1 Supramolecular systems at liquid–solid

interfaces: general discussion†

David Amabilino, Ioan Bˆaldea, Pol Besenius, Peter Beton,

Matthew Blunt, Manfred Buck, Neil Champness, Lifeng Chi,

Stuart Clarke, Giovanni Costantini, Steven De Feyter, Yuri Diaz

Fernandez, Deepak Dwivedi, Karl-Heinz Ernst, Amar Flood,

Brandon Hirsch, Robert Jones, Angelika K¨uhnle, Markus Lackinger,

Trolle Linderoth, Natalia Martsinovich, Andrew Mount, Martin Nalbach,

Claire-Marie Pradier, Talat Rahman, Rasmita Raval, Neil Robinson,

Marco Sacchi, Sebastian Schwaminger, Steven Tait, Phil Woodruff

and Han Zuilhof

DOI: 10.1039/C7FD90074K

(200:[200]200) Ioan Bˆaldea opened a general discussion of the paper by Amar

Flood: Could you please give details on how you model the interaction between

the anion and the molecule?

Amar Flood answered: As noted in the paper (DOI: 10.1039/C7FD00104E), we

geometry optimized the structure of the molecular receptor using DFT and kept

this as xed. We extracted point partial charges for the atoms. The charges were

used to calculate the energy of the bromide ion in the proximity of the receptor.

The locations of the atoms were used as the origins of the vdW radii of the

molecule.

(201:[201]201) Rasmita Raval said: Yesterday we talked about not ignoring

disorder. Today, you have demonstrated that we shouldn’t ignore fuzzy STM

images. Do you think that the natural focus of scientists using SPM techniques to

image beautifully ordered regions is affecting our overview on complex molecule

behavior at surfaces?

Amar Flood responded: Yes and no. You rst have to prove your scientic

credibility in correctly locating, identifying, and then interpreting the ordered

regions. Aer that, you can tackle the harder, more fuzzy and less ordered regions

of the datasets. The same dichotomy is seen with thermodynamics (easier and

with permanence) and kinetics (harder and eeting). “Flaunt it if you got it” is all I

can say.

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7fd90074k

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Cite this: DOI: 10.1039/C7FD90074K 204

DISCUSSIONS

(202:[202]202) Steven De Feyter asked: If you kick out the anion, you go from

one adsorbed phase to the other one? In other words, removing the anion

destabilizes the adsorbed phase it was part of?

Amar Flood replied: Yes, with the correct molecular receptor on the surface,

then ejection of the anions leads to the molecules transforming into another

phase. By “correct”, I mean to say that the receptors with C18 chains in the tails

undergo the transformation. The factors (vdW and dipole) controlling this phase

selection have been reported elsewhere.1 To the second part of the question,

removal of the anion does destabilize the adsorbed phase relative to another

phase. Loss of the anion leads to larger molecular dipoles that introduce dipole–

dipole repulsions that are relieved when the molecule forms the other ordered

(and dipole stabilized) phase.

1 B. E. Hirsch et al., J. Chem. Phys., 2015, 142, 101914.

(203:[203]203) Steven De Feyter enquired: What is the time scale of the shuttling

of the anion, and of the change in adsorbate structure as a result of

a “relocation” of the anion?

Amar Flood responded: The movement of the anion is many orders of

magnitude faster than the change in adsorbate structure. From the model we

created, the barrier to motion of the bromide anion when the tip is very far away

from the anion is on the order of 10 s. As the tip gets closer, the barrier gets

increasingly smaller until it disappears. For the adsorbates reordering on the

surface (with presumed partial desorption into solution), it takes multiple

minutes to see ordered regions by STM.

(204:[204]204) Steven Tait commented: Following on from a previous question,

it would be interesting to attempt these experiments using a constant-height

scanning mode in STM so that the tip-surface distance could be controlled

independent of the STM tip-surface bias. This may allow for more control of the

dynamic behavior in the gap. It is difficult to interpret the dynamic behavior here

because the size of the tip-surface gap is so small that there is room for only a few

molecules in this region. We would like to consider the solution in the simplest

picture of having uniform properties, but that model is obviously inadequate in

the gap where there may be only one or two solvent molecules and they are likely

to be somewhat restricted to a specic orientation, therefore not having much

“liquid” character. Even though the STM tip-surface gap in ultra-high vacuum can

be modeled well, we need more development of our theoretical description of that

gap in solution/surface environments, as well as ambient environments. The work

presented here by Prof. Flood highlights some of the complexity of that interface

in the dynamic behavior of surface-bound anions, but there is much more to be

explored here, including the dynamic behavior of molecules with dipole moments

and the behavior of the solvent.

(206:[206]206) Andrew Mount said: Building on the discussion about the

potential for carrying out experiments at constant height (known distance) above

the surface, having performed a previous topological scan, could a small

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amplitude ac voltage oscillation superimposed on a chosen dc bias voltage

between sample and tip as a function of frequency not then provide interesting

experimental characterisation information? At high frequencies one might expect

to see currents and hence impedances governed by the dielectric (probing solvent

character), whilst at lower frequencies ion movement might be possible, and the

differences between distinct surface states might become evident. Are there any

technical challenges to making such measurements?

Amar Flood answered: Your suggested experiment is, in principle, exactly as

one might imagine. As for the technical challenges and if they exist, those are for

the instrument builders amongst us and that is not my area of expertise; rather, I

am a molecule builder. So if you want a molecule to make this type of behavior

“resonate”, then I and others in my area of expertise can help.

(207:[207]207) Robert Jones asked: Due to the movement of electrons at

a surface, a bromide ion on a metal conductor would have an image charge of

opposite polarity located an equal distance below the surface as the bromide is

above the surface. The bromide and its image form a relatively strong, attractive,

Coulombic interaction holding the bromide on the surface. For the bromide on

graphite case in this paper, does graphite have sufficient mobile electron density

to allow such an image charge to form, and if so, was this taken into account when

calculating the energetics?

Amar Flood responded: The assumption was made that the graphite can

support image charges and there is nothing to suggest that it does not. Yes, the

character of the graphite was taken into account in the form of the dielectric

constant when including the image charge.

(208:[208]208) Robert Jones said: In answering the question about whether an

image charge of the bromide could be formed in the graphite substrate, you

mentioned that the STM tip was metallic, and that an image charge could

therefore be formed in the tip. If such an image charge was formed in the STM tip,

is it likely, given the distances involved, that the attraction of the bromide for its

image in the STM tip could contribute to displacing it from the substrate to the

tip?

Amar Flood replied: Perfection! Yes, that is exactly what we see. As the tip

approaches the surface, the largest effect on the bromide’s overall stability is the

overlapping effects of the two image charges. However, the electric eld and the

receptor’s stabilization of the bromide are what decide which location (tip or

surface) has the lower energy for the anion.

(209:[209]209) Pol Besenius enquired: A supramolecular question from my

side. On your rst slide, you pointed out the importance of the hydrogen bond

between the aryl amide and triazole units of the halogen receptor. The two amide

carbonyl units do get fairly close, while the hydrogen bonds are locked up. Do you

ever observe a change in the hydrogen bonded conformation of the physisorbed

receptor unit on the surface in the absence of the bromide or iodide guests?

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Amar Flood responded: Good question and insight on the molecular details

and mutual differences in conformational energies that we need to consider. We

have never seen the “unfolded” conformation on the surface. We do, however,

have molecules in which some of the amides are missing and observe such

conformations, giving us a little license to make these types of judgements.

(210:[210]210) Giovanni Costantini asked: How do your calculations scale with

the effect of curvature of the tip? I guess it would be possible to have an essentially

at tip (extremely large radius of curvature) with a single atom protruding from it.

This tip would be an excellent STM resolving tip but the electric eld at the

position where the image is generated and in a relatively large region around it

would be essentially constant. How would this affect your results and main

conclusions?

Amar Flood answered: We did not examine the effect of the tip’s curvature on

the electric eld, and thus the relative stability of the bromide anion if the tip was

essentially at. However, if pressed, then I could speculate about this possibility. I

imagine a tip some 100 nm in width with one atom protruding from it at the

center of the 100-nm block (as suggested). At both very high positive or negative

biases (e.g., \_1 V or greater), then all the bromide anions would either be attracted

to or repelled, respectively, from the surface prior to the tunneling atom reaching

the area being imaged. Correspondingly, one would expect to see all bromide ions

sitting in the receptor pockets or the receptors empty. Thus, all the receptors in

the eld of view would be the same, which differs from the curved tip. With the

curved tip, we saw loss of image quality when using negative surface biases of

decreasing magnitude. In this case, the model indicates this effect arises from the

bromide being stable in the surface receptor except when the tunneling region of

the tip gets close to said bromide anions. With a 100-nm at headed tip, all those

anions will be expected to be ejected from the surface receptors at a distance far

away from the tunneling region. In that case, any and all negative biases would

show the empty receptors at the surface on account of the fact that the anions

would have been ejected at times and locations far away from the tunnel region.

(212:[212]212) Brandon Hirsch commented: Pertaining to the nature of the

effects that would impact the anion ejection, it is certainly necessary to consider

local tip shape impacts, but one should also take into account the absolute slope

of the surface when no tting to the raster scan is done. In such a case we oen

see that the surface has a slight slope moving “uphill”/“downhill” depending on

the trace/retrace. This subtle change in tip movement also acts in combination

with tip shape effects to alter the voltage-dependent anion ejection.

(213:[213]213) Peter Beton addressed Amar Flood: I have a question about ion

interaction on the surface, is it mostly bromine you’re using or are there others? Is

there any information about the binding energy?

Amar Flood responded: We have looked at bromide, iodide, and tetra-

uoroborate (BF4

\_) anions. We have quantied their binding energies to the

receptors in homogeneous solutions, which are all about 26 kJ mol\_1 and with

slight drop-offs Br\_ > I\_ > BF4

\_. So we know their relative binding energies in

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solution. We can see binding of bromide and iodide but not BF4

\_ at the surface.

Presumably binding in solution is allowed by expansion of the binding pocket to

accommodate the BF4

\_ anion’s larger size. But this cannot occur in the crystalline

(and xed) receptors on the surface. If you really care to ask about the binding

energies of the anion into the receptor pockets in the surface-arrayed system, then

that is contained in the model. Therein, image charges, and electric elds add

together. From the paper (DOI: 10.1039/C7FD00104E), at 0 V I can pull the

number out at about 64 kJ mol\_1 or \_0.66 eV or \_25 kT.

(214:[214]214) Peter Beton asked: For a bigger ion, would you get a smaller

image charge?

Amar Flood answered: Focusing on the surface-bound anions, bigger ions are

further away from the surface resulting in a smaller energy of interaction coming

as a result of the image charge. I do not know if the image would be bigger or

smaller in size.

(215:[215]215) Peter Beton remarked: Is there a value for the adsorption energy

of one of these ions on the surface, and does it vary between the different ions?

Amar Flood replied: As mentioned previously, the adsorption energy of the

anions inside the receptors is close to 64 kJ mol\_1 or \_0.66 eV or \_25 kT. Without

the receptor, which confers around 26 kJ mol\_1, the adsorption energies are

lower.

(217:[217]217) Peter Beton said: Regarding the counter ions, if it is an image

charge holding the ions on the surface, would there be the same interaction for

the positive ion?

Amar Flood replied: Yes, that is our expectation as well.

(220:[220]220) Steven Tait said: I have a comment following on from discussion

about the tunnelling gap. The question of how to model the STM tip to

surface gap is rather interesting and quite challenging. The gap is so small that

with a molecular adsorbate present there may just be room for a single counterion

(if a charged adsorbate) or a single solvent molecule. Therefore, it no longer

seems reasonable to assume a mean eld characterization for the solvent and one

must question usual ideas about screening ions in solution and other bulk effects

of the solution. In the calculations that Prof. Flood presented, we made a point to

vary the size of the tip–surface gap to explore how this would impact the behaviors

we observed. It would be very valuable to have other groups build on this work

with more detailed and rigorous calculations of adsorbate (charged or neutral)

interactions within the STM tip–surface gap. The study points out that the electric

eld off to the sides of the tunneling junction may affect the adsorbates. It would

be useful to study this for different tip shapes.

(221:[221]221) Talat Rahman asked: Long back we did calculations on the

effect of the shape of the tip in manipulation at surfaces and found that the shape

of a tip could make a difference.1 In our case, the tip was close to the surface,

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while in your case it is probably further away. However, a pointed tip could

make a difference in the presence of the electric eld that you have here. I

wonder how difficult it would be to do a couple of calculations with pointed tips

rather than the shapeless one here, or to do an experiment in which you use

a pointed tip?

1 C. Ghosh, A. Kara and T. S. Rahman, Surf. Sci., 2002, 502–503, 519–526.

Amar Flood answered: This is nice work you cited. We have long considered

the tip a black box. A mysterious entity constantly being shaped and reshaped

during the actual experiments. We expect it to have a gross shape that is illde

ned and extremely difficult to alter or control at will. That said, my personal

opinion is that we could examine all sorts of tip shapes. We may even collect data

that corresponds to one shape over another. But, we will always have to face the

reality that we will never know the tip’s shape. The work on SERS of plasmonically

active particles has the same problem. They got around it by TEM imaging of the

actual particles they got SERS spectra from. Perhaps a similar method may be

viable in this eld. Until then, I worry about drawing too much (or perhaps too

little) insight from such studies?

(222:[222]222) Talat Rahman commented: What we were doing was simpler,

looking at the shape of the tip on the potential energy surface, adatoms diffusing,

manipulation of atoms, and we found that electric eld could concentrate at

sharp tips. It might be something to concentrate on in the future.

(223:[223]223) David Amabilino asked: I’d like to come back to the counterion

effect. I didn’t notice the counterion thing taken into consideration in your

model, could you comment?

Amar Flood replied: You are correct. We were not able to account for the

counter cation. Our model could only account for the energy of a point charge in

the tip-surface region. So, the counter cation’s energy would largely be the inverse

of the anion’s. In addition, we were not able to include the dynamics for ion pair

association and dissociation. That would require a much different approach.

(224:[224]224) David Amabilino enquired: What would happen if instead of

putting an anion in your model, you put an associated dipole (because I guess ion

pairing is tight)?

Amar Flood answered: If we put an associated dipole, let’s call it a permanent

electric dipole, into our model, then we would expect the dipole to orient rather

than move within the electric eld. In addition to that part of the model, we would

need to include features for the dipole binding to the receptor (if the receptor was

designed to bind the dipole), and for the image dipoles in the surface and tip to

also stabilize the dipole. Presumably, the dipole–image dipole interactions would

be weaker in magnitude than the charge–image charge interactions. In such

cases, the receptor binding might play a bigger role than the other factors, which

is not what we saw with the bromide.

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(225:[225]225) David Amabilino remarked: I recognise the fact that this system

is nice as you have a receptor for an anion which is not a good receptor for

a cation, but nonetheless, the cation has to be around there somewhere, right?

When you ip the system with the electric eld, the anion is going to the tip as you

showed, and therefore your cation is going to the surface presumably, but it

doesn’t bind well so is it mobile? Can you design a system where you can control

the dipole orientation, e.g. the example that Giovanni showed (K docking on top

of TCNQ), and can you think about ipping that around to try and control it in

that way and switch orientation of the dipole? Could this be the basis for a device?

Amar Flood replied: Yes, the cation must be present for charge balance. We

also assume that the cation goes to the surface at large negative surface biases but

it cannot settle and order at the surface, and this situation offers no chance to

image the cations by the trace and retrace needed for STM. As to the device idea

you propose, yes, using an electric eld orienting and reorienting dipoles could

work and I believe it is the basis for ferroelectric systems. The dipole reorienting

has also been reported in ref. 1.

1 S.-B. Lei et al., Nano Lett., 2008, 8, 1836–1843.

(226:[226]226) David Amabilino asked: Does ion pairing change with electric

eld?

Amar Flood replied: I amnot exactly sure on this one. We imagine that if a tight

ion pair exists, that it will be a dipolar zwitterion. This dipole will orient in the

eld. However, all tight ion pairs have a nite lifetime. When the two ions

dissociate then they will move in the eld away from each other. So, it is likely that

the electric eld hastens the dissociation of tight ion pairs and destabilizes them.

(227:[227]227) Neil Champness opened a general discussion of the paper by

Manfred Buck: In the systems that you have studied, what are the timescales

associated with the rotation of the guest molecule?

Manfred Buck answered: While the temporal resolution of the STM is far too

low to directly access the time scale of the rotation at the temperature of our

experiments (room temperature), we estimated the range (10–104 s\_1) based on

literature work (the details are described on page 7 of our paper, DOI: 10.1039/

C7FD00115K).

(228:[228]228) Neil Champness remarked: Is there any possibility that the

guest molecule is not rotating, it’s actually ipping perpendicular to the surface?

Manfred Buck responded: Flipping over should be much less likely compared

to rotation, as the latter requires only one arm to be detached from the surface

whereas the former would require a more substantial detachment and/or an

energy-costly deformation of the molecule.

(229:[229]229) Markus Lackinger said: You mentioned that the preparation

sequence is important, or in other words the system evolves under kinetic control.

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I can clearly see this for the system with thiol SAMs as guests, but for C60 as guests

I would expect that the targeted structure is the thermodynamically most stable

one. Could you comment on this?

Manfred Buck replied: For the honeycomb network only, adsorption of seven

C60 molecules results in a thermodynamically stable state, in contrast to thiol

adsorption which, in general, is kinetically controlled and, ultimately, displaces

the network. For this reason the two types of molecules were chosen for the

experiments. For the star-modied network it is, based on the existing data,

difficult to differentiate between thermodynamic and kinetic control, i.e., whether

three fullerenes plus star are more stable than a cluster of seven fullerenes and no

star. Our observation, that the immersion time for C60 is not critical in the case of

the star-modied network, is consistent with a thermodynamically-controlled

assembly process. However, it is also conceivable that once one or two subpores

are lled, the activation barrier to displace the star molecules by C60 (e.g.

due to suppression of the rotational motion with partial detachment) becomes

too high to occur sufficiently fast. It would need in situ experiments to monitor

individual pores in order to decide whether clusters of six or seven C60, as seen

sporadically in Fig. 6 of the paper (DOI: 10.1039/C7FD00115K), form in pores void

of or by displacement of a star molecule.

(230:[230]230) Markus Lackinger asked: You were saying that lateral mobility is

a necessity for replacing the excess network forming PTCDI molecules that are

stably adsorbed within the pores by C60 with guest molecules. Can you explain

this in more detail?

Manfred Buck answered: PTCDI adsorbs strongly, so the desorption channel is

negligible as concluded from our unsuccessful attempts to clean the pores by

immersion of the network into the pure solvent at elevated temperature. That

means an adsorption site occupied by a PTCDI molecule only becomes available

for a fullerene molecule if the former diffuses laterally. Since the highly conned

environment of a subpore eliminates this channel, C60 cannot adsorb in a subpore

if already occupied by a PTCDI molecule.

(231:[231]231) Yuri Diaz Fernandez said: For the adsorption of the star molecules

you have used two different solvents. Have you observed any effect of the

solvent on the occurrence of defects, or on the occupancy of the pores? Is the

choice of the solvent based on the solubility of the molecules?

Manfred Buck replied: While we have not studied this in any depth, no obvious

difference between solvents has been observed. In general, solubility can indeed

be an important criterion but that is dependent on the particular system. Boiling/

freezing points are quite important as they dene the temperature range available

for the preparation. Another point is toxicity.

(232:[232]232) Martin Nalbach asked: If I understood correctly, you adsorb the

molecules from solution and investigate the surface aerwards in air? How do you

remove the solvent?

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Manfred Buck replied: This is done by quickly blowing the sample dry in

a stream of nitrogen when the sample is removed from the solution.

(233:[233]233) Martin Nalbach said: At the moment you take the sample out of

the solution, how do you ensure that any solute in the solvent does not precipitate

on the surface due to a local high supersaturation at the interface which is caused

by the radical decrease of solvent volume? In the experimental part of your paper,

you mention an adsorption time of about 2 min for the star molecules as well as

for C60. How do you ensure that the molecular structures you observe on the

surface are formed during the 2 min and not at the moment you locally supersaturate

the molecule concentration at the interface?

Manfred Buck answered: Usually our solutions are rather dilute (typically in

the range of 1mMto 100 mMor even below). We exclude a signicant contribution

due to supersaturation as the coverage scales with the immersion time.

(235:[235]235) Marco Sacchi enquired: Could you say that C60 could jump from

one nanopore to another?

Manfred Buck responded: We have no indication that C60 molecules jump

spontaneously. However, even at the low currents used in the work we observed

some tip-induced movement of C60 molecules, revealed by occasional streaks or

only a fraction of the molecule being imaged.

(236:[236]236) Marco Sacchi remarked: Did you consider the possibility that

the 3BPEB molecules could sit on top of one another inside the nanopores, or is

this not energetically possible?

Manfred Buck responded: There is no indication that the molecules are

systematically arranged on top of each other in a well-dened geometry. The

possibility that they are exactly on top of each other is energetically unfavourable

and should also give rise to a different tunneling contrast compared to a single

molecule. Also, on uniform layers of 3BPEB (no network) the shapes of the

molecules are clearly seen with no differences in contrast indicative of stacking.

However, partial overlap (e.g. two arms of two different molecules) cannot be

completely excluded to occur occasionally. It could give rise to irregular features

such as the one highlighted by the dotted circle in Fig. 3 of the paper (DOI:

10.1039/C7FD00115K). It is noted that these features are different from the

regular ones which arise from a stochastic rotational motion of a single molecule

in a network pore.

(237:[237]237) Steven De Feyter asked: You image by STM under ambient

conditions. Is there a specic reason why you don’t do the imaging at the liquid–

solid interface?

Manfred Buck responded: This comes from our motivation to build structures

which are sufficiently stable to allow sequential assembly. The advantage is that

very different types of molecules and different assembly schemes (e.g. hydrogen

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bonding molecules and thiols) can be combined. Furthermore, it also enables

kinetic control, thus adding another dimension to the assembly process.

(238:[238]238) Steven De Feyter commented: The liquid–solid interface might

promote solvation of the on-surface impurities and their desorption, favouring

subsequently the adsorption of the guest species.

Manfred Buck answered: For some components this might work. For example,

excess melamine present aer the synthesis of a melamine-PTCDI network could

be removed as its interaction with the surface is not that strong and its solubility

sufficiently good at elevated temperature. However, for the more strongly

adsorbing PTCDI this is not an option as the temperature required for solvation

seems to lie above the temperature where the network is stable in a solution

environment. Our attempts to clean the network pore by solvent treatment were

unsuccessful.

(239:[239]239) Peter Beton asked: You mentioned that you tried some molecules

that hadn’t been successful. What are the essential ingredients for a molecule

to be captured by the pores?

Manfred Buck responded: For the pores compartmentalised by the star

molecules, the bottleneck is their adsorption strength. While C60 was not critical,

thiols easily displace the star molecule as documented in Fig. 8 of our paper (DOI:

10.1039/C7FD00115K). So it is a balance between sufficiently strong adsorption

(also to remove impurities) and a sufficient difference in the time scale of pore

lling and displacement to allow for a kinetic control. Different thiols tried all had

similar effects, i.e., easily displaced the pore modier.

(240:[240]240) Peter Beton said: Just as a related question, in your schematic,

you’ve got the melamine being ‘nudged out of the way’. Is the lling of the pores

completely random? Is there evidence that what’s going on in a neighbouring

pore affects this?

Manfred Buck replied: We do not have any evidence that processes in adjacent

network pores affect each other. For example, the orientation of the stationary star

molecules is random. With regard to C60 adsorption in subpores, our present data

base does not allow an analysis as any correlation effects and blocking of sites by

impurities would be hard to disentangle.

(241:[241]241) Brandon Hirsch enquired: Have you attempted to position the

tip over the pore and monitor the tunnelling current uctuations?

Manfred Buck responded: Our experiments were performed at room temperature

in an ambient environment. The dri under these conditions did not allow

this type of experiments.

(242:[242]242) Neil Champness opened a general discussion of the paper by

Natalia Martsinovich: In your model, when you have introduced hydroxy groups

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to the terephthalic acid core, the hydroxy groups are involved in intramolecular

hydrogen bonding. Are you condent that this is the most stable arrangement?

Natalia Martsinovich replied: Yes, we are condent that the structure involving

intramolecular hydrogen bonding is the most stable one. We have calculated four

isomers of 2HTPA, with different positions of the OH group: next to carboxylic OH

or carbonyl oxygen, with or without intramolecular hydrogen bonding (the last

four structures shown in Table S1 of our paper, DOI: 10.1039/C7FD00112F). The

structures with intramolecular hydrogen bonding were 6–10 kcal mol\_1 more

stable (the most stable isomer has the hydrogen bonding to the carbonyl oxygen).

These energies are shown in the Supporting Information in Table S1.

(243:[243]243) Neil Champness said: If the intramolecular hydrogen bonds

involving the hydroxy groups represent the more stable arrangement, can you rule

out intermolecular hydrogen bonds to adjacent chains?

Natalia Martsinovich replied: We cannot rmly rule out intermolecular

hydrogen bonding, but we have not observed them in our search of 2D structures.

In all our 2D arrangements, the starting structures involved intramolecular

hydrogen bonding, and all the resulting minimum-energy structures preserved

this bonding. There was no ipping of OH to form intramolecular bonds.

However, we did not use alternative starting 2D structures without intramolecular

hydrogen bonding – these structures would be more likely to lead to intermolecular

hydrogen bonds to adjacent chains. I would expect such 2D arrangements

to be less stable than with intramolecular bonds: our calculations of various

isolated dimers (Table S1) showed the 2HTPA dimer with ipped OH groups as

unfavourable; intramolecular hydrogen bonds are favourable here because they

lead to formation of stable 6-membered rings.

(244:[244]244) Brandon Hirsch asked: In Fig. 5b of your paper (DOI: 10.1039/

C7FD00112F), it appears that you have placed the OH group in a random orientation.

Is there a substantial basis for this? From the STM image it appears that

there are double rows, which have epitaxial turns possibly due to kinetic trapping

between two relatively degenerate states. Is it not then likely that the double rows

result from the interactions between OH groups from molecules in neighbouring

rows?

Giovanni Costantini answered: The molecular structures proposed to interpret

Fig. 5b are only tentative but the orientation of the OH groups has not been

assigned in a random way. It is rather based on the measured intermolecular

distances (as shown for three specic molecular pairs in the same gure) which

we believe to be indeed determined by the interaction between the lateral OH

groups. What should be noted is that there is much disorder in the arrangement

of the double rows, which are extremely short and have quite a wide distribution

of inter-row distances.

(246:[246]246) Matthew Blunt addressed Natalia Martsinovich: For terephthalic

acid (TPA), no self-assembly was observed at the graphite–phenyloctane

interface for the experimental section of your presented work. However, the

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results of your molecular mechanics/dynamics calculations on this system, when

analysed as part of the Born–Haber cycle, suggest a small enthalpic gain associated

with two-dimensional self-assembly by this system (\_9.8 kJ mol\_1). In the

paper and in your presentation, you state that as the enthalpic gain is small it may

be offset by the entropic losses associated with self-assembly. Do you have any

idea what size of enthalpy gain as obtained from your calculations would provide

a unambiguous prediction for self-assembly?

Natalia Martsinovich responded: We cannot at this stage make an exact

prediction of the enthalpy gain that is sufficient to ensure self-assembly, because

of the difficulty and complexity of calculating the entropy term. We can make only

qualitative estimates. First, based on comparison with entropy calculations for

similar systems (\_TDS ¼ 3–13 kJ mol\_1 for related dicarboxylic acids1,2), the

enthalpy gain should be at least 5–10 kJ mol\_1, dependent on the system. Second,

by comparing the calculated enthalpy gains in the systems where self-assembly

was observed (DH ¼ \_22 kJ mol\_1 and larger) and the system where selfassembly

was not observed (DH ¼ \_9.8 kJ mol\_1), an enthalpy gain of at least

10 kJ mol\_1 is necessary and 20 kJ mol\_1 is sufficient. However, this value would

also depend on the nature and concentration of the solvent and solute and, in

particular, on the number of solvent molecules that are associated with one solute

molecule in solution.

1 W. Song et al., J. Am. Chem. Soc., 2013, 135, 14854–14862.

2 W. Song et al., Phys. Chem. Chem. Phys., 2014, 16, 13239–13247.

(247:[247]247) Matthew Blunt asked: Do you have any idea how accurate the

calculations are that are used to obtain values for the entropic losses associated

with 2D self-assembly (i.e. TDS terms)?

Natalia Martsinovich replied: They are not very accurate. First, the calculated

entropy term depends on the structure and concentration of the solute and on the

assumption of the free volume of the solvent,1 leading to perhaps a few kJ mol\_1

uncertainty in TDS. The second and larger source of uncertainty is the assumption

on the number of solvent molecules that are associated with one solute molecule

and are released during adsorption and self-assembly – here the uncertainty may

be as large as several tens of kJ mol\_1 (e.g. ref. 2).

1 M. Mammen et al., J. Org. Chem., 1998, 63, 3821–3830.

2 W. Song et al., J. Am. Chem. Soc., 2013, 135, 14854–14862.

Markus Lackinger responded: I believe the accuracy and reliability of TDS

estimates is rather poor. For the calculation several assumptions have to be made,

where the most crucial ones relate to the solvation shell. Here we do not even

know the number of solvent molecules involved and also the corresponding

structure is not known. However, both factors signicantly affect the outcome of

the simulations. In this respect, it appears more reasonable to refrain from an ab

initio calculation of TDS, and rather benchmark theoretical against experimental

results.

(248:[248]248) Steven De Feyter said: It’s tricky to conclude something based

on the fact you don’t see anything, especially using STM. I’msure there were many

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attempts to visualize this system. However, I was wondering if you looked, for

instance, into the impact of bias polarity and TPA concentration? Bias polarity

might have a strong inuence on the probability to “see” a monolayer. Furthermore,

to what extent is the relative surface coverage of the different polymorphs

dependent on annealing or TPA concentration?

Giovanni Costantini communicated in response: Several attempts were done

to image TPA in PO by varying the tunnelling conditions (both current and bias

voltage, at positive and negative values), but none of them produced an appearance

of any ordered molecular layer. Concerning the effect of polymorphism

(observed for 2HTPA but not for TPA), we did not explore the effect of concentration,

although we expect this to potentially play a role.

(250:[250]250) Markus Lackinger addressed Natalia Martsinovich: Do the

solvation energies you quote for heptanoic acid vs. phenyloctane refer to vacuum,

and are those experimental or theoretical values? I’m surprised to see an even

slightly higher value for phenyloctane, given the fact that TPA can form strong

solute–solvent hydrogen bonds in heptanoic acid. Can you explain what accounts

for the relatively high solvation energy in phenyloctane?

Natalia Martsinovich responded: The solvation energies reported in the paper

are with respect to an isolated molecule in vacuum. These are theoretical values

(experimental determination of solvation energies was not attempted in this

work). I believe that the high solvation energy in phenyloctane is caused by strong

p-stacking interactions of the phenyl rings of the solvent and solute molecules. A

solute molecule can have two solvent molecules stacked above and below it. As an

upper limit of the p-stacking energy, we can consider the energy of adsorption of

one phenyloctane molecule on a TPA monolayer, \_87.4 kJ mol\_1 (Table 5 of the

manuscript, DOI: 10.1039/C7FD00112F) – larger than the carboxylic acid dimer

hydrogen bond energy (\_60–68 kJ mol\_1), although this adsorption energy also

contains the interaction of the alkyl chain. The contribution of the dispersion

interaction with the solvent’s alkyl chain (which is longer in phenyloctane than in

heptanoic acid) is also non-negligible: for comparison, the solvation energy of

TPA in a longer alkanoic acid, nonanoic acid, was calculated as \_115.1 kJ mol\_1

(also with respect to vacuum),1 larger than the value obtained here for heptanoic

acid (\_93.8– \_98.6 kJ mol\_1). Thus a longer and, therefore, more exible alkyl

chain will also improve solvation. I also note that there is a signicant error bar in

the energies obtained in these molecular dynamics simulations: the standard

error of the mean of the solvation energies is up to 20.5 kJ mol\_1 in phenyloctane

and up to 41.9 kJ mol\_1 in heptanoic acid (manuscript section 3.3.2), therefore the

calculated solvation energies in heptanoic acid are not very accurate.

1 W. Song et al., J. Am. Chem. Soc., 2013, 135, 14854–14862.

(251:[251]251) Steven Tait opened a general discussion of the topics raised at

the session: What analytical techniques can be used at liquid/solid interfaces to

complement scanning tunneling microscopy (STM)? We have discussed the

complexity of self-assembly and have seen several examples of effectively

combining structural analysis, spectroscopic analysis, and computational

modeling to better understand these systems. Please respond with your ideas for

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effective analysis tools for molecular assembly in ambient or at liquid/solid

interfaces. Please give a brief statement about what type of information can be

obtained and what are the essential system requirements and key features of the

technique.

Han Zuilhof communicated in reply: Laser Ablation Electrospray Ionization

(LAESI) MS would be useful, as long as the liquid is water/protic. In this technique

the surface is irradiated with a pulsed red/IR laser. This heats up the water very

rapidly, leading to an ‘explosion’ at the surface and a plume bursting upwards.

This (vertically moving) plume with the materials of interest can be crossed by

a (horizontal) ESI spray, which transfers desorbed materials from the surface to

the MS. This technique currently offers spatial resolution in the 10’s of

micrometers, and of course coupling it to a high-resolution mass spectrometer

yields very specic molecular information. For ambient conditions this is also

ne. In those cases DART-MS might also work well and complement STM and

other techniques.

Deepak Dwivedi communicated in response: I think small angle neutron

scattering can be an alternative technique for characterizing solid/liquid interfaces.

It has been widely used for this purpose.1 Our recently published book

chapter describes the role of small angle neutron scattering for lm characterization

and we discussed the application of this technique in corrosion science.2

1 W. C. Forsman and B. E. Latshaw, Polym. Eng. Sci., 1996, 36, 1114–1124.

2 D. Dwivedi and K. Lepkov´a, SAXS and SANS Techniques for Surfactant Characterization:

Application in Corrosion Science, in Application and Characterization of Surfactants, ed. R.

Najjar, InTech, 2017, DOI: 10.5772/intechopen.69290.

(252:[252]252) David Amabilino said: Rachel Barnard and Adam Matzger used

thermal analysis to study heat of adsorption.1 Simple alkane derivatives on

graphite, but in principle you could use that technique more generally.

1 R. A. Barnard and A. J. Matzger, Langmuir, 2014, 30, 7388–7394.

(253:[253]253) Stuart Clarke communicated: There are a number of experimental

methods that can be used for the study of particular aspects of molecular

species adsorbed from liquids to solid surfaces. In general, a combination of

these methods is recommended to give a clear picture of these complex and

challenging systems. The ESI† of this discussion section presents an outline of

several of these and some references for the interested reader. It is not intended

as a full review of all the methods one might consider, nor a comprehensive

literature review, but a suggestion of some methods that might be used to

complement STM measurements, as prompted by the question raised by Steven

Tait at the Faraday meeting. There are also other more established techniques

that colleagues from a UHV background will be familiar with, such as XPS, SIMS,

EDX, BSED, FIB-TEM, EELS, EXAFS etc. which are generally available through

national and local services that are not included, that should also be employed to

characterise surfaces before and/or aer adsorption from solution. Other

methods not discussed in detail include QCM and SPR, which are helpful in

identifying that something has adsorbed, but do not identify the species. In

simple terms these approaches may be considered in several broad groups: a)

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structural methods, 2D – in plane diffraction and structure normal to the surface;

b) spectroscopic methods, e.g. surface-specic methods (such as SFG) and surface

sensitive approaches (such as RAIRS, ATR and PM-IRRAS) and related methods

such as AFM-IR; c) thermodynamics/calorimetric methods, such as Differential

Scanning Calorimetry (DSC), solution depletion adsorption isotherms and

surface titration; d) methods to investigate dynamics of adsorbed species, which

include low and high eld NMR and incoherent neutron scattering (IQNS),

exploiting ‘dynamic contrast’; e) and others, such as the Surface Force Balance.

(254:[254]254) Angelika K¨uhnle commented: Regarding further techniques for

investigating the solid–liquid interface, I would like to add that scanning force

microscopy is not limited to 2D images. It allows for acquiring 3D maps of the

interfacial region. From these maps, one can deduce conventional images parallel

to the surface, but also slices perpendicular to the surface. In these vertical slices,

you see the position of the solvent molecules above the surface.1,2 With this

technique, we can study the impact of the solvation structure on molecular selfassembly.

For many systems, the solvation structure will be crucial to understand

molecular self-assembly at the solid–liquid interface.

1 H. S¨ongen et al., Rev. Sci. Instrum., 2016, 87, 063704.

2 H. S¨ongen et al., Langmuir, 2017, 33, 125.

Deepak Dwivedi communicated in response: Thank you, Professor K¨uhnle, for

sharing these nice papers. I would like to ask if you could comment about the

image processing technique which gets used for making 2D and 3D images? Is it

possible to gure out phase segmentation by scanning force microscopy as was

done with X-ray nano-computed tomography?1

1 T. M. M. Heenan et al., Fuel Cells, 2017, 17, 75–82.

(803:[255]255) Angelika K¨uhnle communicated in reply: The AFM imaging

technique is based on probing the interface with a sharp tip mounted on

a mechanical resonator. As the tip is scanned directly in real space, 2D images and

3D data are directly recorded. Thus, no elaborate image processing is necessary.

Both 2D and 3D AFM allow various pieces of information about the tip–sample

force to be obtained (see ref. 1). With AFM, a phase boundary could therefore only

be identied based on the force measurement.

1 H. S¨ongen, R. Bechstein and A. K¨uhnle, J. Phys.: Condens. Matter, 2017, 29, 274001.

(300:[300]300) Neil Robinson opened the discussion of the paper by Steven De

Feyter: Could you tell us a little more about the possible applications of the

transfer of chiral information from solvent to the solid–liquid interface? In your

opinion, could such processes be applicable to the separation of miscible liquids?

Steven De Feyter responded: In my view, this approach has no direct applications.

While I don’t think it can be used for the separation of miscible liquids,

there are other possibilities. For instance, as we have shown some years ago in

a collaboration with David Amabilino, chiral physisorbed monolayers can be used

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to trap analytes in an enantiospecic fashion, akin to processes that happen in

chromatography.

(301:[301]301) Claire-Marie Pradier asked: What happens if you change the

solvent? Are these arrangements reversible? What happens if you dry the system?

Steven De Feyter responded: Changing the solvent has an important impact on

the appearance and the stability of certain phases. In short, the outcome of the

self-assembly process at the liquid–solid interface can be quite different,

depending on the solvent used. This certainly also relates to the impact of the

solvent used on the dynamics at the liquid–solid interface. For instance, the time

scale of out-of-plane dynamics, i.e. adsorption and re-adsorption, is system- and

solvent-dependent. Under conditions where the dynamics of individual molecules

can be traced, the residence time is shown to range from sub-milliseconds

to several hours, depending on the molecular system and solvent probed. Obviously,

the dynamics and the time scale of the dynamics are inuenced by the

presence of the solvent. Solvent evaporation or removal may lead to “freezing” and

stabilizing the molecular pattern. However, one should note that the appearance

and stability of a pattern oen depends on the concentration of the molecule in

the solution phase. A change in concentration, e.g. as a result of solvent evaporation,

may induce the formation of a new, oen higher-density phase. However,

for some systems, it is possible to kinetically trap a metastable pattern.

(306:[306]306) Talat Rahman asked: What are the essential elements in terms

of where theory is at this point? In a sense, MD is the obvious answer, since it has

the ability to include all the effects of temperature and pressure in a natural way.

The problems with MD, of course, are the length and time scales, particularly for

ab initio MD simulations. The good news is that we are not too far away from

getting there. Also, the combination of DFT and kinetic Monte Carlo simulations,

for which you need to have prior knowledge of all mitigating processes, is very

promising and some efforts are being made in that direction. To get back to your

experiments, do you get an indication of whether nucleation is important? I

assume it is. Could we then get some idea about nucleation sites from experiments?

This would save a lot of computational time.

Steven De Feyter replied: For sure, nucleation is important. And indeed, there

are efforts to use MD to gain insight into the nucleation process itself, but as you

mention, it’s time consuming. Getting experimental information on the nucleation

sites is possible, though not trivial, at least not at the liquid–solid interface,

where stable STM imaging oen goes hand in hand with the presence of

a monolayer. We are looking now into new experimental designs that could

overcome that problem, and allow us to directly visualize the nucleation process

itself.

(307:[307]307) Talat Rahman noted: Regarding these systems containing

molecules with 50–100 atoms, it may be possible to carry out ab initio MD

simulations for them. For the record, I think I can give you a reference of where

people are doing this kind of work, free energy calculations.1

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1 M. A. Caro, T. Laurila and O. Lopez-Acevedo, J. Chem. Phys., 2016, 145,

244504.

(308:[308]308) Trolle Linderoth remarked: Your detailed analysis shows that

the chiral induction by the solvent is likely to occur in the nucleation stage on the

surface. Could UHV-STM experiments at low temperatures help to pinpoint and

identify the nucleation complexes by co-adsorbing the DBA molecules and the

chiral octanol solvent?

Steven De Feyter responded: I believe that this is indeed possible. In particular,

the aspect of temperature control in a UHV environment is attractive. It may allow

the nucleation step to be recorded or visualized and provide meaningful insight

into the intermolecular interactions that are involved.

(310:[310]310) Karl-Heinz Ernst commented:We have heard several times about

nucleation. But the most stable nuclei are oen not the ones that are viable to grow.

This can be due to the fact that with increasing coverage the self-assembled layer

does not t perfectly to the substrate, and strain in the overlayer is increased.

Moreover, grain boundaries play a very important role. If they can’t accommodate

the right-handedness, certain domains may be unfavorable and become rearranged

into themore favored one. A comment to Trolle Linderoth: Concerning experimental

methodology, I wouldn’t focus always on STM here. These questions may be

addressed by high-resolution electron or photoelectron microscopy (LEEM/PEEM)

working under ambient pressure (as for ambient pressure XPS today). It would be

difficult to build this, but not impossible.

(311:[311]311) Lifeng Chi remarked: We tried vacuum deposition with molecules

which have a rigid core and three arms (alkyl chains). The molecules form

very complex structures, not only coverage- but also process-dependent. I mean

that with different deposition speed and substrate temperature, the structure

could be different. We observed at least ten phases. In contrast, when liquid

preparation was used for the same molecule, much fewer phases were observed.

For this reason, this kind of molecules may be suited for liquid preparation rather

than vacuum preparation.

(312:[312]312) Phil Woodruff commented: It would surely be nice if it were

possible to adapt the LEEM and PEEM instruments to operate at ‘near ambient’

pressures, but there are likely to be insurmountable technical problems. These

instruments achieve their high spatial resolution by operating the electron optics

at \_20–30 keV, and this is achieved with electrons emerging from the surface at

only a few eV by applying voltages of 20–30 kV across a very narrow gap between

the sample and the last optical element. Clearly at higher pressures this will lead

to breakdown. By contrast, in ‘near ambient pressure’ XPS, the ‘only’ challenge is

to have differential pumping such that the pressure in the electron energy analyser

is much lower than that in the narrow space in front of the sample.

(313:[313]313) Manfred Buck addressed Steven De Feyter: An odd-even effect in

the chiral selectivity has been observed for chain lengths between 10 and 14. What

is the explanation and is this effect limited to this narrow range of chain lengths?

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Steven De Feyter replied: We don’t have a clear view on the reasons behind this

“odd-even” effect. Only a few molecules with an odd number of carbon atoms in

the alkyl chains were tested. In all cases, a clear difference with the response of

the “even” analogues was obtained.

(314:[314]314) Karl-Heinz Ernst commented: We have environmental scanning

electron microscopy (SEM) that works with higher voltages. The same applies to

transition electron microscopy. If there would be higher interest in having

systems (PEEM, LEEM) that would probe self-assembly at the solid interface, they

would probably exist. There is no fundamental reason not to be able to build

something that I just proposed. The design, of course, would be completely

different from what we have for UHV machines.

(315:[315]315) David Amabilino opened the discussion of the paper by

Sebastian Schwaminger: I really enjoyed your presentation and your paper. I have

some questions about the magnetite nanoparticles that you prepare. You

prepared them with a covering, what was that covering? You show a binding with

your peptide immobilised on paper, what’s happening at the interfaces there?

How do you immobilise the peptide in this way? What’s the change in the

covering of your nanoparticle in the process of adsorption to the peptide? Finally,

how do you get the nanoparticle off the paper to study it?

Sebastian Schwaminger responded: Thank you. The nanoparticles are bare

particles which are not coated but are terminated with hydroxy groups, which can

be proven with XPS and ATR-IR. Furthermore, in most experiments, buffers

containing different ion species are used, which means that the surface should

contain bound species of sodium ions, chlorine ions and other buffer components

as well. It is a good question regarding what is really happening on the

interfaces between peptides and nanoparticles. We assume that there is a mixture

of electrostatic interaction and coordinative binding between the peptides and

particles. However, this experiment is not able to tell us much about the local

interactions between single peptide molecules and particle surfaces, but can be

used as a screening method which hints global interactions and, to some extent,

the affinity of the used peptides to the nanoparticles. The cellulose membrane

(basically paper) is amine-terminated, where the peptide can be linked to via its Cterminus

by peptide synthesis methods. The membrane we used is commercially

available and the peptide composition can be designed by the user. We think that

a lot of molecules are playing a role in the binding process. We think it is possible

to have a direct coordination between peptides and metal ions (here the surface

composition is changed and one bound molecule is replaced by a peptide) as well

as a binding mediated by H-bonds and electrostatic interactions between buffer

components bound to the particles and peptides (here the surface composition

will not change). We are able to elute the particles from the Glu8 and Glu6

peptides with citrate and phosphate-based buffers.

(316:[316]316) David Amabilino asked: How do you think the peptides are

binding to the magnetite; what’s the chemical process? What are the functional

groups involved (amino acid residues) and chemical interactions? You looked at

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XPS; what are the main interactions with the surface? Where is the optimum

point on your surface for binding?

Sebastian Schwaminger answered: I think there is a mixture of electrostatic

interactions and coordination chemistry possible. For example, in the paper (DOI:

10.1039/C7FD00105C) we were able to show a monodentate coordination between

a Glu8 peptide and magnetite nanoparticles. So it is denitely reasonable that

hydroxy groups can be replaced by carboxy groups. However, it is also possible

that H-bonds between the hydroxy groups and carboxy groups are formed. An

electrostatic interaction between negatively-charged peptides and the nanoparticles

is possible as well. I think it is really difficult to exactly dene the

interactions for such complex systems. Usually we are only able to observe

interactions between charged amino acids and magnetite nanoparticles. The

amount of bound peptide type is strongly dependent on pH and buffer. However,

the results shown in the article do demonstrate interactions between magnetite

and aromatic peptides as well. This behavior was only observed in unbuffered

saline. In most buffers used, usually either negatively- or positively-charged

peptides are favored for the binding with magnetite particles. From XPS, it is

difficult to say what the main interactions with the surface are, as Fe 2p spectra

are quite difficult to interpret. Furthermore, it is always difficult to describe an

ambient system ex situ with an in vacuo technique. However, a reduction of

hydroxy groups can be interpreted as an at least partial replacement by carboxy

groups. The optimum point for binding can only be answered globally and not

locally for this system. We observed the best binding conditions for negativelycharged

peptides in MES (pH 6) and acetate buffer (pH 5).

(317:[317]317) Claire-Marie Pradier enquired: If you do XPS on a layer of your

peptide on your nanoparticles, you claim there is no change in the Fe peak, but

would you detect a change on the Fe peak, coming from the surface layer?

Sebastian Schwaminger replied: This is indeed a really good question. The aim

of our statement in the paper was to show that magnetite does not oxidise and

change its physical properties upon adsorption and processing. As XPS is a very

surface-sensitive technique, it should be possible to detect changes in the

outermost layer. However, the high-spin multiplets of Fe3+ and Fe2+ compounds

and their resulting Fe 2p 3/2 peaks are quite difficult to analyse. Therefore, I think

for these nanoparticles, I am not able to distinguish between OH-terminated

magnetite surfaces and surfaces coordinated by carboxy groups with the XPS

device used for this study. Further experiments with M¨ossbauer spectroscopy,

which is less surface-sensitive, were also not able to detect a change of the electron

density and the magnetic eld at the iron ions upon adsorption of amino

acids.

(318:[318]318) Claire-Marie Pradier said: Then you do IR spectroscopy and you

look at the shi of the amide bond. Is it with the same coverage of peptide as the

one used for XPS measurements? You deduce there is a change in the conformation,

but does this not assume that you have a thick enough layer, of at least

several peptides?

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Sebastian Schwaminger replied: Yes, the IR measurement at pH 7 is of the

same sample as the one investigated with XPS. We also see changes of the amide

band with different pH values. However, the peptides are quite short and therefore

even small changes like adsorption or orientation of some side chains to the

surface can induce a conformational change. Furthermore, the pH is critical for

the peptide conformation as well, and there is an overlay of amide bands and

carboxy groups. Here, glutamic-based homopeptides were investigated and

therefore the carboxy group is very dominant in the IR spectrum. The change in

conformations does not necessarily result in layers of several peptides but,

especially for lower pH values, lateral interactions between peptides will denitely

inuence the binding.

(321:[321]321) Yuri Diaz Fernandez asked: You mentioned the formation of

peptide multilayers around the particles, but for a wide pH range poly-glutamate

molecules are negatively charged and hence repulsive interactions will dominate,

preventing formation of a multilayer. How could you explain, then, the relatively

strong circular dichroism signals observed, that seem too large for a monolayer?

Sebastian Schwaminger replied: In the case of circular dichroism, we do not

only measure the adsorbed peptides but a dened amount of peptides mixed with

a small number of nanoparticles. So what we see in the paper (DOI: 10.1039/

C7FD00105C) is how some of the peptides are affected and not a multilayer,

but otherwise you would be right. The peptides are negatively charged for all pH

regions which were investigated.

(322:[322]322) Yuri Diaz Fernandez remarked: In the experiments of attachment

of the particles to cellulose, you mentioned that depending on the pH, the

nanoparticles are detached, suggesting that the interactions with the peptides are

reversible with the pH, as expected due to the protonation/deprotonation equilibrium

of the peptides and the change in the charge of the iron oxide nanoparticles.

When you discuss your model, even at acidic pH at which you may

expect glutamates to be fully protonated, you still consider the peptides to be

bound to the surface of the particle. What evidence do you have that the peptides

are still attached?

Sebastian Schwaminger replied: Yes, we were able to detach the particles from

the peptides by changing the buffer, which is not shown in the article. We were

able to release the particles by adding citrate-buffered saline. Thereby we change

the charge of the particles to a negative charge and coordinated peptides can be

replaced by citrate ions which are added in excess. At lower pH values the

magnetite surface is charged more positively, while the Glu8 peptide is still

negatively charged at pH 4. We measured adsorption isotherms at pH 4, 5, 7, 9

and 10 and by analyzing the supernatant, we were able to determine the amount

of peptide. Hence, at all pH values an adsorption can be observed, while the

highest loading capacity can be monitored at low pH values.

(323:[323]323) Claire-Marie Pradier asked: In the last part of your paper, the

attachment of the protein, you said that proteins have a behavior similar to that of

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peptides. Does that mean that the interaction of the protein with the nanoparticles

is dominated by electrostatic interactions?

Sebastian Schwaminger replied: In our case, using green uorescent protein

(GFP) with a Glu6 tag, electrostatic interaction plays an important role in the

binding to the magnetite nanoparticles. Furthermore, from experiments where

we used mixtures of Glu6- and Gly6-tagged GFP, we can conclude that the binding

is via the tag and that the affinity is denitely inuenced by the tag. However, this

can be completely different when other particles or other proteins are used. In

this case, electrostatics are most probable to dominate the interaction.

(324:[324]324) Claire-Marie Pradier said: Can you detect by IR spectroscopy

some change in the conformation of the protein upon adsorption?

Sebastian Schwaminger replied: We have not analysed the protein binding

with IR spectroscopy, yet. However, this would be very interesting, and as GFP is

dominated by a b-barrel structure, such measurements might prove or disprove

the interaction of magnetite and GFP via a glutamic acid-based tag.

(325:[325]325) Neil Champness asked: What are your opinions on the

comparison between nanoparticles and at surfaces? What have we learned from

studies on at surfaces and how do these inform nanoparticle studies?

Sebastian Schwaminger responded: I think it is really important to think about

similarities of at surfaces and nanoparticle surfaces. There is a reason why I like

to address a nanoparticle problem to a surface science community. In my

opinion, it is always better to know what happens on a at dened surface before

changing to a more complex system. It is always easier to simplify a system and

understand the basics of what is possible (chemically) here. Many ways of

analyzing and understanding surface/interface properties have their roots in

surface science and are based on at surfaces. However, it will always be difficult

to make the transfer from at to curved surfaces.

(326:[326]326) Claire-Marie Pradier commented: Comparing results on NPs

and on planar surfaces enables us to apply complementary techniques, like NMR

on powders and “surface science” techniques on planar surfaces. As another

example, IR in various modes can be applied to nanoparticles or to at surfaces.

It’s very interesting to compare results from those various techniques for a similar

system (same molecule, same substrate in the form of either powder or of a single

crystal).

Sebastian Schwaminger replied: Yes, this might be very valuable to compare

single crystal behaviour to nanoparticles with orthogonal techniques. We thought

about this and actually wanted to start with single crystal surfaces. Actually,

techniques like IRRAS or AFM using a tip with attached peptides would denitely

improve the understanding of interactions and only work on at surfaces. The

problem hereby is that the behaviour is very different, as small spherical nanoparticles

do not possess dened regular surfaces, and more manpower, knowledge

transfer and interdisciplinarity is necessary to understand two systems. I

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think that aer more than four years, I am still far away from wholly understanding

the behaviour of magnetite nanoparticles and I do not believe that it will

be so much easier to understand the interactions of peptides and proteins on

a single crystal.

(328:[328]328) Rasmita Raval opened the discussion of the paper by Deepak

Dwivedi: Corrosion in pipes is a big problem and can involve bacteria and marine

species in the corrosion process. Do we know how corrosion inhibitors work with

respect to such living species?

Deepak Dwivedi responded: Thanks, Prof. Raval, for raising this question.

Corrosion of pipelines is a big issue and has been addressed in our recently

published article. I have not worked with microbiological corrosion, but I am

familiar with the concept that inhibitor selection depends on the type of microorganism

present in the pipeline. If it contains S-reducing bacteria, we should try

to avoid S-containing inhibitor molecules. In another article which is on the

corrosion of ancient artifacts, we have described the effect of microbiological

corrosion on ancient ship wrecks, buried inside the sea. I must say that this

problem is a big issue for oil and gas companies and still the corrosion mechanism

is not yet well understood, as described in ref. 1. The microorganisms alter

the interfacial chemistry between corrosive uid and substrate, and anaerobic

sulfate-reducing bacteria (SRB) is the most common type of bacteria which we

encounter in pipelines. Various inhibitors such as imidazolines, amino-amines,

fatty acids, p-dodecyl benzene sulfonic acids etc. are inhibitor compounds (a

complete list is mentioned in a review article, ref. 2) and organisms present

degrade the inhibitive lm formed on the steel (as organisms cause enzymatic

attack on specic functional groups of inhibitors such as benzene rings, CN

groups etc.) As far as characterization is concerned, environmental microscopy,

Raman spectroscopy and X-ray CT are various techniques which are getting used

currently by researchers. Techniques for inhibitor characterization are still

a challenge, and we have discussed this issue in our Faraday Discussions article in

detail (DOI: 10.1039/C7FD00092H).

1 K. M. Usher et al., International Biodeterioration & Biodegradation, 2014, 93, 84–106.

2

(329:[329]329) Martin Nalbach asked: How do you saturate your test solution

experimentally with CO2 and how do you quantify or measure that it is really

saturated?

Deepak Dwivedi answered: Thanks, Martin, for asking this question. For CO2

corrosion, we usually try to keep the oxygen ppm level as low as possible, and by

observing the turbidity and color of the solution, we can judge about the

saturation.

(330:[330]330) Manfred Buck remarked: Most of us at this meeting work on

rather simple systems involving well-dened substrates like single crystals, which

allow studies down to the level of atomic/molecular resolutions. For your much

more complex steel surfaces, how much information do you have on the initial

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stages of lm formation? To what extent can you relate nucleation to topography

such as screw dislocations or surface heterogeneities and/or chemical effects?

Deepak Dwivedi answered: We are thankful to Prof. Buck for pointing out the

complexity associated with lm formation on carbon steel surfaces. There are

various factors such as the texture of carbon steel, the surface energy of carbon

steel, phases such as ferrite and pearlite, and microstructure (grain size and grain

boundaries etc.). We have characterized these factors with the help of various

characterization techniques. Film formation has been characterized with in situ

synchrotron XRD and in situ Raman spectroscopy, which illustrated the phases

formed at the initial stages of the lm formation. From our point of view, the

initial hierarchical lm formation promoted the screw dislocation formation,

which was further supported with the stacking fault energy, inclusion etc. Surface

heterogeneities were characterized with FESEM and SIMS, and we have noticed

the screw dislocation loop with hierarchical morphology. In situ AFM experiments

are in our future plans.

(331:[331]331) Steven De Feyter commented: In your conclusions, you write

that sodium thiosulphate serves as a performance enhancer in corrosion inhibitor

formulations. What is the impact of other ingredients in the formulation on

the process that you describe here?

Deepak Dwivedi replied: Thanks, Prof. De Feyter, for raising this issue. As

discussed during the meeting, we have investigated the interaction of sodium

thiosulphate with other organic inhibitors (surfactants) under similar CO2

corrosion conditions and we have noticed that the corrosion inhibition efficiency

was improved. Various techniques such as in situ synchrotron XRD, in situ Raman,

ex situ Raman etc. have been utilized for investigation.

(332:[332]332) David Amabilino said: Very nice presentation and nice work.

Out of curiosity, I was wondering if you’d tried looking at the rst steps of lm

formation? Those initial steps are presumably what gets the lm going. To try and

see that nucleation, maybe it’s a common theme in this session, did you try using

atomic force microscopy to see the initial stages of the formation of the lms?

Deepak Dwivedi responded: Thank you, Prof. Amabilino, for this nice

suggestion. We believe that in situ AFM could be a nice technique to investigate

about the initial steps formation. It is worth trying and, as mentioned earlier, it is

in our future experiment list which is going to be conducted.

(333:[333]333) David Amabilino said: To make the surface smoother, maybe

you could polish it. I seem to recall seeing corrosion studies where they look at it

using electrochemical STM, though roughness is of course a big issue. Systems

like yours, it’s those rough points where nucleation is starting, and I suppose you

want to look there. STM and AFM in liquid could be useful, could you try? To

make controlled defects and see what happens there in terms of nucleation is

a really interesting opportunity. Can you comment on this?

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Deepak Dwivedi responded: It is a nice suggestion. As discussed, we plan to

perform in situ AFM with the electrochemical cell. The application of STM, as you

suggested, could be another interesting technique and this has been highlighted

by our review article published recently as well. We will follow this nice advice to

get further insights about a dislocation formation process.

(334:[334]334) Andrew Mount asked: Following on from the discussion about

applying electrochemical measurements (e.g. in SECM), there is the potential in

this corrosion system for S2O3

2\_ to undergo oxidation to form S4O6

2\_ (and there

may also be other oxidised species). Might these be implicated in nucleation and

lm formation, and which of the characterisation techniques could distinguish

such species? Electrochemical measurement, or control, of the substrate potential

should be able to probe the importance of such effects. Have such

measurements been carried out, and if so, what do they show?

Deepak Dwivedi answered: Prof. Mount, your suggestion to use scanning

electrochemical microscopy for investigating the ionic species formation and its

impact on screw dislocation-derived lm formation is nice. I agree that these

species may affect nucleation and growth. It is also worth mentioning that surface

roughness of the substrate as well as inherent defects and/or inclusions may also

act as nucleating sites. We have not used SECM, but we have discussed SECM and

its application in corrosion science in our review article; we have not used this

technique yet and it is a nice suggestion to include this technique in our project.

(335:[335]335) Neil Champness opened a general discussion of the topics

raised at the session: A general theme that is coming out of the discussion is

nucleation; what is the real question that needs to be answered and how do we

answer that particular question?

(337:[337]337) Karl-Heinz Ernst commented: I’d like to emphasize the

importance of better understanding nucleation in the liquid phase, which is

relevant for polymorphism, and therefore for crystallization in general, but in

particular also for pharmaceutical drugs. Because it requires lower supersaturation,

nucleation basically occurs only on surfaces, hardly ever as homogeneous

nucleation. So surface structure plays an important role. If one thinks about the

role of impurities at the stage of nucleation, the ripening of the colloidal nucleus

into more stable crystallites under the exclusion of solvent: this is not understood

at all. Recent progress in environmental microscopy has revealed or proved new

forms of ripening, like Viedma ripening, where stereoselective fusion of small

crystallites into larger ones occurs. So the importance and impact to materials

science demand new approaches and techniques towards better insight.

(338:[338]338) Talat Rahman remarked: In terms of theory, ab initio MD is the

best way to go as this captures the dynamics of the system and you don’t have to

put the forces from empirical potentials. How to do time- and length-scales large

enough to capture what’s going on? There have been promising recent advances.

Someone has been able to show, for molecules in solvents, at the liquid–solid

interface, that you could do MD ab initio at timescales large enough to be able to

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capture the free energies of these systems. Promising steps are being taken by

a number of groups.

(340:[340]340) Talat Rahman commented: There are some new experimental

setups in which they can measure the vibrational density of states while reactions

are happening, using inelastic M¨ossbauer scattering (Prof. Roldan’s group at

Ruhr University Bochum). These are very promising as they allow investigation of

the surface in operando. They also provide measures that can relate directly to

theory.

(341:[341]341) Neil Champness asked: The crystal engineering community

talks about similar issues relating to nucleation. What can we learn from those

who work on crystal structure prediction?

Deepak Dwivedi communicated in response: Thanks, Prof. Champness, for

raising this nice question. I would like to highlight a paper by C.-Y. Wu et al. who

have used synchrotron-radiation-based infrared nanospectroscopy (SINS).1 The

application of such in situ synchrotron techniques may enable the nucleation and

growth phenomenon to be described in great detail.

1 C.-Y. Wu et al., Nature, 2017, 541, 511–515.

(342:[342]342) Talat Rahman commented: I am more interested here in

..phenomena than the crystal structure – how are things happening in.a lot of

factors are involved, and we need to understand under what kinds of conditions

you could stabilise structures. In this context, I agree that DFT calculations may

not be the optimal way to proceed. A lot can be learned from molecular dynamics

and kinetic Monte Carlo simulations using empirical and semi-empirical

potentials, which include the effects of temperature either directly through the

lattice (molecular dynamics) or indirectly (kinetic Monte Carlo). While molecular

dynamics simulations can be achieved to microseconds, kinetic Monte Carlo

simulations can be run to seconds and minutes, as in the lab. For accuracy

checks, DFT calculations can then be performed for selected cases and ratelimiting

parameters validated. Of course, it is imperative that contact be made

with relevant experimental data at all stages possible.

Amar Flood responded: To address these types of phenomena, we have been

thinking about using multi-scale simulations. However, aer some involvement

with molecular dynamics and multi-scaling from that starting point, it is clear

that 10-fold speed-ups are what are expected (and are applauded) from within that

community. However, and as noted by many others already, we do not need to go

from one to ten microseconds but to get into seconds and minutes.

(345:[345]345) Talat Rahman said: Minutes is when we see something that’s

beyond nucleation stage.

Amar Flood answered: The only solution we have for the use of MD and multiscale

simulations to understand the self-assembled structures is the same

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strategy used with DFT, and that is to start as close as possible to the thermodynamic

equilibrium point.

(347:[347]347) Talat Rahman remarked: Relying on DFT for everything may not

be the best way to go. Classical MD with empirical or semi-empirical force elds

are good enough now to give us a starting point, but I think you still need that

accuracy that you get from DFT to check things. In the ab initio MD simulations

that I mentioned earlier, the point is not to carry out simulations for nanoseconds

or microseconds, but rather to use analytical methods to obtain information from

the trajectories you get for short time scales (\_10 ps, or 1 ns). It appears that you

can get reliable values of free energies from such procedures. That beats looking

at trajectory... that could take forever. The point is, we are addressing these issues

in the computational modelling of materials.

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