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DISCUSSIONS

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Properties of self-assembled nanostructures: general discussion

Javier Reguera, Edward Malachosky, Matthew Martin, Moritz Tebbe, Bruce Law, Lucio Isa, Helmuth Moehwald, Yangwei Liu, Fernando Bresme, Dhanavel Ganeshan, Christopher Sorensen, Suvojit Ghosh, Andreas Fery, Petr Král, Asaph Widmer-Cooper, Christina Graf, Almudena Gallego, David Schiffrin, Brian Korgel, Gunadhor Okram, Subramanian Sankaranarayanan, Yifan Wang, Toshiharu Teranishi, K. Michael Salerno, Sean McBride and Xiao-Min Lin

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Subramanian Sankaranarayanan presented his invited discussion remarks ("Sub-nanometer ligand asymmetry leads to Janus-like nanoparticle membranes"): We had interesting presentations on the mechanical properties of self-assembled nanoparticle membranes and the optical properties of nanodisks. The ligand dynamics and conformation play a key role in dictating the properties of these self-assembled structures. To explore the ligand dynamics, we have performed coarse-grained molecular dynamics simulations of the self-assembly process. We find that the ligand shell around the self-assembled nanoparticle membranes has an asymmetric distribution with the density being higher at the air-facing side. The presence of this asymmetry leads to the folding of membranes into tubes when exposed to e-beams, as observed experimentally by the first speaker of this session.[1] Coarse-grained simulations further suggest that the asymmetry originates due to mobility of the ligands on the nanoparticle surface, and is a strong function of the ligand coverage. The findings of our simulations are corroborated by X-ray scattering studies. Our experimental and simulation study demonstrates that a small change in molecular distribution can impact the macroscopic properties of self-assembled nanostructures.[2]

1 Y. Wang, P. Kanjanaboos, S. P. McBride, E. Barry, X.-M. Lin and H. M. Jaeger, *Faraday Discuss.*, 2015, DOI: c4fd00243a.
2 Z. Jiang, J. He, S. A. Deshmukh, P. Kanjanaboos, G. Kamath, Y. Wang, S. R. S. Sankaranarayanan, J. Wang, H. M. Jaeger and X.-M. Lin, *Nat. Mater.*, 2015, DOI: 10.1038/nmat4321.

Christopher Sorensen opened a general discussion of the paper by Yifan Wang: The high strength of the membranes is interesting. Below eqn (2) in your paper,[1] you state that "the nanoparticles are interacting *via* the interpenetration of shells of short alkanethiol ligands". Do you think that this is the only source of the membrane strength? What about the van der Waals attractions between the gold particles?

1 Y. Wang, P. Kanjanaboos, S. P. McBride, E. Barry, X.-M. Lin and H. M. Jaeger, *Faraday Discuss.*, 2015, DOI: c4fd00243a.

Yifan Wang answered: In our system the ~5nm diameter gold nanoparticles are separated ~1.7nm by organic ligands. As estimated in ref. 30 in our manuscript,[1] at this separation the van der Waals attraction between nanoparticle cores contributes less than 10% of the overall membrane strength. So we believe the high strength of membranes comes indeed from the ligand–ligand interactions in the interstices between particles. This conclusion is also supported by simulations in other publications.[2,3]

1 K. E. Mueggenburg, X.-M. Lin, R. H. Goldsmith and H. M. Jaeger, *Nat. Mater.*, 2007, **6**, 656–660.
2 P. Schapotschnikow, R. Pool and T. J. H. Vlugt, *Nano Lett*, 2008, **8**, 2930–2934.
3 K. M. Salerno, D. S. Bolintineanu, J. M. D. Lane and G. S. Grest, *Phys. Rev. Lett.*, 2014, **113**, 258301.

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Christopher Sorensen discussed: We have measured the enthalpy of dissolution of dodecylthiol-ligated gold nanoparticles with a gold diameter of *ca.* 5 nm in a toluene solvent. From this we find that the depth of the attractive potential between these gold nanoparticles is 0.3–0.4 eV per nanoparticle, which was surprisingly high to us. This large potential seems to be consistent with the high membrane strength.

Yifan Wang replied: From our experiments we roughly estimate the energy needed to separate two nanoparticles as: $U \approx \sigma^* \cdot (\pi d^2)/4 \cdot (\sigma^* d)/E = (\pi d^3 \sigma^{*2})/(4E)$, where σ^* ~11 MPa is the fracture strength, d ~7 nm is the nanoparticle diameter, and E ~1 GPa is the monolayer Young's modulus. These values correspond to U ~0.2 eV, which is close to the attractive potential measured in the nanoparticle solvent. However, it is important to note that our mechanical measurements were performed on membranes that were completely dry, *i.e.*, long after both the solvent (toluene) and the water had evaporated.

Andreas Fery continued the discussion of the paper by Yifan Wang: Have pre-stress and surface tension effects been taken into account in the atomic force microscopy (AFM) deformation experiments? How exactly was the Young's modulus of the membranes determined in the earlier publication you refer to?

Yifan Wang responded: In our previous work,[1,2] both the pre-stress and the Young's modulus of the nanoparticle membranes were extracted from AFM indentation measurements on freestanding membranes across a hole. The pre-stress and Young's modulus were determined by fitting the linear and cubic components, respectively, of the force–indentation curve to models based on the deformation of thin elastic plates.

1 K. E. Mueggenburg, X.-M. Lin, R. H. Goldsmith and H. M. Jaeger, *Nat. Mater.*, 2007, **6**, 656–660.
J. He, P. Kanjanaboos, N. L. Frazer, A. Weis, X.-M. Lin and H. M. Jaeger, *Small*, 2010, **6**, 1449–1456.

Javier Reguera addressed Yifan Wang and Subramanian Sankaranarayanan: Regarding the bending of the nanoparticle monolayer, and the interpretation of

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the remark that was made during the conference, it was claimed that this bending was due to the rearrangement of the ligands that took place when the nanoparticles were situated at the water–air interface. It was discussed that this took place at the defect of ligands covering the nanoparticles. I have some questions regarding this:

1. Was the ligand density (or the ligand : gold ratio) measured experimentally?
2. What is the cleaning process that was performed to achieve the claimed lack of ligands?
3. Regarding the simulation, once the ligands rearrange due to the water–air interface, what happens when the nanoparticle monolayer is transferred to the air and there is no longer an interface? Would they rearrange again if the time scale is long enough?
4. Have the free ligands been considered in the explanation and in the simulation?

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Subramanian Sankaranarayanan responded: The bending is attributed in part to the asymmetry in the distribution of the ligands on the self-assembled nanoparticle membrane. The answers to the specific questions are below:

1. It is not possible with the current characterization techniques to directly measure the ligand density or distribution on the nanoparticle surface. Although a thermogravimetric analysis (TGA) measurement was performed, it cannot give atomistic details regarding the ligand distribution. For example, there can be enhanced coverage on the under-coordinated sites such as edges and corners compared to the faces. Such details are difficult to probe experimentally.
2. The nanoparticles were washed multiple times to remove the excess ligands as well as to make the nanoparticles deficient in ligand coverage.
3. The asymmetry persists even after the nanoparticle membrane is transferred since the ligand–ligand interactions post-reorganization are strong enough to maintain this asymmetry.
4. No, these were simulated for microseconds and we observed no rearrangment. Free ligands are not considered in the set of simulations presented. The assumption is that washing the experimental samples removes the free ligands. We are studying the role of excess ligands as part of the ongoing work.

Yifan Wang responded: We would like to clarify that the bending under electron beam exposure simply exploits an asymmetry in ligand density that pre-exists because of the monolayer preparation at a liquid–air interface. We have direct evidence of this asymmetry from detailed quantitative measurements using X-ray scattering.[1] The electron beam irradiation is not expected to produce the asymmetry. Further responses to the questions are below:

1. We have attempted to measure the ligand density through TGA. As indicated in the supporting material of ref. 26 in our paper,[1] TGA tends to overestimate the accurate ligand density on nanoparticle crystal facets, so the exact ligand density on crystal facets is difficult to obtain. However, we can compare the particle spacing of monolayers formed from different washing steps from the same nanoparticle solution, and show that it continues to decrease after each washing step. From this, we infer that after multiple washing steps, the surface ligand is becoming deficient.[1]
2. The Au nanoparticle solution was cleaned by adding a certain amount of ethanol to a toluene solution to precipitate the nanoparticles. The supernatant

was decanted, and the same process was repeated multiple times, and aided by centrifugation.

3. We found in the simulation that the ligand rearrangement depends on the mobility of the ligand.[1] If the thiol head group is not mobile, the asymmetry which develops at the air–water interface is purely due to conformational changes, and can disappear after water is removed. However, if the thiol head group is mobile, then the ligand rearrangement is more robust, and can resist changing back to its symmetric conformation after the water is removed due to ligand–ligand bundling. These simulations were performed using coarse-grained models and carried out over long time periods (500 ns), suggesting that the result is close to what we observe experimentally.

4. The role of free ligands was not considered in the simulation, but is explicitly considered in our explanation. A large amount of the free ligand is not the reason that causes the asymmetry to develop in the membrane. On the contrary, we find that adding a large amount of free ligand back into solution causes the nanoparticles to be well ligated and the ligand asymmetry to disappear.

1 Z. Jiang, J. He, S. A. Deshmukh, P. Kanjanaboos, G. Kamath, Y. Wang, S. R. S. Sankaranarayanan, J. Wang, H. M. Jaeger and X.-M. Lin, *Nat. Mater.*, 2015, DOI: 10.1038/nmat4321.

Helmuth Moehwald returned to the general discussion of the paper by Yifan Wang: As the Au nanoparticles are very strong scatterers it is difficult to measure the ligand by small-angle X-ray scattering (SAXS). How then do you measure it?

Xiao-Min Lin replied: We did not directly measure the distribution of the ligand by SAXS. Instead, we transferred the nanoparticle monolayer from the air–water interface onto a silicon substrate through either a stamping or draping process, so that either the air-facing side or the water-facing side of the monolayer make contact with the substrate. We then measured the grazing-incidence small-angle X-ray scattering (GISAXS) pattern of these monolayers and fit the data using a multilayer distorted wave Born approximation (DWBA) model, and determined the distance between the center of the nanoparticle monolayer with respect to the substrate, taking into account both the particle size distribution as well as the variation of particle height relative to the substrate. Subtracting the particle radius from this height value, we can obtain the ligand shell thickness sandwiched between the particle core and the substrate. Using this technique, we found a ligand asymmetry of roughly 6 Å between the water-facing side and the air-facing side of the membrane.

Helmuth Moehwald opened a general discussion of the paper by Toshiharu Teranishi: The coupling scheme described in Fig. 4 of your manuscript[1] involves a redistribution of the oscillator strength between the two absorbing states, but conservation of the integrated intensity. Experimentally, however, a change in intensity upon interaction is observed. How can one understand this?

1 L. Chen, M. Sakamoto, R. Sato and T. Teranishi, *Faraday Discuss.*, 2015, DOI: c4fd00239c.

Toshiharu Teranishi replied: The in-plane plasmon coupling of the face-to-face assembled nanodisks induces a blue shift of the localized surface plasmon

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resonance (LSPR) peak and a decrease in optical density. The out-of-plane plasmon coupling of the face-to-face assembled nanodisks induces a red shift of the LSPR peak and an increase in optical density. A decrease in the absorption intensity in Fig. 4 results from the precipitation of long nanodisk arrays.

Helmuth Moehwald asked: Compared with metals, semiconductors have a lower electron density, which makes the plasmon band sensitive to changes in the free electron density. Hence a covalent bond between thiols and the metallic particle would change the density of free electrons, thus changing the spectra. What is expected for a weaker ligand bond, *e.g.* a coordination bond or electrostatic bond?

Toshiharu Teranishi responded: As you suggested, the plasmon band of semiconductors is very sensitive to changes in the free carrier density. A coordination bond is intrinsically similar to a covalent bond. Therefore, the ligand exchange of amine-protected copper sulfide nanodisks with thiols does not lead to a significant change in the hole density. Electrostatic bonds would not affect the carrier density of semiconductors.

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Suvojit Ghosh continued the general discussion of the paper by Yifan Wang: The scanning electron microscopy (SEM) images were obtained after transferring the cracked films from the PDMS substrate to silicon. Do the authors have any comments on how the fractures are preserved and/or affected by this transfer, especially considering that this transfer may cause a release in the strain that caused the cracks?

Yifan Wang responded: The PDMS transfer process was performed as gently as possible, and the amount of strain applied to the PDMS during the transfer was undetectable within experimental error. To study the effect of the transfer process on the nanoparticle membranes, we did control tests by transferring unstrained membranes, and no cracks were observed after the transfer process. Hence we believe the PDMS transfer process adds very little strain and does not cause fractures in the sample.

Suvojit Ghosh remarked: The observed stiffness of the "scrolls" are an order of magnitude higher than the predicted values. However, the authors predict the values by considering there to be no out-of-plane linkages between the particles. Is it possible that considering such linkages will change the prediction? If so, will that provide a better estimate of the heightened stiffness?

Yifan Wang answered: It is important to note that the stiffness enhancement of the scrolls refers to an enhancement of the bending stiffness, not the stiffness to stretching. The large effective thickness is simply another way of stating this. We indeed believe that the reason for the large bending stiffness is rooted in the fact that the particles cannot be treated as point particles connected by in-plane nearest neighbor springs (as in simple continuum mechanics). Instead, the finite particle size and the way that these particles interact through their interpenetrating ligand shells seems to be key in hindering the bending while leaving the stretching unaffected. One way to understand the question posed here is that out-of-plane linkages correspond to ligand-mediated interactions beyond nearest

neighbors that oppose changes in the 'bond angle' between nanoparticles. A larger effective thickness in this scenario is then equivalent to a more effective hindrance of out-of-plane bending. This is our current understanding of the enhancement phenomenon and, as suggested by the questioner, it gives a consistent explanation of the observed behavior.

A second way to understand the question is to consider the linkage between layers in our multilayer-walled scrolls. If the interaction strength between layers is similar to the intra-layer particle–particle interaction, this would give an enhancement of < 3 times of the bending stiffness, far less than the 1–2 orders of magnitude we measured. Thus we believe this huge enhancement has to come from the discrete microstructure, and especially the finite particle size, in our system.

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David Schiffrin and **Fernando Bresme** commented on the paper by Yifan Wang: The study of the fracture mechanics of membranes constructed from alkanethiol-capped nanoparticles can give valuable information on the nature of interparticle interactions, and predict the superlattice stability. The nature of the forces responsible for their mechanical properties requires careful consideration. The authors propose in their analysis of the critical tensile strength (eqn (2)) that nanoparticles interact through the interpenetration of the dodecanethiol ligand.

The interaction energy between C_{12}-capped Au nanoparticles required for the formation of superlattices has been previously analysed employing the Hamaker formalism for the calculation of dispersion interactions.[1] Khan *et al.* demonstrated that both repulsive ligand mixing and core–core attractive interactions must be taken into account in the calculation of the interparticle energy required for the formation of superlattices in the case of 5 nm Au nanoparticles capped by dodecanethiol.[2] These authors considered nanoparticles in a solvent with similar properties to the hydrocarbon chains, and one may argue that the hydrocarbon–hydrocarbon interactions considered in that work would be different from those in vacuum, *i.e.*, in conditions similar to those of nanoparticle arrays. They argue, however, that due to the differences in the Hamaker constants, one only needs to consider the Au–Au Hamaker constant through the ligand medium. In the case of large particles, 5.2 and 9.1 nm, as employed by Wang *et al.*,[3] it could be that the main energy contribution approaches that of two slabs of Au separated by a hydrocarbon layer. Answering in full this question would require further understanding on how the behaviour of Au in small clusters differs from that in bulk gold.

The equilibrium interaction energy minimum calculated by these authors with the Hamaker constant from ref. 4 corresponds to a ratio of core–core centre distance to nanoparticle diameter of 1.33, from which a 1.7 nm core–core separation distance can be calculated. From the results reported by Wang *et al.* (Fig 1b),[3] the average core to core separation in the superlattice formed by solvent evaporation of the nanoparticle solution is 1.8 nm, in good agreement with the prediction above. In addition, it is interesting to note that a model without chain interpenetration, but only considering indentation of the ligand shells, predicts equally well the observed core–core equilibrium separation distance between the nanoparticles.

The interactions between nanoparticles have also been investigated using atomistic computer simulations.[5,6] These simulations indicate that large cohesive

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energies can result from the van der Waals chain–chain interactions between alkanethiols coating neighbouring molecules. For small nanoparticles ~2 nm in diameter, the interaction is strongly dependent on the chain length; for dodecane-coated particles this results in pair energies of ~3 eV, which are significant. For larger nanoparticles, 5 nm in diameter, where the interactions should be stronger,[6] simulations show that the van der Waals interactions between alkanethiol chains can drive the formation of close-packed arrays at the water surface with distances between the gold core edges of ~1.3–1.4 nm for octanethiol ligands, which are consistent with the distances inferred from reflectivity experiments,[7] and with phenomenological models based on the ratio of the hydrocarbon chain length to core radius.[6] For dodecanethiol ligands, the estimated edge-to-edge distance, using the phenomenological model in ref. 6, would be ~1.9 nm, in reasonable agreement with the experiments. These atomistic simulations thus show the importance of the van der Waals interactions in defining the interparticle distance too, but it is important to note that, almost invariably, it is assumed in these computations that the cores are fully coated. The work by Wang *et al.*[3] shows that this might not always be the case. In that situation, core–core interactions may play a more important role. Indeed the Young's moduli reported, several GPa in magnitude, indicate a large energy density. For characteristic nanoparticle–nanoparticle distances and diameters of ~6 nm, and using simple scaling arguments, the pair interactions should be orders of magnitude higher than the characteristic pair energy inferred from existing simulations considering van der Waals interactions only. Interestingly, it was shown in ref. 6 that the Young's modulus of nanoparticle superlattices depends strongly on the temperature, particularly on the melting temperature of the hydrocarbon chains. Below the melting transition, Young's moduli of the order of GPa were observed, whereas above the transition, the Young's modulus decreased to 10^{-2}–10^{-1} GPa, which would give nanoparticle pair energies more in agreement with what is expected from previous simulation estimates (~10s of eV).

From the above, it can be concluded that, for nanoparticles where there is no full coverage, and where the ligands are above the melting temperature, core–core interactions may play a role in defining the stability and mechanical strength of nanoparticle membranes.

1 H. C. Hamaker, *Physica*, 1937, **4**, 1058–1072.
2 S. J. Khan, F. Pierce, C. M. Sorensen and A. Chakrabarti, *Langmuir*, 2005, **21**, 487–497.
3 Y. Wang, P. Kanjanaboos, S. P. McBride, E. Barry, X.-M. Lin and H. M. Jaeger, *Faraday Discuss.*, 2015, DOI: c4fd00243a.
4 P. C. Ohara, D. V. Leff, J. R. Heath and W. M. Gelbart, *Phys. Rev. Lett.*, 1995, **75**, 3466–3469.
5 K. Tay and F. Bresme, *Mol. Simul.*, 2005, **31**, 515–526.
6 U. Landman and W. D. Luedtke, *Faraday Discuss.*, 2004, **125**, 1–22.
7 J. Reguera, E. Ponomarev, T. Geue, F. Stellacci, F. Bresme and M. Moglianetti, *Nanoscale*, 2015, **7**, 5665–5673.

Yifan Wang replied: We agree that the details of the interactions that control the mechanical strength of nanoparticle superlattices are complex and that additional experimental measurements, especially of the temperature dependence of this strength, coupled with further atomistic simulations, will be required to make progress. Prior experiments by our group as well as others[1–5] demonstrate that mechanical properties such as the Young's modulus can be controlled and tuned by the choice of ligand. As estimated in ref. 4, the van der

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Waals attraction between the nanoparticle cores contributes less than 10% of the overall membrane strength. In ref. 3, we demonstrated that by changing the ligand crosslinking with e-beam exposure, we created in-plane stress in the nanoparticle monolayers and extracted Poisson's ratio. This shows the in-plane stretching behavior of the monolayers is directly related to the ligand interactions. In ref. 5, we showed the Young's modulus measurements of monolayers of Au nanoparticles with different diameters (2–12nm), and found a very weak Young's modulus–diameter dependence. In our current work,[6] only a 40% fracture strength enhancement was found by increasing the particle diameter from ~5.2nm to ~9.1nm. According to ref. 1 and 4 cited in the above comment, however, the core–core van der Waals adhesion should depend much more significantly on the core diameter, which contradicts with our experimental results.

Recently, fully atomistic simulations by Grest and coworkers[7] showed explicitly how changes in the ligand chemistry, specifically replacing the CH_3 termination at the free end by COOH, significantly affect the mechanical strength and fracture behaviour of self-assembled nanoparticle monolayers. Earlier simulations by Schapotschnikow, Pool and Vluigt[8] extracted the potential of mean force between alkanethiol-capped gold particles and found a center-to-center separation of 1.25 particle diameters. Importantly, these simulations show that the direct core–core interactions contribute only little to the total interactions and that the potential of mean force is dominated by the interactions between the ligands. This is certainly in line with the results from ref. 5 and 6 cited in the comment.

Variations in ligand coverage will affect the interparticle spacing, as most recently shown in detailed simulations using coarse-grained models[9] or a sufficiently large ligand deficit, the most noticeable effect is likely to be sintering of adjacent cores.[8] Note that the top–bottom asymmetry in ligand coverage that we exploit in order to curl up freestanding membranes does not reduce the ligand density in the portion of the interstices between neighboring particles where these particles come closest.[9] We therefore believe that, at least in our system, as long as the particles are separated by ligands, direct core–core interactions do not control the mechanical properties of nanoparticle superlattices.

1 A. Dong, J. Chen, P. M. Vora, J. M. Kikkawa and C. B. Murray, *Nature*, 2010, **466**, 474–477.
2 W. L. Cheng, M. J. Campolongo, J. J. Cha, S. J. Tan, C. C. Umbach, D. A. Muller and D. Luo, *Nat. Mater.*, 2009, **8**, 519–525.
3 P. Kanjanaboos, A. Joshi-Imre, X.-M. Lin and H. M. Jaeger, *Nano Lett.*, 2011, **11**, 2567–2571.
4 K. E. Mueggenburg, X.-M. Lin, R. H. Goldsmith and H. M. Jaeger, *Nat. Mater.*, 2007, **6**, 656–660.
5 J. He, P. Kanjanaboos, N. L. Frazer, A. Weis, X.-M. Lin and H. M. Jaeger, *Small*, 2010, **6**, 1449–1456.
6 Y. Wang, P. Kanjanaboos, S. P. McBride, E. Barry, X.-M. Lin and H. M. Jaeger, *Faraday Discuss.*, 2015, DOI: c4fd00243a.
7 K. M. Salerno, D. S. Bolintineanu, J. M. D. Lane and G. S. Grest, *Phys. Rev. Lett.*, 2014, **113**, 258301.
8 P. Schapotschnikow, R. Pool and T. J. H. Vlugt, *Nano Lett.*, 2008, **8**, 2930–2934.
9 Z. Jiang, J. He, S. A. Deshmukh, P. Kanjanaboos, G. Kamath, Y. Wang, S. R. S. Sankaranarayanan, J. Wang, H. M. Jaeger and X-M. Lin, *Nat. Mater.*, 2015, DOI: 10.1038/nmat4321.

Fernando Bresme opened a general discussion of the paper by K. Michael Salerno: Your computations predict the mechanical properties of membranes and compare well with the experimental observations, see Wang *et al.*[1] This is very interesting as these classical models do not incorporate explicitly the

polarizability of the gold core. This result is in line with computations using similar models, which have been shown to predict surface energies in close agreement with experiments (see Reguera *et al.*[2]). Hence, one would conclude that the organic passivating aliphatic layer is the main factor defining the particle–particle interactions that ultimately controls the mechanical strength of the nanoparticle layers. This is a very interesting result.

Experiments on the other hand indicate that the ligand shell can feature deviation from full coverage, which may favour ligand interpenetration between nanoparticles, hence influencing the mechanical response of the nanoparticle layers. Your simulations using full coverage do not provide evidence for ligand interpenetration. Have you tried to compute the dependence of the mechanical response with the ligand surface density? Would you expect significant differences between low and full coverages, particularly since direct gold–gold interactions may become significant in this case?

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1 Y. Wang, P. Kanjanaboos, S. P. McBride, E. Barry, X.-M. Lin and H. M. Jaeger, *Faraday Discuss.*, 2015, DOI: c4fd00243a.
2 J. Reguera, E. Ponomarev, T. Geue, F. Stellacci, F. Bresme and M. Moglianetti, *Nanoscale*, 2015, **7**, 5665–5673.

K. Michael Salerno replied: We have not studied low coverages. It is interesting to ask whether coverage density influences the ligand conformation and interpenetration. For the COOH-terminated ligands there is a clear effect of the number of hydrogen bonds on membrane stiffness. Though the number of ligands would go down with decreased surface coverage, there could be a compensation due to ligand mobility that would allow ligands to relocate (roughly) within the membrane plane and form hydrogen bonds with neighboring nanoparticle ligands, where in the full coverage case they could not. In the CH_3 case, presumably the membrane stiffness would decrease, although again, there is an open question of ligand mobility and its effect. As mentioned in the previous question, the effects above would be difficult to address without accurately modeling the potential movement of ligands along the surface at low coverage. To summarise, these are interesting questions, but the role of the gold–thiol interaction makes them difficult to answer. As noted in the question, the role of the gold core would become more important with decreasing coverage and would also need to be considered in order to study the low coverage case.

Moritz Tebbe continued the general discussion of the paper by Yifan Wang: Is it possible to use buckling instabilities to measure the E-modulus of the nanoparticle films supported by the elastomeric PDMS by compressing the film?

Yifan Wang answered: Yes, it is possible to use buckling instabilities and the resulting characteristic wrinkle patterns to estimate the Young's modulus of nanoparticle films supported on soft PDMS substrates under compression. In ref. 1, the Young's modulus was estimated from the buckling of nanoparticle monolayers as 3.5–6 GPa, consistent with our previous AFM measurements.[2,3]

1 Y. Wang, P. Kanjanaboos, E. Barry, S. McBride, X.-M. Lin and H. M. Jaeger, *Nano Lett.*, 2014, **14**, 826–830.
2 K. E. Mueggenburg, X.-M. Lin, R. H. Goldsmith and H. M. Jaeger, *Nat. Mater.*, 2007, **6**, 656–660.

3 J. He, P. Kanjanaboos, N. L. Frazer, A. Weis, X.-M. Lin and H. M. Jaeger, *Small*, 2010, **6**, 1449–1456.

Bruce Law said: In Fig. 2b of your manuscript[1] you do not observe very, very large fractured structures, which extend throughout your whole nanoparticle membrane. What role will slippage, between the nanoparticle membrane and the PDMS substrate, play in explaining your observations?

1 Y. Wang, P. Kanjanaboos, S. P. McBride, E. Barry, X.-M. Lin and H. M. Jaeger, *Faraday Discuss.*, 2015, DOI: c4fd00243a.

Yifan Wang responded: In the paper we propose that a finite crack length originates from the plasticity of nanoparticle membranes at high stress. Our model is based on the assumption of no slippage and it explains the observations very well up to about a 30% applied strain. However, other explanations are possible. For example, slippage between nanoparticle membranes and the PDMS substrate might occur at the crack tips, where stress is highly concentrated.

Matthew Martin asked: You explained the details of stretching/fracturing, and briefly mentioned that you have performed the reverse process: compression/buckling experiments. In all of these stress experiments, have you seen any evidence of the hexagonal symmetry dependence playing a role in the strength? Have you tried to stretch along a specific crystal axis, twist 60 degrees, and then stretch again? In other words, does the twist angle between the stretch/compression direction and the superlattice planes have an effect on the monolayer's mechanical strength?

Yifan Wang answered: The monolayers in our experiments consist of locally close-packed domains, but they are randomly orientated from domain to domain. Therefore, we could not align the applied stress with any particular symmetry axis. Furthermore, in the multi-layers there is no registration between layers stacked on top of each other (because of the fabrication process *via* stamping). Certainly, the fracture path will have to respect the geometry of the particle arrangement, *i.e.*, within locally crystalline regions, following along one of the symmetry axes. However, we did not observe sudden changes in crack direction at the domain boundaries. Instead, we find fracture patterns that are, on the scale of tens of particles or larger, consistent with expectations based on continuum models for thin film materials (including the 'zig-zag' pattern at angles characteristic of surface instabilities). At smaller length scales the fracture patterns exhibit fluctuations that we interpret as being due to variations in local coupling strengths between the particles (mediated by the ligands). Thus, at least in our experiments, we cannot directly connect the monolayer strength to the crystalline orientation. A related question is whether the fracture strength we observe is dominated by the behavior of the locally crystalline regions, or by grain boundaries. In Fig. 3 in our manuscript, we plot the decrease in average crack spacing L up to strains of around 20%. In data where we trace this behavior out to 60%, we find that L changes much more slowly beyond about 30%.[1] A likely interpretation is that at these large strains there is some slippage between the nanoparticle film and the underlying substrate, which would prevent L from growing further. However, because this change in

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behavior coincides with the crack spacing L becoming comparable to the size of locally crystalline domains (this happens at $L \sim 200$ nm, corresponding to a couple of dozen particles across), an intriguing alternative explanation is that we are seeing a crossover from grain boundary-dominated behavior to behavior dominated by the larger strength of locally ordered domains. Still, at this stage we cannot say anything definite about how the mechanical strength varies when the angle between the applied stress and the superlattice axes of symmetry is varied.

1 Y. Wang, P. Kanjanaboos, E. Barry, S. McBride, X.-M. Lin and H. M. Jaeger, *Nano Lett.*, 2014, **14**, 826–830.

Helmuth Moehwald continued the discussion of the paper by K. Michael Salerno: In the structure model the C_{12} chains are given in the all-*trans* configuration. Experimentally, however, one finds the chains in a state with many kink defects. How can one explain this?

The thiols with terminal COOH groups should couple *via* hydrogen bonds. These bonds would be broken near 350 °C, explaining the change in slope in Fig. 2 in your manuscript.[1] Is this interpretation correct?

1 K. M. Salerno and G. S. Grest, *Faraday Discuss.*, 2015, DOI: c4fd00249k.

K. Michael Salerno answered: In our model we make no assumption about the configuration of the C_{12} chains, instead, the atomistic force field determines the fidelity of the model. For the OPLS-AA force field that we utilize there is a recent study which examined the properties of hydrocarbons simulated with the OPLS-AA and then performed an optimization to improve the agreement between the simulated model and experimental data.[1] In particular, the authors found that for all models there are many chain defects at room temperature, though one can better match the experimental data by optimizing the potential. We are currently studying the influence of the force-field by using the modified OPLS potential presented in this reference. So far we have found results which are consistent with Siu *et al.*,[1] that the melting temperature is shifted from model to model, but the qualitative behavior and temperature dependence is comparable.

The kink in the lattice-temperature curve occurs for the CH_3-terminated ligands, so this would not be explained by the COOH hydrogen bonding. We did not investigate the cause of this kink.

1 S. W. I. Siu, K. Pluhackova and R. A. Böckmann, 2012, **8**, 1459–1470.

Dhanavel Ganeshan returned to the general discussion of the paper by Toshiharu Teranishi: How do you see the scattering effect under UV, and what is seen when using different sized nanoparticles?

Toshiharu Teranishi responded: Absorption and scattering effects can be separately measured by changing the positions of the detectors. In general, the scattering is dominant at longer wavelengths. When the size of the nanoparticles becomes larger than 80 nm, one should consider the contribution of scattering, for example see Jain *et al.*[1]

1 P. K. Jain, K. S. Lee, I. H. El-Sayed and M. A. El-Sayed, *J. Phys. Chem. B*, 2006, **110**, 7238.

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Lucio Isa resumed general discussion of the paper by Yifan Wang: How large can you make these membranes? If they are cut, how long can they be rolled and how thick can they be made?

Yifan Wang responded: The size of freestanding nanoparticle monolayers depends on the particle size and ligand type. For ~5 nm diameter Au nanoparticles with dodecanethiol ligands, the largest hole diameter we can cover is ~10 μm. If larger freestanding membranes are cut and exposed to the e-beam, we expect them to roll into more layers than smaller membranes, while the radius is always set by the ligand asymmetry from both the air and water sides.

Christopher Sorensen addressed Yifan Wang: What is the thermal stability of the free-standing film? If you were to heat it up, would it return to the same film when it was cooled back down?

Yifan Wang answered: At this stage there are only very preliminary results regarding higher temperatures. Earlier simulations of related nanoparticle superlattices by Landman and Luedtke[1] (see Fig. 10 in their manuscript) indicated that the modulus should vanish at temperatures above ~40 °C. Our measurements on freestanding monolayers[2] showed that they survive mechanically to significantly higher temperatures. Eventually, of course, ligands will desorb and particles will start to sinter. Experiments are currently being conducted in our laboratory to address these questions in more detail.

Sean McBride commented: The topic of the thermal stability of the free standing films is an ongoing area of research being investigated in our laboratory. We are using an atomic force microscope to examine how the mechanical properties (*i.e.*, stiffness and Young's modulus) of the free-standing films change as a function of temperature. Preliminary and previously unpublished results have shown that free-standing films can be heated well past the expected ligand melting temperature and still span 6.5 micron diameter pores, as evidenced by standard optical microscopy (100× magnification). High resolution transmission electron microscopy images of the free standing films as a function of temperature, mechanical properties as a function of increasing and decreasing temperature showing any hysteresis, and higher temperatures reaching the failure point are all needed and being collected to address this exact question.

1 U. Landman and W. Luedtke, *Faraday Discuss.*, 2004, **125**, 1–22.
2 K. E. Mueggenburg, X.-M. Lin, R. H. Goldsmith and H. M. Jaeger, *Nat. Mater.*, 2007, **6**, 656–660.

Matthew Martin remarked: You showed free standing membranes over ~2 micrometer holes and how they roll up into scrolls. If you were to use much larger free standing monolayers (> 500 micrometer diameter, for example), would you expect different scroll formation? For example, would you see a different scroll radius or would you expect the same curvature you observe, but with many more layers in the rolled up structure?

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Yifan Wang answered: The curvature of the nanoparticle scrolls is, we believe, set by the asymmetry in ligand packing density on different sides of the monolayer.[1] For a given nanoparticle synthesis and assembly method, the rolling curvature is therefore expected to be the same. As a result, larger freestanding monolayers are expected to roll into scrolls of similar curvature (and thus similar diameter) but with walls comprised of more layers under e-beam exposure.

1 Z. Jiang, J. He, S. A. Deshmukh, P. Kanjanaboos, G. Kamath, Y. Wang, S. R. S. Sankaranarayanan, J. Wang, H. M. Jaeger and X.-M. Lin, *Nat. Mater.*, 2015, DOI: 10.1038/nmat4321.

Brian Korgel continued the general discussion of the paper by Yifan Wang: Is there a way to probe the effect of temperature on the suspended nanocrystal monolayers using GISAXS? GISAXS is definitely sensitive enough to pick up subtle changes in structure and *in situ* heating is possible without too much trouble. If sagging of the membrane is an issue, is it possible to tighten up the membrane and then heat it?

Xiao-Min Lin answered: The suspended nanoparticle monolayer actually recedes inside the hole by attaching part of the membrane along the substrate wall of the hole, and then stretching across the hole. This process tenses up the membrane, which is the source of the pre-stress in the membrane. But this also makes GISAXS measurement directly on the suspended monolayer impossible to do. Ligand melting and the possible influence of the mechanical properties of the membrane are important question to address, and we are currently conducting *in situ* heating experiments with AFM to probe this behavior.

Edward Malachosky resumed the general discussion of the paper by Toshiharu Teranishi: You nicely describe and demonstrate the effects of ligand-induced oxidation and reduction on the LSPR of your copper sulfide nanodisks. I was curious if you thought it would be interesting or worthwhile to investigate the same effect using electrochemistry, either *in situ* or on a thin film of your particles.

Toshiharu Teranishi replied: Thank you for your interesting question. I have never tried electrochemical redox reactions of copper sulfide nanodisks, but it could be possible to do either *in situ* or on a thin film. The electrochemical redox reactions would change the hole density in a wider range than the chemical redox reactions do.

Christina Graf asked Subramanian Sankaranarayanan: You suggest that on particles with a reduced ligand density (for example due to extensive washing) the ligands are moving on the surface, so that when the particles are ordered on a surface some parts of the nanoparticle surface become ligand-free. My question is, nanocrystals have a faceted surface. How can the ligands move from one crystal plane to another by passing edges and corners of the particle? I think when a significant part of the nanoparticle surface becomes ligand-free such a process is necessary.

Subramanian Sankaranarayanan answered: The coarse-grained (CG) model assumes a spherical nanoparticle and hence the asymmetry is represented by

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some parts being ligand deficient. When you have a faceted surface, then the initial distribution itself would be such that the edges and corners probably have higher density than the faces. The spatial variation upon washing would probably be represented by the faces being much more ligand deficient than the edges and corners. The exact diffusion mechanism leading to such a distribution when the ligands are washed off is still not understood.

Fernando Bresme addressed K. Michael Salerno: Experiments and Density Functional Theory computations indicate that thiolate molecules can adsorb through the so-called staple motif where the structure RS–Au–RS is formed.[1] Did you take into account this effect in your model? Do you expect reconstruction of the gold surface, and could this be modeled using classical force-fields, either atomistic or coarse-grained?

1 M. Askerka, D. Pichugina, N. Kuz'menko and A. Shestakov, *J. Phys. Chem. A*, 2012, **116**, 7686–7693.

K. Michael Salerno responded: We did not take into account the possibility of "staple-motif" structures in our model. I am not aware of any particularly good classical force-field models of the Au–S interaction. I believe that this is a difficult question and could have considerable impact on the modeling of nanocrystals, particularly at far-from-full coverage.

Subramanian Sankaranarayanan also commented: This is a very valid question. There can be absorption of thiol molecules on the motifs where RS–Au–RS is formed. These were not taken into account in the coarse-grained model as the intention was to look at the self-assembly of the membrane over microsecond timescales. These features can be captured using all-atom classical force fields. For example, the latest ReaxFF force field is capable of capturing the resulting reconstruction on the gold surface. We are currently investigating these effects using atomistic simulations on a smaller-sized model system.

Andreas Fery returned to the discussion of the paper by Toshiharu Teranishi: Your systems could be interesting candidates for enhancing second harmonic generation effects plasmonically. This could be tested by intercalating or simply adsorbing a second harmonic generation dye on the disc superstructures.

Toshiharu Teranishi replied: Thank you for your interesting comment. A second harmonic generation dye would be easily intercalated in the disk arrays by using dye-modified ligands. However, in our case, we can enhance only in the in-phase bright mode. I'm not sure, but I think that enhancing second harmonic generation effect could be observed by using the in-phase dark mode, which induces near-field enhancement. If the out-of-plane mode of nanodisks can be plasmonically excited, I will try the experiment that you suggested.

Dhanavel Ganeshan queried: Why is it called a LSPR mode? Can you explain how plasmon coupling works?

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Toshiharu Teranishi responded: Localized surface plasmons are collective free carrier (electron or hole) oscillations in conductive and semiconductor nanoparticles that are excited by incident light waves. Because the oscillations are localized in nanoparticles, we call them localized surface plasmon resonance (LSPR). For plasmon coupling, see Yang *et al.*[1]

1 S.-C. Yang, H. Kobori, C.-L. He, M.-H. Lin, H.-Y. Chen, C. Li, M. Kanehara, T. Teranishi and S. Gwo, *Nano Lett.*, 2010, **10**, 632–637.

Yangwei Liu returned to the general discussion of the paper by Yifan Wang: The Au nanoparticle membrane forms fracture patterns under stretching. Although the strength of the membrane is due to multiple interactions, I would assume that the cracks begin at specific locations where there are defects and thus have a lower strength than the surrounding area. Would the extent of defects affect the mechanical properties of the membrane? Were you able to examine the relationship between the defect amount and locations with the fracture pattern? Do you have any comments on that?

Yifan Wang responded: Indeed, the cracks first start at larger defects, which sets the initial crack separation, as stated in the paper. The as-deposited monolayers in our experiments were highly uniform but it consists of close-packed polycrystalline regions separated by grain boundaries. For < 5% strain, a few channel cracks appear, mainly at large-scale residual deposition defects or occasional multiparticle voids in the film. These are a few micrometers apart and act as nucleation sites for the initial cracks, setting the largest crack distance in our experiments. Since we did statistical analysis on the crack separations, the fracture strength is an average value considering all local defects. Experiments on monolayers with different types or amounts of local defects were not carried out, but we expect that fewer local defects will increase the fracture strength.

Petr Král commented in relation to the paper by K. Michael Salerno: Atomistic modeling shows that nanoparticle membranes do not develop pores for the observed passage of molecules (filtration). Only after the imperfection of sizes and ligand densities are included (as in experiments), are pores between the nanoparticles observed. The results then fit the observed sizes of molecules passing through the membranes; see Fig. 1–4 and Fig. S1 and S6 in He *et al.*[1]

J. He, X.-M. Lin, H. Chan, L. Vukovic, P. Král and H. M. Jaeger, *Nano Lett.*, 2011, **11**, 2430–2435.

Asaph Widmer-Cooper asked Subramanian Sankaranarayanan: In your simulation studies of nanoparticle membranes you have allowed the ligands to move on the surface of the particles. Have you looked at how temperature affects the distribution of ligands on the particle surface, *e.g.* does it change substantially as the ligands order and align with one another at low temperature?

Subramanian Sankaranarayanan answered: We have not looked at the temperature effect, but we expect the mobility of the ligands to be higher at higher temperatures. The extent of asymmetry and the coverage at which it occurs is likely to be different depending on the temperature.

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Bruce Law resumed the general discussion of the paper by Yifan Wang: I would like to suggest an experiment which may be rather difficult to perform in practice. Can you apply strain to the PDMS substrate while observing your nanoparticle membrane using TEM and see if the fractures develop at nanoparticle defects within the membrane?

Yifan Wang answered: This is a very good suggestion. The main difficulty in our setup is that PDMS is not conductive, leading to strong charging effects and preventing high resolution imaging by SEM. It is also not transparent for electrons, as is required for TEM.

Petr Král commented: We have modeled ligated nanoparticles arranged in planar and spherical assemblies (see Fig. 1, 2, 4–6 and 9 in ref. 1). When the nanoparticles were stretched on a spherical surface, they switched from a multilayer to monolayer and changed their numbers of neighbors from 7 to 6 and 5 as the stretching progressed. The number of neighbors correlated well with the stretching. At small stretching the nanoparticle distances were more random, while at high stretching they were very regular. nanoparticles with longer ligands formed more disordered systems.

1 H. Chan and P. Král, *Nanoscale*, 2011, **3**, 1881–1886.

Almudena Gallego communicated to Yifan Wang: Did you study the optical properties of the layers and compare it with the nanoparticles in solution? In that case, did you see any enhancement due to the assembly of the nanoparticles?

Yifan Wang communicated in response: We have not done any quantitative studies on the optical properties of nanoparticle monolayers. However, we do observe color changes of monolayers at an air–water interface for different ligand concentrations in the nanoparticle solvent. For example, monolayers with excess ligands usually reflect purple colors, while monolayers with not enough ligands reflect light blue colors. This suggests that the spacing between nanoparticles during the assembly process could relate to the excess ligand concentration in the solvent.

Almudena Gallego communicated: Did you consider using a conductive organic polymer as a capping ligand in order to create nanowires, or do you think that the interpenetration between particle shells would not be efficient enough to form the layers?

Yifan Wang communicated in reply: The organic ligands currently used (dodecanethiol) are insulating and the conductivity across nanoparticle monolayers is very small.[1] However, it is possible to replace the dodecanethiol with conductive ligands to enhance the conductivity to a level where transport can be observed that appears band-like.[2]

1 T. B. Tran, I. S. Beloborodov, X.-M. Lin, T. P. Bigioni, V. M. Vinokur and H. M. Jaeger, *Phys. Rev. Lett.*, 2005, **95**, 076806.
2 J. S. Lee, M. V. Kovalenko, J. Huang, D. S. Chung and D. V. Talapin, *Nat. Nanotechnol.*, 2011, **6**, 348.

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Gunadhor Okram communicated: Will the inverse proportionality relationship between the width and the applied strain be the same for any type of ligand–water interface or monolayer cracking, and why?

Yifan Wang communicated in response: We do not anticipate that the general, inversely proportional relationship between the average fracture width and the applied strain will change for different types of ligand. On the other hand, the prefactor of this proportionality will change because different ligands will produce different fracture strengths. Different ligands might also affect when the data start to deviate from this inverse proportionality at large strain, for example by controlling the binding strength between the monolayer and the underlying substrate.

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