same as those found earlier in exchange Monte Carlo simulations, in particular showing the order–disorder transition in the core as a melting precursor.[1] These results are consistent with the optical absorption and low energy ion scattering measurements indicating the presence of an alloy within the core and the high stability of the silver shell, even when the nanoparticles are embedded in alumina.[2]

1 F. Calvo, E. Cottancin and M. Broyer, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **77**, 121406(R).
2 E. Cottancin, M. Gaudry, M. Pellarin, J. Lermé, L. Arnaud, J. R. Huntzinger, J. L. Vialle, M. Treilleux, P. Mélinon, J.-L. Rousset and M. Broyer, *Eur. Phys. J. D.*, 2003, **24**, 111–114.

Alexis Front replied: Well, our results are not really similar. Here, the equilibrium structure has a L11 ordered core at low temperature (also determined experimentally[1]). The order–disorder transition in the core is not a melting precursor. In our case, the melting precursor comes from the surface, in particular the (100) facets. Then the melting propagates to layers beneath the (100) facets leading to the partially melted core.

1 J. Pirart, A. Front, D. Rapetti, C. Andreazza-Vignolle, P. Andreazza, C. Mottet and R. Ferrando, *Nat. Commun.*, 2019, **10**, 1982.

Alexis Front communicated in reply: I don't understand the question. Our conclusions concern bimetallic nanoparticles…

Catherine Amiens opened a general discussion of the paper by Wolfgang E. Ernst: Can helium be replaced by another noble gas to perform the growth of the NPs at a different temperature?

Wolfgang E. Ernst replied: Helium is the noble gas with the least interaction with dopants. Other noble gases will easily form van der Waals complexes with the dopant atom or molecule. Beyond this, the superfluid helium matrix allows for unhindered motion of the dopants inside the droplets.

Christian Kuttner asked: You mention that the size of helium nanodroplets can vary between 5 and 1000 nm (**https://doi.org/10.1039/d2fd00089j**). What role does the size of the superfluid droplet play, and does it influence the quality of the nanoalloy clusters at all?

Wolfgang E. Ernst answered: For the aggregation of nanoclusters in helium nanodroplets, a respective number of corresponding atoms – here metal atoms – have to be picked up by the droplets where these atoms can form the clusters of interest. Upon each pickup of an atom and each formation of a new bond during the aggregation, energy is released into the droplet where it is dissipated, leading to the evaporation of helium atoms. In this way, the stability temperature of the droplet (0.4 K) is restored, *i.e.*, the larger the desired metal cluster, the larger the helium nanodroplet has to be so that it is not completely evaporated before the desired cluster has grown. For example, the binding energy per silver atom in a large silver cluster is 3 eV, *i.e.* for the formation of a silver cluster of 10^5 atoms, 3×10^5 eV energy are released into the helium nanodroplet. For each 6×10^{-4}, one helium atom is released from the droplet (helium binding energy). So, we should have a helium nanodroplet of about 10^9 to 10^{10} helium atoms to be on the safe side. If you just want to create a silver dimer, you can work with small helium nanodroplets. Practical examples are given in the open access article, ref. 1.

1 W. E. Ernst and A. W. Hauser, *Phys. Chem. Chem. Phys.*, 2021, **23**, 7553–7574.

Ewald Janssens remarked: The thermodynamics aspects of nanoparticle formation in helium droplets is very peculiar: you have the superfluid He droplet, the hot vapor in the pick-up zone and finally the room temperature substrate on which the particles are deposited. You characterize the particles carefully after landing on the support, but do you also know something about the structures in the (remainder) of the He droplets? Is a (nearly) equilibrium growth path followed or are the structures at this moment far from equilibrium and possibly not at all compact?

Wolfgang E. Ernst responded: It is correct that we deal with rather different thermodynamical aspects. For the nanoparticle formation inside the He droplet, there should be fast energy dissipation up to a certain nanoparticle size. As long as the heat transport is only determined by the thermal conductivity of the superfluid helium, dissipation leading to helium atom evaporation should be on a nanosecond or sub-nanosecond time scale. This estimate is based on the ratio of a typical droplet size over the thermal velocity in superfluid helium. This should be valid for the formation of dimers, trimers, … and higher (see for example ref. 1) until one can speak of a volume of the created cluster which would prevent the fast dissipation by the large mismatch of thermal velocities (bulk metal *vs.* superfluid helium) and most probably result in nanoparticle formation at a higher temperature (how high is difficult to answer). Small molecules or aggregates where cooling is fast, are known to be sometimes created in local potential minima or metastable configurations. Large nanoparticles seem to show equilibrium configurations indicating a higher temperature during formation. However, the pickup cell temperature is no issue, rather the local heating in the droplet before the slowed-down dissipation (due to the mentioned mismatch). We can assume that the obtained nanoparticle configuration is then frozen during the millisecond flight time before the shell material is added. A different matter is the thermodynamics upon heating of the deposited nanoparticles, see for example ref. 2.

1 A. W. Hauser, A. Volk, P. Thaler and W. E. Ernst, *Phys. Chem. Chem. Phys.*, 2015, **17**, 10805–10812.

2 M. Schnedlitz, D. Knez, M. Lasserus, F. Hofer, R. Fernández-Perea, A. W. Hauser, M. P. de Lara-Castells and W. E. Ernst, *J. Phys. Chem. C*, 2020, **124**, 16680–16688.

Miguel Jose Yacaman remarked: Your tomography data indicate that some of your particles were concave. Can you elaborate on why?

Wolfgang E. Ernst responded: I would not call it concave. The particles are clearly flattened where they touch the substrate. Please refer to the original paper and the supplementary information.† In some pictures, there seems to be a weaker contrast in the center of the flat part but that could be a result of the imaging.

Riccardo Ferrando asked: Can you estimate at what temperature the growth takes place in the helium droplets? This question is made because the nanoparticle shapes obtained inside the helium droplets are quite compact and regular, so that they seem to originate from atomic-scale rearrangements whose rate would be extremely low at the typical temperatures of liquid helium.

Wolfgang E. Ernst responded: This is of course one of the important open questions. While the energy dissipation in pure superfluid helium would translate into thermal relaxation within less than a nanosecond, the heat transfer will be inhibited as soon as the grown nanoparticles reach a size where the Kapitza effect might take over, *i.e.* the mismatch between the thermal speed in the grown material and the helium. However, it is not as simple as this when it comes to the details. The heat transfer from the grown material to the helium should take place through coupling to collective modes of the superfluid droplet such as phonons (volume compressional modes), ripplons (surface modes), and vortices (rotation modes). The finite size of the helium nanodroplets leads to a discrete excitation spectrum depending on the droplet size. While metal dimers, trimers, … should undergo fast relaxation to 0.4 K, nanoparticles are probably formed at higher temperature, and then frozen in their formed configuration during the flight time to the pickup of the shell material (milliseconds). However, the temperature during formation is not known yet and is an interesting topic that may be theoretically approached with respect to the coupling of the named modes.

Catherine Amiens said: What can you expect if the Au and V_2O_5 nanostructures were produced in the reverse order? Could it be a way to optimize the material and get more regular gold NPs (with possible catalytic properties) somehow supported on V_2O_5?

Wolfgang E. Ernst responded: Unfortunately we have not tried to dope first with V_2O_5 and add gold afterwards. Our intention was to produce a plasmonic core (*i.e.* gold) that should enhance possible photocatalytic properties of the formed nanoparticles. It seems that the two materials do not wet properly and therefore, I would not expect much difference regarding formation of a core–shell structure. However, the observed Janus-like structure of Au–V_2O_5 may still have interesting catalytic properties that should be explored in the future.

Alessandro Fortunelli remarked: What is the estimated temperature of growth inside the He droplets? I would expect it to be much larger than the temperature of the droplet itself and perhaps at least 200–300 K to justify the nice structures you observe and this may be due to retarded dissipation of the binding energy released by adding a metal atom to the cluster.

Wolfgang E. Ernst responded: I agree, the formation is most probably taking place at a higher temperature. Dissipation of the binding energy of the formed cluster may be hindered by Kapitza resistance, *i.e.* the reduced heat flux from the cluster to the surrounding superfluid helium due to the acoustic mismatch, the large difference of the speed of sound of the two. I cannot give a temperature value but think that the formed cluster structure will be frozen during the time of flight (around 1 ms) to the next pick-up region that adds the shell atoms.

Fuyi Chen communicated: The binding energy of a single Au atom with $(V_2O_5)_4$ in the Janus structure, obtained by the same calculation, is 3.30 eV, which is within the theoretical range. Why does the single cluster test of Au atoms fail to reach the distance convergence value?

Wolfgang E. Ernst communicated in reply: I am not sure about this question and what is meant by the “distance convergence value”. There may have been a misunderstanding concerning the word “converge”. This is not related to the theoretical treatment. It means that while the binding energy per unit quickly reaches a constant value for clusters of V_2O_5, the binding energy per unit (*i.e.* per atom) for Au is only slowly growing from dimer, trimer, … towards a much larger value for large clusters and finally the bulk. Many-body interactions cause the binding energy per gold atom to grow and finally to “converge” to the Au bulk value.

Christian Kuttner addressed all: Some groups are working on nanoalloys with a record number of different metals. I think the highest number I have seen as a preprint is up to 50; but that’s where compositional characterization becomes extremely difficult. What does the community think about the push toward such record nanoalloys and the current instrumental limitations for their analysis?

Miguel Jose Yacaman replied: I really think that the maximum number of metals should be 6. Increasing to more metals might lead to a change in the electronic structure of the Mott insulator because of electron interactions. I think that for many applications to keep a metallic state is much better.

Damien Alloyeau responded: To me, it seems more difficult to control the composition, size and atomic structure of nanoalloys made of more than 10 metals, than characterizing their atomic structure by TEM. For example: the quantitative analysis of single nanoparticle composition by STEM EDX is not much more difficult on HEA nanoparticles than on bimetallic nanoparticles, if the nanostructures have the same size.

Stephan Barcikowski answered: Maybe that goes towards an Olympic discipline rather than a scientific one.

Jonathan Quinson addressed all: I think that experimental work is actually a limit for HEA (I feel that the work is actually driven by theory so far, at least for nanoparticles for catalysis). I think that strategies to address the range of options that HEA opens might gain to shift gear a bit and for now 'limit' the importance of fully detailed characterization. Especially when we know that under catalytic conditions so many things can change. One way to bypass (for now) characterization (or live with minimal characterization) is to use machine learning, see poster "*Optimizing multimetallic nanoparticle compositions with machine learning towards high entropy alloys: case study of PtRuPdRhAu for the CO oxidation reaction*" or ref. 1.

1 V. A. Mints, J. K. Pedersen, A. Bagger, J. Quinson, A. S. Anker, K. M. Ø. Jensen, J. Rossmeisl and M. Arenz, *ACS Catal.*, 2022, **12**, 11263–11271.

Damien Alloyeau communicated in reply: I disagree with you. If the experimental works on high-entropy nanoalloys was a child, theoretical works would be a new born, since the atomic potentials describing properly these complex systems does not exist yet. Given the very vast compositional space of HEA, machine learning can potentially help design more efficient HEA nanoparticles (notably for catalytic applications). Nevertheless, beyond composition, the properties of HEA nanocatalysts will also depend on their size, shape and atomic structure and it is then essential to understand the interplay between all these parameters and to develop synthesis methods that allow their control. On this topic, there is a lack of both experimental and theoretical work to establish the link between the structure of HEA nanostructures and their catalytic properties. I agree on the fact that nanomaterials undergo strong modifications under catalytic conditions. Therefore, understanding the dynamics of HEA nanocatalysts in their application media is an important challenge to understand why they are efficient (or not) for catalytic applications. This crucial challenge can be met with atomic-scale operando analyses such as gas-cell TEM (see for example ref. 1).

1 A. Nassereddine, Q. Wang, D. Loffreda, C. Ricolleau, D. Alloyeau, C. Louis, L. Delannoy, J. Nelayah and H. Guesmi, *Small*, 2021, **17**, 2104571.

Christine Aikens opened a general discussion of the paper by Alessandro Fortunelli: Your method that combines molecular dynamics, machine learning, and DFT is very exciting (**https://doi.org/10.1039/d2fd00107a**). Does this method provide significant time savings over standard DFT with a nudged elastic band approach for finding transition states? What other advantages does the method have?

Alessandro Fortunelli replied: The nudged elastic band (NEB) approach you mention requires that initial and final structures are input by the user, and then finds the energy barrier connecting the two structures. So if you have a good idea of the initial and final structures, *i.e.*, of the reaction mechanism, you do not need to follow the complex procedure we derived and you can directly use DFT/NEB, as indeed we have also done ourselves in many previous studies of catalytic processes. However, if you do not trust your chemical intuition about the mechanistic steps because the process and the configurations involved are too complex, then you will need to explore the potential energy surface in some systematic way to find initially unknown paths. You can certainly do this exploration using pure DFT. However, since in doing this you will need to calculate energy and forces of very many configurations not too dissimilar/distant in the configurational phase space, it makes sense and it actually significantly accelerates this exploration/search if you interpolate DFT *via* a machine learning force field (or neural network potential (NNP)), to make the exploration/search using this much faster approach, and then validate your NNP findings or predictions by double checking *via* DFT *e.g. via* DFT/NEB as a final stage. Finally, let me also recall that we use meta-dynamics (m-Dyn) to accelerate kinetics, *i.e.*, to do the exploration of the reactive phase space of the system, and we perform a final check of the predictions obtained *via* m-Dyn/NNP using a rigorous DFT/NEB approach.

Graham J. Hutchings said: For your catalyst you show that leaching of manganese occurs. Is this leaching crucial for the catalytic effect that is observed? If the leaching helps create the active site then if the leaching continues, eventually all the manganese is lost and so will the catalyst activity if they are linked.

Alessandro Fortunelli answered: Thank you for your question. At the present stage of our understanding, this should be confirmed hopefully in the near future by further experiments and simulations and by control validations, leaching is crucial for catalysis only in the sense that it leaves behind unique pure-platinum configurations that have however a greater catalytic activity than those created by usual synthesis methods. In this picture, the electropositive element only plays an indirect, sacrificial role, as we believe also happens in other catalytic processes in solution under harsh oxidative conditions, such as the oxygen reduction reaction.[1] If this picture is realistic, the improved catalytic activity will then continue even after all the Mn has leached.

1 A. Fortunelli, W. A. Goddard, L. Sementa, G. Barcaro, F. R. Negreirosa and A. Jaramillo-Botero, *Chem. Sci.*, 2015, **6**, 3915–3925.

Rasmus Svensson said: Very interesting work! You have chosen (111)-slabs when modeling the behavior over nanoparticles, with rate determining steps around 1 eV. Why have you chosen to omit more under-coordinated metal sites, where the rate-determining step might be considerably lower?

Alessandro Fortunelli replied: Thank you for your interesting question. We chose the (111) facet for two reasons. First, (111) is the facet that is thought to be catalytically active, as was indeed confirmed in a parallel study of APR reaction mechanisms (to be published), so that we could compare one-to-one oxidation and APR on the same facet. Second, (111) is the most compact facet, so if oxidation proceeds on this surface it will likely proceed and probably more easily so on other facets (as you rightly suggest), such as the (100) we are currently investigating.

Riccardo Farris commented: Have you tried your machine learning force field, trained on slab models, to simulate nanoparticles?

Alessandro Fortunelli replied: We have not tried yet: this is the next step we have planned, after we include the NNP parametrization data on the (100), and perhaps the (110), facets.

Cameron J. Owen asked: Could you provide more context regarding your choice of collective variables? Is it possible that the selection of this variable could bias sampling towards one section of energy surface?

Alessandro Fortunelli replied: Thank you for your question. The collective variables (CVs) we employed, as defined in the computational details section and especially in the ESI file (that may have been difficult to access in the preprint stage but to which I refer as it is complete with technical details), are: CV-PtMn, CV-MnO, and CV-SurfMnO. They were calculated *via* the Plumed code, please see ref. 1. The first two were summed over all atoms (*i.e.*, CV-PtMn means summing over all pairs of all Pt atoms with all Mn atoms), and were used mostly to perturb the system out of equilibrium *i.e.* to explore a wider section of the energy basins. The CV-SurfMnO descriptor was instead used to promote the actual reaction.

Clearly, by definition the meta-dynamics approach depends on (is biased by) the user's choice of the CVs employed to "force" the system out of equilibrium and to promote the transformation, thus in our case especially on CV-SurfMnO. Note in this respect that in Fig. S5 of the ESI published alongside our article, it is shown how the CV-SurfMnO descriptor is able to differentiate between metastable states, which is one important feature of a CV. Note also that the actual mechanisms suggested by the meta-dynamics have then been validated by DFT/NEB. Finally, we were not able to think of (our chemical intuition could not think of) a more natural CV and reaction mechanism which our system could give rise to, in particular with respect to oxidation/leaching.

1 **https://www.plumed.org/doc-v2.7/user-doc/html/_colvar.html**.

John McGrady said: Is it easy/possible to track formal oxidation states of Mn through this cycle, perhaps using computed spin densities? Does the oxidation amount to a Mn(II)/Mn(IV)/Mn(VI) cascade, or does charge transfer from the Pt surface buffer the electron deficiency at the Mn to some extent?

Alessandro Fortunelli responded: Thank you John for your interesting question. We have not performed this analysis, although it is very interesting we have all the data and we can/will do this. My expectation is that oxidation of Mn will follow the MnO_x cascade you mention, but I think that the spin density part is more open and more intriguing.

Swathi Swaminathan said: What according to you drives the adoption of oxygen?

Alessandro Fortunelli answered: The adsorption of O_2 molecules even on pure platinum FCC (111) surfaces is an exothermic process. Adsorption energies are also sufficiently large to overcome gas-phase entropy of O_2 under standard conditions. Adsorption of oxygen is thus thermodynamically favorable. O_2 can then dissociate on the surface, and this is also thermodynamically favored. All these processes are even more favorable when manganese atoms lie in the topmost surface layer, given the higher oxygen affinity of Mn with respect to Pt, and therefore the higher adsorption energies and dissociation reaction energies.

Vincenzo Amendola said: Thank you for your inspiring talk.

Do you think the addition of a third element just to the surface of the Pt(2)Mn alloy may enable the formation of a passivating monolayer of oxide which avoids further leaching of Mn from the nanoalloy, while still preserving the availability of catalytically active Pt sites?

Alessandro Fortunelli replied: Thank you for your excellent question. We have been thinking how to solve the problem of changing the PtMn catalyst in such a way that its enhanced catalytic activity is preserved while Mn leaching is suppressed, and the addition of a third element is one interesting possibility, especially if as you suggest, one manages to create a buffer layer that protects the surface without inhibiting its catalysis. So far however we have not identified a way to do this that is promising enough to invest effort in this direction, so this interesting challenge is still open, and we will keep thinking about it.

Cameron J. Owen asked: Did you explore the effect of changing the architecture of the neural network on the accuracy of the final potential (*e.g.*, changing the depth or width)? Are the dynamics stable, given that the force error is relatively high?

Alessandro Fortunelli answered: In the parametrization stage we did test the effect of changing the architecture of the neural network on the accuracy of the final potential. Note that 30 neurons per layer is normally good enough, please see ref. 1, and indeed we found that changing the architecture had a minor effect, improving only slightly the NNP while implying a huge burden in the training effort.

Note also that we are not aware of many NNPs for three elements with a final accuracy of 10 meV A^{-1} in the forces.

We believe that this level of accuracy is sufficient to provide a sound input for a final DFT/NEB check, as we did in our work.

Finally, we were able to run MD and m-Dyn simulations using the most accurate NNP19 force field for 100 ps with zero warnings. To be reproducible, in the ESI of this discussion section† we provide one such example: there you can find the MD and Plumed input files and the file of coordinates so that anyone can re-run this MD (together with the information on NNP19 from the ESI of our article).

1 N. Artrith, B. Hiller and J. Behler, *Phys. Stat. Solid. b*, 2012, **250**, 1191–1203.

John McGrady commented: You emphasised the point that machine learning allows us to make progress without relying on chemical intuition. Could you comment on how much information as a whole, you have told us that you think would not have emerged if you had relied on chemical intuition alone? Has machine learning told us anything completely unanticipated, in this case?

Alessandro Fortunelli answered: Thank you John for your interesting question. Difficult to answer as it depends on whose chemical intuition… I would say that in this case we might have generated the same knowledge using a more traditional approach based on our experience and chemical intuition. However, I would like to stress that: (1) a systematic search such as those allowed by machine learning force fields (neural network potentials) give us more confidence on the thoroughness of our study; (2) the NNP19 we generated (to be integrated by further studies on other facets) can now be used to investigate more complex phenomena such as oxidation of nanoparticles perhaps exceeding chemical intuition and certainly exceeding our available computational resources.

Fuyi Chen communicated: The initial structures for the oxidized system are surface O on metal configurations, how do the subsurface O structures affect the fitted NNP?

Alessandro Fortunelli communicated in reply: Thank you for your question. We assumed as a starting point of the oxidation process the one generated by adsorption and dissociation of oxygen molecules on the reduced state of the catalyst surface, therefore with the initial positions of oxygen adatoms exohedral (external) to the metal slab, as in the initial configurations in Fig. 1–5 in our article. We then did not specifically test the issue of subsurface oxygens. However, please note that in the Int5 configuration of Fig. 5 an oxygen atom fills a subsurface vacancy, and that this does not introduce any particular problem in the corresponding MD, m-Dyn/NNP19 (whence DFT/NEB) simulations.

Charlie Paris opened a general discussion of the paper by Michael Bowker: How do your Pd-containing catalysts compare, in terms of catalytic performance (activity, selectivity, stability, …), with respect to the conventional CuZn-based catalyst?

Michael Bowker responded: In terms of overall productivity the standard CZA ($Cu–ZnO–Al_2O_3$) catalysts are superior. However Pd loadings are much lower here (**https://doi.org/10.1039/d2fd00119e**) than metal loadings in the CZA catalyst and so productivity per mol of metal is similar. CZA catalysts have a similar selectivity at low conversions, but are approximately 5 times more active per gram of catalyst (low temperature, low loading).

Jette K. Mathiesen commented: From the presented heat of mixing calculations, PdCu alloy structure is found not to be favored. Is the structure instead intermetallic or is Pd and Cu just not able to mix?

Furthermore, how do you think the structure of PdCu (*i.e.*, disordered alloy *vs.* intermetallic) or other possible intermetallic Pd–M compositions contribute to the methanol synthesis properties?

Michael Bowker replied: First of all, let me say that, of course, PdCu is a stable alloy system, with a fairly well-defined phase diagram. Indeed we have just published work concerning the adsorption and decomposition of formic acid and ethanol on CuPd(110) a BCC alloy surface,[1] where both species exist at the surface. However, the CuPd alloy is not stable/preferable in the presence of ZnO and a reducing environment because the PdZn alloy is so much more thermodynamically favoured (mixing energy -0.6 eV per atom *vs.* ~ -0.1 for PdCu).

Pure Pd makes three main products, methane, CO and methanol, and is mainly a reverse water gas shift catalyst under these conditions. Alloying with Cu knocks out CO dissociation and methane formation, but can still provide a hydrogenation function.

1 M. Bowker, R. Holroyd and N. Perkins, *J. Phys. Chem. C*, 2022, **126**, 15703–15709.

Didier Grandjean asked: You have presented a very extensive *in situ* XRD characterization of the Pd and PdZn catalysts supported on ZnO and Ga_2O_3, but what type of information can you get about the surface sites/phases that are actually active in the catalysis as this technique is bulk-focused? What are then the active sites/phases in the CO_2 hydrogenation reaction that you are envisaging?

Michael Bowker responded: Of the techniques we use the reactor data only relates to the surface of the material investigated; in that sense it is the most surface-sensitive technique. However, you're right, that does not tell us directly what the active site is, and many of the other techniques (XRD, XAS) are indeed bulk analysis techniques. We are engaged in *in situ* studies of the reaction by IR, which will help identify surface intermediates. Perhaps, more importantly, we may be able to image the active site by ACSTEM, combined with environmental cells to carry out the reaction, while imaging, at elevated temperature/pressure. We are developing that capability at Cardiff. Of course the experiment under those circumstances (with X-rays, high and low energy electrons in the mix) needs careful experimentation and interpretation.

My mental image of the reaction is as follows (at steady state). There will be anion vacancies present at a certain level on the oxide, if it is a suitable one (that is of the correct reducibility), enhanced by the presence of metal which can provide hydrogen atoms for the reduction. Then CO_2 is adsorbed on these vacancies, next to the metal. The CO_2 is then hydrogenated to formate, which is bidentate with one anchor on the metal and one in the oxide. The formate is then hydrogenated through to methanol, the rate determining step generally being considered to be the first hydrogenation of the formate.

Hazar Guesmi asked: Given the very low melting temperature of Ga and In, I was wondering what state (solid or liquid) the alloy could be in under reaction conditions?

Michael Bowker replied: This is a good question and one I have thought about quite a bit since it seems somewhat contradictory that such materials with low melting point elements are stable. The main reason for this is probably seen in Fig. 10 of our paper, that is, a highly exothermic mixing enthalpy of the alloy, which in turn means stronger binding of, for instance, Ga and In in a Pd lattice rather than in their own lattice.

Swathi Swaminathan asked: Trying to comprehend the mechanism, CO_2 and H_2 are both being activated on the surfaces of Pd and Zn. It makes sense that H_2 is activated on the Pd surface, and that CO_2 transforms into a bent $CO_{2\neg}$ structure. Do you see the appearance of ZnO on the surface of the nanoparticles, post reaction, if the bent CO_2 adsorbs on Zn *via* the oxygen end?

Michael Bowker responded: We don't have specific evidence regarding where exactly the CO_2 adsorbs, but it is our feeling that it adsorbs at Zn sites adjacent to the metal nanoparticles, possibly anion vacancy sites produced by reduction with spillover hydrogen. Of course, it could be that it adsorbs at Zn sites (they are very oxophilic) on the surface of the alloy nanoparticle. Ongoing theoretical calculations will hopefully shed insight into these different pathways.

Pinkie Ntola communicated: The use of Cd is restricted, most likely due to its toxicity, but what do you envisage would be the difference if you used a PdCd alloy for instance? That is, support on cadmium oxide seeing as Zn and Cd have similar electronic properties?

Michael Bowker communicated in reply: Thanks for your question. As you say, due to the toxicity of Cd we don’t generally use it in catalyst synthesis. However, so far alloying with any of the metals we have used (*e.g.* Zn, Ga, In) increases selectivity (but not necessarily activity) and so we think Cd would do the same. It may be that the main effect of alloying is a Pd ensemble-limiting one.

Fuyi Chen communicated: Pd/ZnO, Pd/Ga_2O_3 and PdZn/Ga_2O_3 catalysts display enhanced methanol productivity, due to Pd alloy formation under reaction conditions. How about PdGa/ZnO? Is it better than Pd/ZnO?

Michael Bowker communicated in reply: As we show in our paper (Fig. 5, 6 and 7c), when we put Pd and Zn on Ga_2O_3 we cannot obtain the Pd_2Ga alloy. Thanks for your interesting suggestion, but so far we have not made the structure you suggest, but we are aiming to do so in the near future. It would be very insightful to know, when made that way round, if the Ga would alloy with the Pd.

Fuyi Chen communicated: The introduction of Zn into Pd can efficiently improve the methanol productivity and selectivity. In PdZn/Al_2O_3 and PdZn/TiO_2 catalysts, what is the effect of Pd/Zn molar ratio on methanol productivity and selectivity?

Michael Bowker communicated in reply: We have not varied the ratio for the alumina case, but have for PdZn on TiO_2. In that case increasing the ratio of Zn to Pd from zero to equimolar decreases methane production with little effect on methanol selectivity. In that range Zn is in the metallic, alloy form. Increasing Zn further results in a big increase in selectivity to methanol and some increase in conversion.

Francesca Baletto asked Michael Bowker and Graham J. Hutchings: Could both authors address what is the importance and role of structural and chemical reordering within one nanoparticle – or alternatively the variety of structural motifs and chemical ordering. Could they address better the influence of the substrate?

Michael Bowker responded: We believe that ordering of Pd to PdZn probably starts form the surface (shell–core model) until the Pd particle is saturated. As stated above this then strongly affects CO dissociation on the metal and methane formation. The role of the support depends on the support - if it is titania, then methanol selectivity is poor, but if there is ZnO on the surface of the titania, then there is high selectivity to methanol.

Conflicts of interest

There are no conflicts to declare.