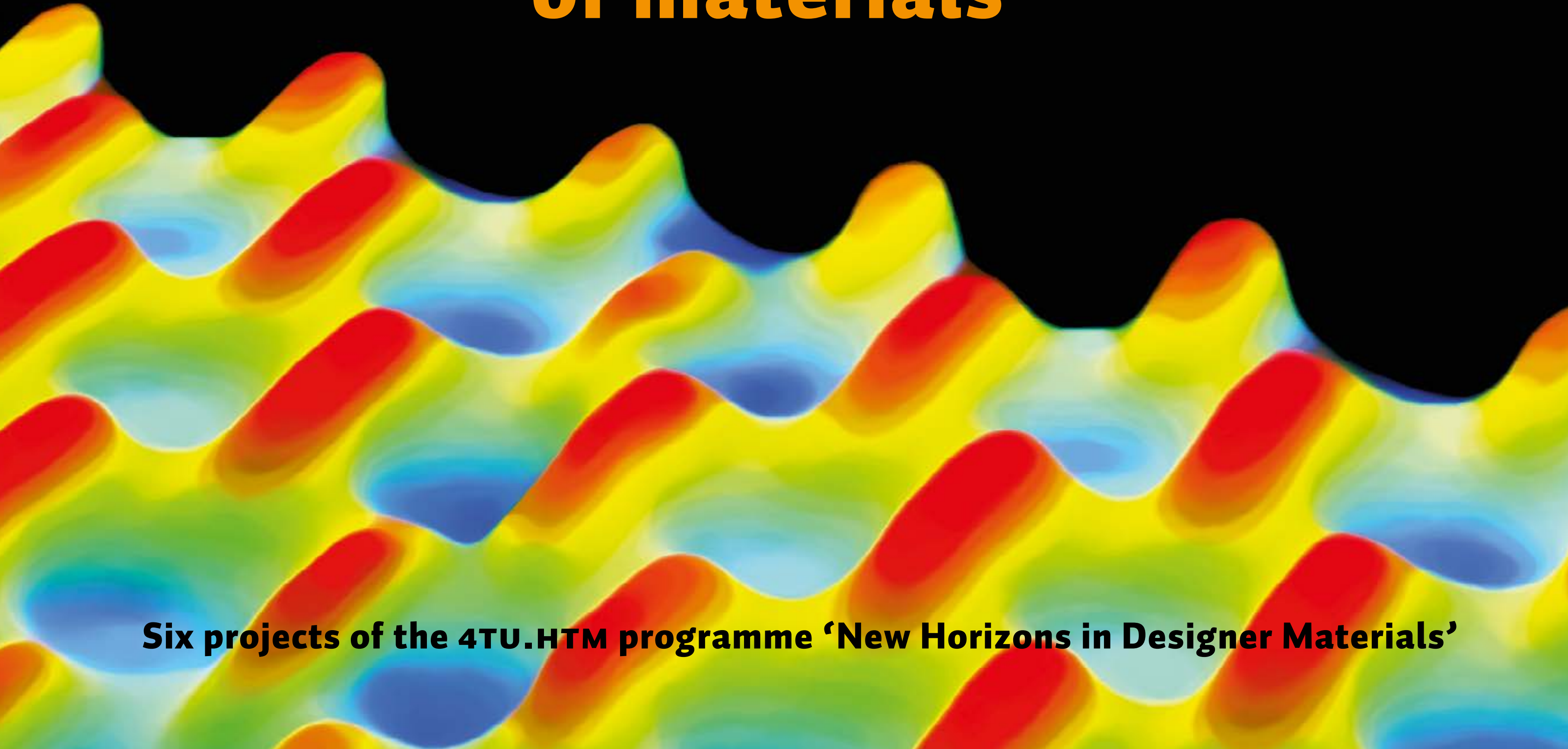
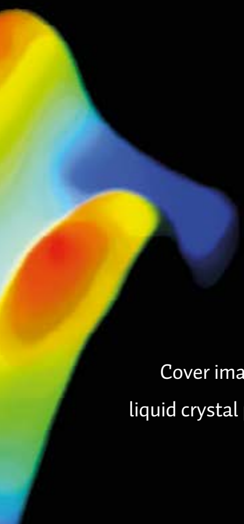
Stretching the boundaries of materials



Six projects of the 4TU.HTM programme 'New Horizons in Designer Materials'



Cover image: Graphic designer’s impression of ‘Surface protrusions formed in a liquid crystal polymer network’. [Danqing Liu, Eindhoven University of Technology]

Stretching the boundaries of materials

Six projects of the 4TU.HTM programme New Horizons in Designer Materials

4TU.Research Centre
High-Tech Materials

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Photo p.6 – RAMLAB
Photo p.11 – Marieke de Lorijn
Graphic design – Nieuw-Eken Ontwerp
Print – Mstra Drukkers

Publication
4TU.Research Centre High-Tech Materials
March 2020

www.4tu.nl/htm

4TU.HTM

Content

The Boundaries of Materials

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Use this code to hear
a reading of this poem

www.samillingworth.com

These are the essential building blocks of life
And non-life
Materials that are imbued
With barely believable features,
Pushing beyond limits that others
Define as traditional.
Following pathways of conservation
And least resistance,
Their dynamic, vibrant features
Slowly begin to emerge:
Stiffening,
Softening,
Healing,
Radiating light,
Resisting translucency.

These are the molecular manipulations that we
Must strain to stimulate,
Embracing entropy with every unformed idea,
Every swirl of caffeine,
Every shattered dream.

W*e race to create an elixir of life;*
Designer macromolecules
That extend their existence
Beyond the blink of an eye,
Radically tricking their termination
To bind their ions and bend their chains.

And yet,

A*s we enter into the second century of our co-existence*
We are still to reach the sophistication of nature;
A macromolecular nirvana where
Environmentally friendly, oxygen-tolerant,
And easier to use materials cast off the
Diabolical characteristics of their surfaces,
To finally embrace their borders
With our external world.

“The issue of sustainability is reshaping the field”

The 4TU.HTM programme New Horizons in Designer Materials (2016-2019) was set up by the 4TU.Federation, a collaboration of Delft University of Technology, Eindhoven University of Technology, University of Twente and Wageningen University & Research. Materials science is one of the scientific fields where the 4TU partners establish joint activities. How do 4TU scientific director for the field of materials Prof. Jilt Sietsma (Materials Science and Engineering, Delft University of Technology) and programme manager Reina Boerrigter look back on the six projects exploring New Horizons in Designer Materials?

WAAMpeller: the world’s first class-certified 3D-printed ship’s propeller. Built by RAMLAB in Rotterdam in 2017, the prototype consists of 298 layers of nickel aluminium bronze alloy.

“Sometimes the very first publications in a scientist’s career make all the difference.”

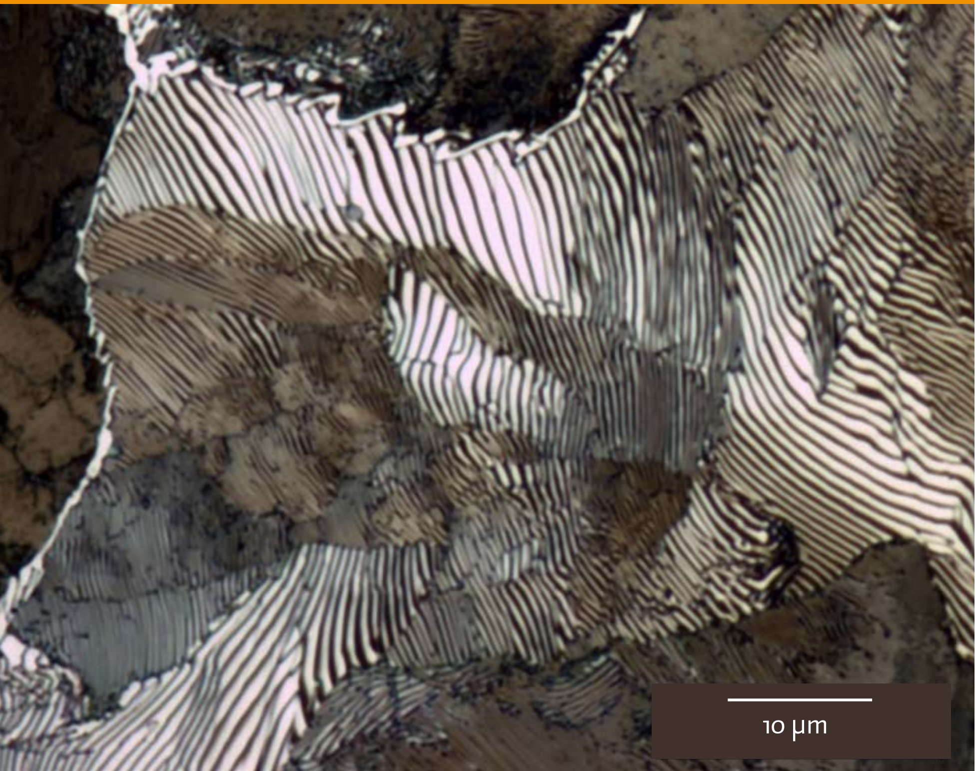
How is materials science in the Netherlands doing? Sietsma: “It is difficult to answer that question across the board, since materials science is a very extensive field considering many different aspects of many different materials. What I find very encouraging is that when we reach out to international colleagues to establish a collaboration, as we did for this research programme, the response is always positive. That is a reflection of the good reputation of Dutch materials science.”

Tell me about the genesis of the New Horizons programme. Boerrigter: “In 2015, the three universities of technology of the Netherlands, working through the 3TU.Federation (Wageningen joined the federation later), established a research centre on high-tech materials, HTM in short. The centre aims to stimulate and intensify the academic research and development of innovative materials in the Netherlands. The New Horizons in Designer Materials programme provided an impulse of 2 million euro. A call was published inviting proposals for three-year research projects to be executed by talented postdocs / young researchers at the beginning of their career. We received eighteen proposals from which a committee with representatives from the three universities selected six. These projects have now been finalized. It is great to see how all the postdocs found new positions, some as tenure-track professors, others in industry. In 2017 the 4TU.Federation decided to shift the research funding from smaller blue-skies research programmes to larger and more integrated programmes. Therefore, at the moment there is no 4TU research programme aimed solely at materials science.”

What can be expected from postdocs working on a materials science topic for three years? Sietsma: “Of course, three years is too short a time to really change prevailing paradigms. What is most important is that it can provide a launching pad for a successful career in materials science. Sometimes the very first publications in a scientist’s career make all the difference.”

Was a new funding programme needed for that? “What I really like about this New Horizons in Designer →

Microstructure of a steel grade for bearings in an intermediate stage of its production process. It consists of a mixture of ferrite (almost pure iron) and cementite (a compound of iron and carbon). [Natalia Luzginova, Microstructure and Transformation Kinetics in Bainitic Steels, Ph.D. thesis, Delft University of Technology, 2008]



Materials programme is that it provided an opportunity to do blue-skies research. Curiosity-driven research. There is little room for that in the Dutch academic system of today. Most programmes need to be co-funded by industry, which means that the topics need to have proven themselves already. There needs to be credible potential for a return on investment in a few years' time. That is understandable, but we also need a more fundamental type of research, even if it yields materials hypes that fizz out before a product can be made but that do generate valuable fundamental knowledge."

The New Horizons programme was about fundamental research? "We are universities of technology. Designing and building is what we do. So, even if we look at the fundamental properties of a material, we do so because in the end we want to use this material to construct something with functionalities that are based on the materials used."

The programme is about high-tech materials. What about low-tech materials? "There is no such thing as

"The engineers we are educating now will find themselves in a very different world in 20 to 30 years' time."

a low-tech material. Whether it is nanotubes or polymers, materials are key to the next generation of technologies. Even all materials that have been around for ages, like steel and concrete, are witnessing continuous developments. Most of today's steel grades were developed less than 15 years ago. Development is always necessary because of new demands by the technologies using the materials and because of increasing sustainability constraints."

Is the definition of 'designer materials' just as broad?
"To be honest, yes. Materials are inseparable from design. Both in terms of materials scientists designing new materials by playing around with how atoms form larger structures, and in the sense that materials are the main tools for designers to really make something. Materials are crucial for the designs that are made into technological objects."

What major developments do you see on the horizon?
"The issue of sustainability is reshaping the field. More and more people now understand that materials play a key role in solving the complex challenges that are facing society due to for example greenhouse gas emissions, fossil-fuel and resource scarcity. There is a growing awareness that materials contribute to how we can maintain and develop technologies in the future. I think that materials are now where energy and oil were about 40 years ago: we recognize the challenges and are slowly starting to move into new directions."

This must have an impact on prospects for university-educated engineers. "I am convinced that the engineers we are educating now will find themselves in a very different world in 20 to 30 years' time. They will have less materials resources to rely on, and more challenges to deal with. They will need to design for recyclability, low-waste manufacturing, longer product lifespans. At the same time, products still need to be economically viable."

Do young people understand what they are in for?
"Young people understand the environmental challenges very well. It is important to explain to them how materials fit into this context. I am a bit worried about the awareness of the role of materials in high schools and Bachelor's

"The combination of learning and teaching makes being a professor one of the best professions in the world."

programmes. In designing new technologies or structures, students first learn to base their designs on materials that are available. Only later they realise that this choice of materials has a major influence on the designs. Designers should challenge materials scientists to come up with better materials. We need to educate them in this respect. Currently, there is no Bachelor's programme in Materials Science in the Netherlands. Such a programme would mean a lot for our engineering education."

What about students in other programmes?
Boerrigter: "Our partners in industry often signal that graduates from the engineering programmes have insufficient knowledge about materials. The 4TU.HTM research centre would like to support materials science education in the broadest sense, for example by stimulating the development of courses for students in other disciplines."

With the advent of artificial intelligence taking care of materials design, can't we pull humans out of the loop altogether? Sietsma: "Computers can help us process lots of data and simulate our designs before we build them. They are important tools in the evolution of materials. Can they trigger a materials revolution all by themselves? I don't think that is very likely. Computers help us deal with information but the human factor remains indispensable."

What techniques should we look out for? "Additive manufacturing, also known as 3D printing, may look like a bit of a hype today but I think it will become very important in the future. It is a very efficient way of tuning materials properties, for example by creating graded materials in which the properties gradually change from one point to the next. It will help us make shapes that were previously very difficult or even impossible to fabricate, and it will greatly reduce material loss during manufacturing. Many people know that 3D printers can make small plastic structures, but the principle has already been used to manufacture huge ship propellers from metal and similarly large structures from concrete."

What material system would you buy stocks in?

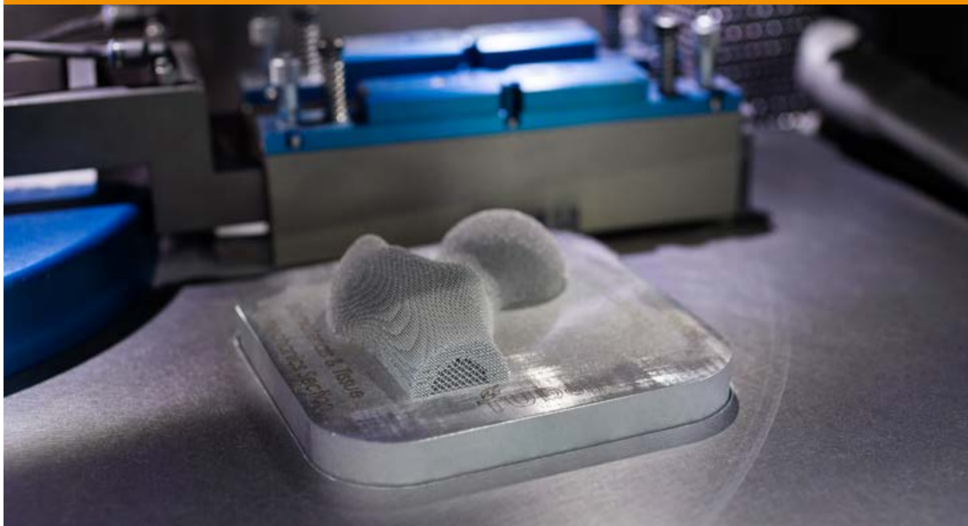
"That is a difficult question, not because there are no options, but because there are so many good options. Many completely new materials are in development and will be needed to keep advancing technology in a sustainable manner. But on the other hand, as I said before, the 'conventional' engineering materials are also constantly in development and will remain the backbone for our technology and infrastructure for decades to come."

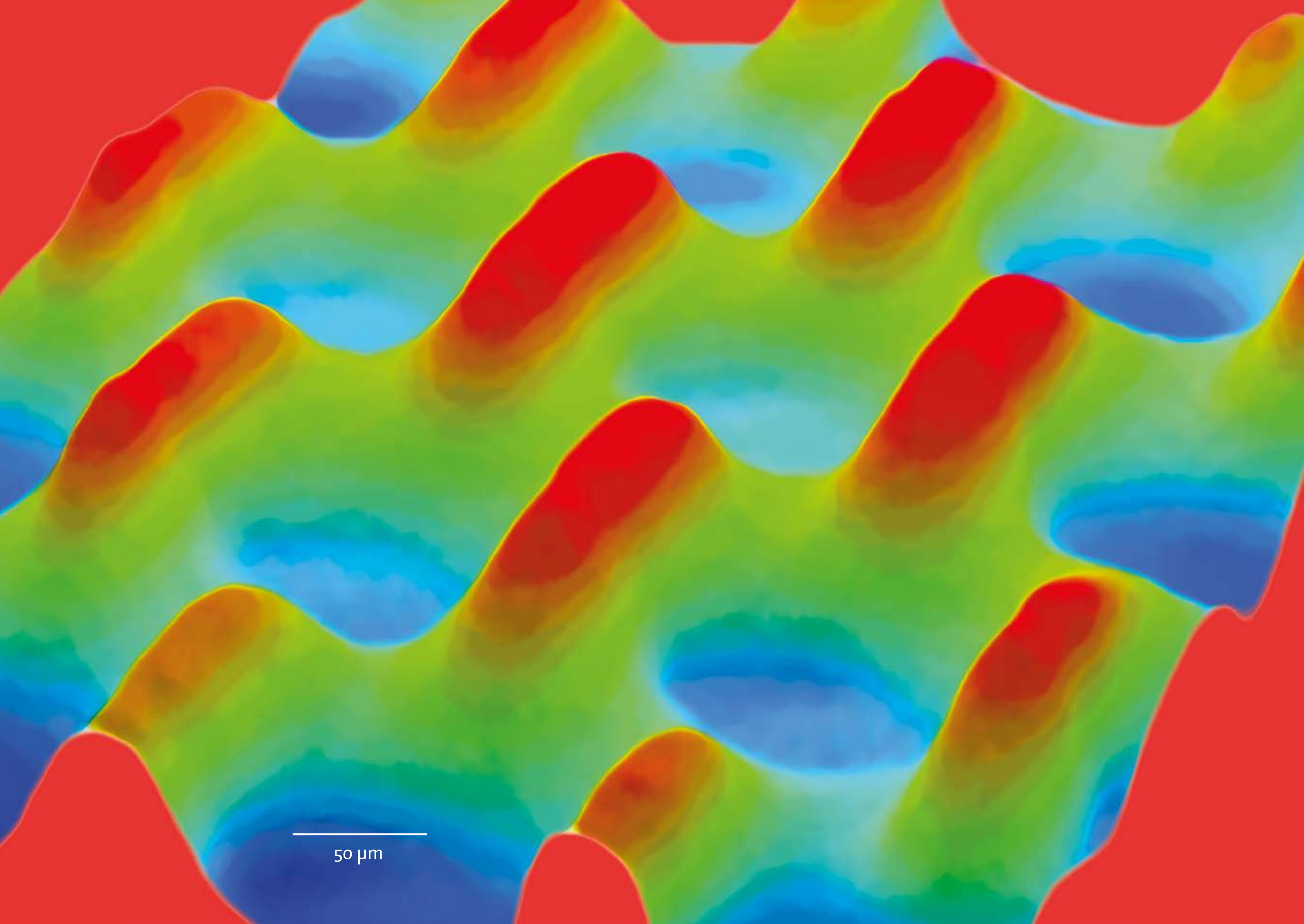
Finally, any word of advice to the postdocs who worked on the New Horizons programme?

"Wherever your career takes you, keep on looking for new insights and transferring that knowledge to the next generation. The combination of learning and teaching makes being a professor one of the best professions in the world. Even if it is not the professorship you hoped for, be confident that you can develop your knowledge, and find alternative ways to instil it onto others." Boerrigter adds: "I hope you will all hang on to the ambition and enthusiasm that you displayed for the past three years!"

"Whether it is nanotubes or polymers, materials are key to the next generation of technologies."

Additively manufactured porous metallic biomaterials aimed for bone tissue regeneration: hip stems with external and internal porous structures. [Amir Zadpoor, Additively manufactured porous metallic biomaterials, Journal of Materials Chemistry B, 7, 4088-4117, 2019]




50 µm

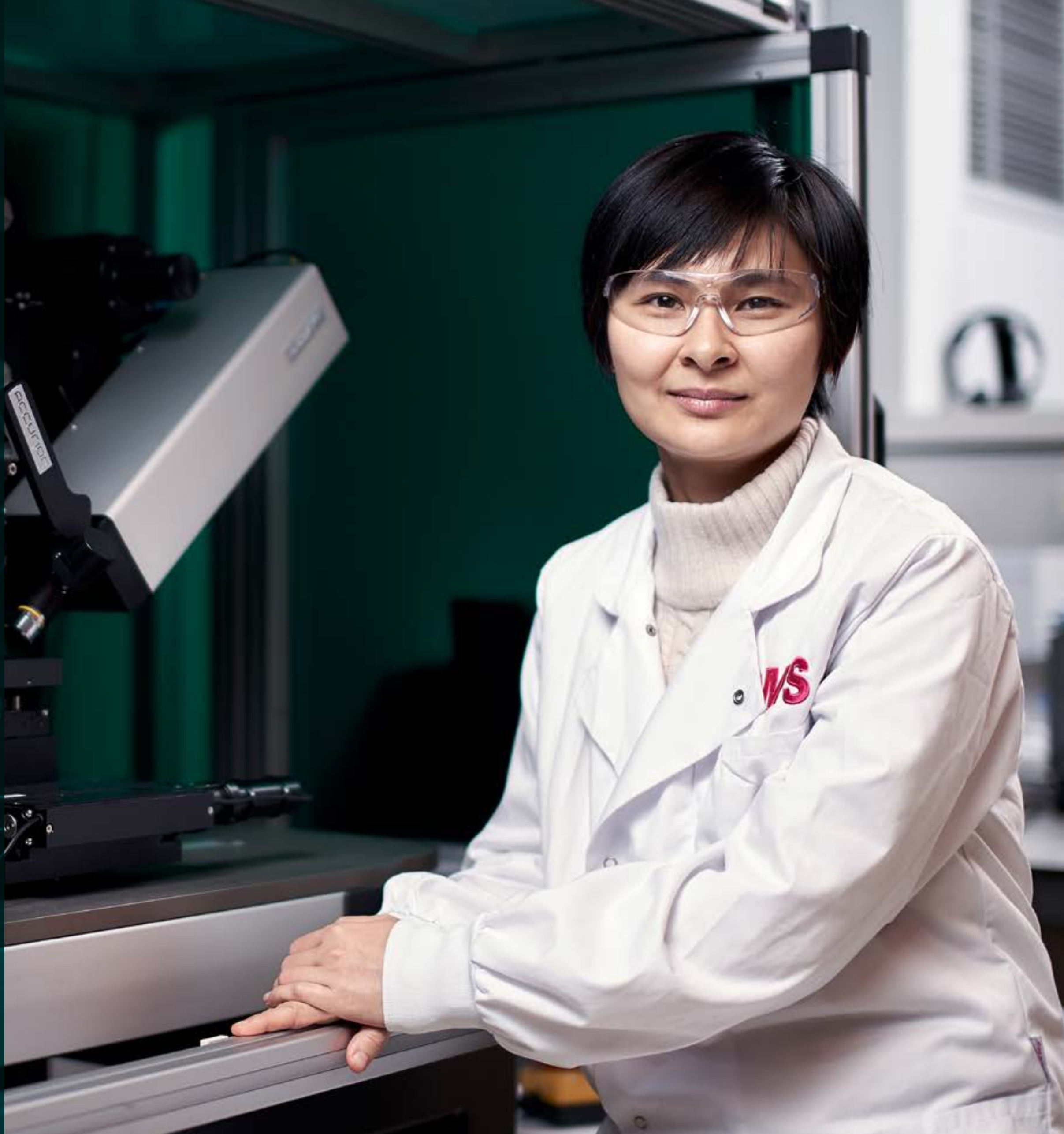
Project title: Communicating Surfaces
Postdoc: Dr. Danqing Liu
Supervisor: Prof. Dirk J. Broer
University: Eindhoven University of Technology
International expert: Prof. Peter Palffy-Muhoray (Kent State University, USA)

Can robots get goose bumps?

"Surfaces are the interface between man and material," Dr. Danqing Liu writes in the prestigious journal *Nature Communications*. They therefore play a crucial role in the exchange of information between the two. While we are used to endlessly watching and listening to our smartphones, computers and televisions, these devices do not appeal much to our sense of touch. Touchscreens feel what our fingers are doing, not the other way around. And that is strange, since touch is a sense that is not to be underestimated. Research from 2013 suggests that our fingers can feel extremely small height differences, down to a nanometre. "We can make materials smarter by making them adapt their surface texture as desired," says Danqing. But how do you make a surface change its texture in a controlled manner so that it can give a human finger something to feel? "Layers of piezoelectric materials, electro-active polymers and hydrogels are well-known to change shape under the influence of an electric field, but only if you place an electrode under and on top of them and apply a large voltage of up to 1000 V. They are therefore not very practical as layers to be touched and felt." The objective of the 4TU.HTM project 'Communicating Surfaces' was to develop a polymer surface that safely and in a controlled way converts electrical signals into touchable surface patterns.

Postdoc: **Dr. Danqing Liu**

Dr. Danqing Liu studied electrical engineering at Delft University of Technology. Keen to explore a different field, she moved to mechanical engineering, which is where she became interested in materials. She obtained her Ph.D. in the field of responsive polymers at Eindhoven University of Technology. During her postdoc project at the Department of Chemical Engineering and Chemistry, she wrote the 4TU.HTM proposal. “HTM stands for high-tech materials, and that term describes exactly what I am working on.” Her work on the project resulted in a string of publications in journals such as *Nature Communications*. This success and Danqing’s ideas were rewarded with a Veni grant from the Netherlands Organisation for Scientific Research (NWO). In 2015 Danqing was a Research Fellow at the Institute of Complex Molecular Systems in Eindhoven. From 2019 she is appointed as Assistant Professor (Tenure) at the Department of Chemical Engineering and Chemistry, Eindhoven University of Technology.



“We had the Mars Rover in mind, the famous space vehicle.”

Ripples in plastic To cut a long story short, Danqing and her team succeeded with flying colours. “We created a thin electrode structure underneath a layer of liquid crystals trapped in a polymer network. The electrodes have an interdigitated structure, like interlocking fingers separated by about 10 micrometres. If we apply a voltage of 70 V, an electric field in the plane of the polymer layer is generated that is strong enough to force the liquid crystals in the polymer network out of their preferred arrangement.” This arrangement is preferred because it has the molecular structure that takes up the least volume. If the molecules are forced to arrange themselves differently, the volume of the layer increases. In other words: a thin corrugation or ripple is created in the plastic layer where the electric field is applied, which disappears when the voltage is removed. “This was an important breakthrough for us. Integrating electrodes underneath the polymer layer was a completely new approach. It was also the first time that this type of organic material was actuated by an electric field.” Danqing is poised to bring the voltage down even further by turning to softer polymer networks that make it easier for the liquid crystals to move when an electric field is applied.

Shaking off extra-terrestrial dust It is not just electric fields actuating the coatings. Other possible triggers are temperature, light, acidity or environmental changes. The potential applications are manifold and Danqing has no shortage of appealing examples. Visions of programmable braille, tactile keys on touch screens and self-cleaning surfaces found their way to the national and international news. For example, in a particularly convincing video clip, Danqing demonstrates that a thin, transparent polymer layer can shake off an amount of sand with the help of a single voltage pulse. “In developing this proof of principle, we had the Mars Rover in mind, the famous space vehicle.” Mars is home to planet-wide dust storms. If this dust covers the Rover’s solar panels, it will lose power and eventually stop functioning. Danqing’s polymer layers could help keep those panels free of sand. NASA has already contacted the scientists. “This project

"This technique could help machines communicate with each other through a very human type of interaction: physical contact."

was a direct spin-off from the innovation that we developed in the 4TU.HTM project."

Hard and soft robots But Danqing is mainly interested in the use of the responsive layers to facilitate communication between man and machine or between machines. Robots now consist mainly of hard materials that do not invite being touched. The alternative technical development of soft robotics has the disadvantage that it, precisely because of its softness, can exert small forces only, for example to pick up or move an object. The communicating polymer layers developed by Danqing can become an attractive interface between man and machine. "The topography of the surface contains information that can be passed on. Think for example of virtual reality, not only for entertainment purposes but also for surgeons to practice delicate procedures. Virtual reality now only gives them visual cues to base their movements on. What if they can also feel something when they almost puncture the training tissue and therefore have to be extra careful? Haptic feedback is an important development to help surgeons operate more safely and accurately," says Danqing. This technique could also help two machines to communicate with each other through a very human type of interaction: physical contact. "A robot will be able to feel the surface topography offered by another robot, like scanning a finger print or sensing goose bumps."

Firm grip In another proof of principle in the field of robotics, Danqing showed that the electrically controlled surface topography can also be used to finetune the surface friction. "Imagine a robot holding something fragile," Danqing explains. "We need ways to finely tune the robot's grip and to allow it to release the object in a controlled fashion. The materials used for soft robotics are often sticky, making the release something of a challenge. Surface friction could mean the difference between abruptly dropping the object and letting it go gently."
By actuating a polymer surface to go from flat to a fingerprint-like pattern of corrugations of less than a micrometre in height, Danqing showed that the effective contact area between robot and object decreases, resulting in lower

friction and therefore in the smallest possible easing of the robot's grip.

Sweaty polymer layers The most recent development that resulted from the 4TU.HTM project also attracted a lot of attention. For this, Danqing went from polymer layers that change the volume on demand to polymer layers that absorb or release a quantity of liquid when triggered. "We use the same principles to get thin sponge-like layers, filled with liquid, to squeeze themselves and release the liquid. This can be a local effect, activated by an optical or electrical signal." Why do you want a polymer layer to sweat? "These layers can be used to apply a liquid locally and in a controlled manner, for example some type of medicine, a lubricant or a dirt-repellent coating. The great thing about our polymer layers is that they can be refilled over and over, if needed with different liquids."

Commercial products Looking back at the string of publications and proofs of principle realised, it is clear the 4TU.HTM project was a success. "We were very well →

New opportunities for familiar crystals

The materials that Danqing successfully set in motion are based on liquid crystals, a type of material that is mainly known as the magical ingredient of thin liquid crystal displays (LCDs). As the name suggests, the molecules form crystal-like structures. The rod-shaped molecules are arranged in a spiral structure in which each molecule is slightly rotated relative to its neighbour. This arrangement causes the polarisation direction of the light passing through the crystals to change. But where a traditional crystal is stuck in a certain ordering, the liquid variants are easier to deform. For example, the arrangement of the molecules and thus the polarisation direction of the light can be changed by exposing them to an electrical voltage. This property forms the basis of the LCDs: electrical signals determine the optical properties of the display material.

Danqing uses a similar principle, but with the tactile properties of the layer. "Producers of chemicals such as Merck find that the liquid crystals in displays are slowly but surely being replaced for example by quantum dots or OLEDs. So, they are looking for new applications of the old materials."

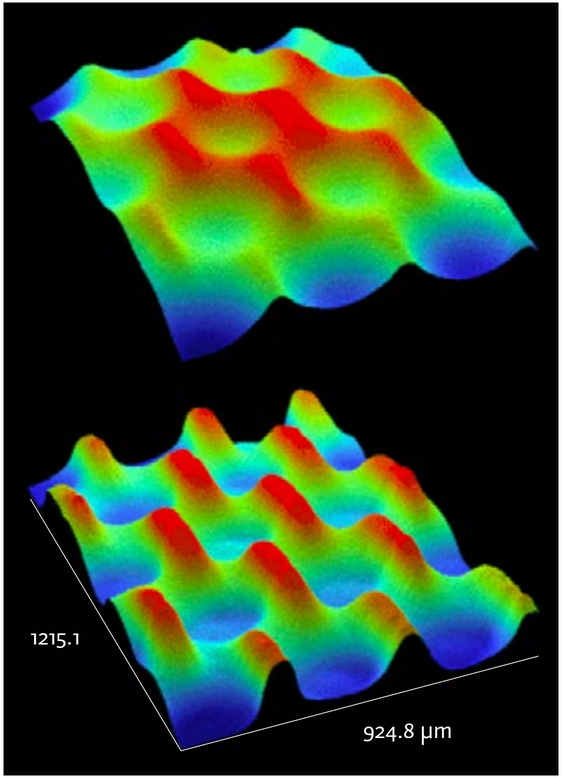
The silent force behind this effort is Prof. Dirk J. Broer, Eindhoven University of Technology's long-time liquid crystal expert. Thirty years ago, he started working on liquid crystals embedded in polymer networks. The polymer network provides flexible crosslinks between the crystals, which ensure that the material returns to its original configuration after a deformation under the influence of, for example, an electrical voltage. It is this type of material that forms the basis for the 4TU.HTM project.

"How do we translate molecular functions to functional materials?"

prepared, and lucky," explains Danqing. She hopes that within 10 years her materials will be used in technology that we use every day. Isn't that very fast? Danqing emphasises that she wants to focus primarily on pioneering new concepts and the scientific aspects thereof. Nonetheless, behind the scenes, the heat is on to scale up the processes. Together with international chemicals manufacturer Merck, the team patented their findings, and in collaboration with South China Normal University they established an institute to demonstrate the feasibility of commercial products. In 2015, Prime Minister Mark Rutte opened this Laboratory for Device Integrated Responsive Materials (DIRM) in Guanghzou. Prototypes are made here based on the ideas from Eindhoven University of Technology. The programmable ripples are not yet in production as the team wanted to start with a simpler system: glass panels covered with liquid crystals that go from transparent to opaque at the touch of a button.

Knowledge gap Reflecting on the field of designer materials, the topic of the 4TU.HTM funding programme, Danqing stresses a particular challenge: "How do we translate molecular functions to functional materials? Only a few people have that expertise. A single molecule can have a fancy functionality but this is not easily translated into the collective behaviour of many such molecules in a material. I think there is a huge knowledge gap. Perhaps future funding programmes could address this gap and stimulate synergy between molecular chemistry and materials science." Danqing and colleagues are committed to closing the gap between disciplines, and currently developing a new course in this area. "We really want to make students aware," she concludes. Students can learn from the Eindhoven team indeed: supported by the 4TU.HTM programme, Danqing has successfully covered the *entire* development chain, from molecule to material, and even a step further to a proper device, ready to be turned into a viable technology.

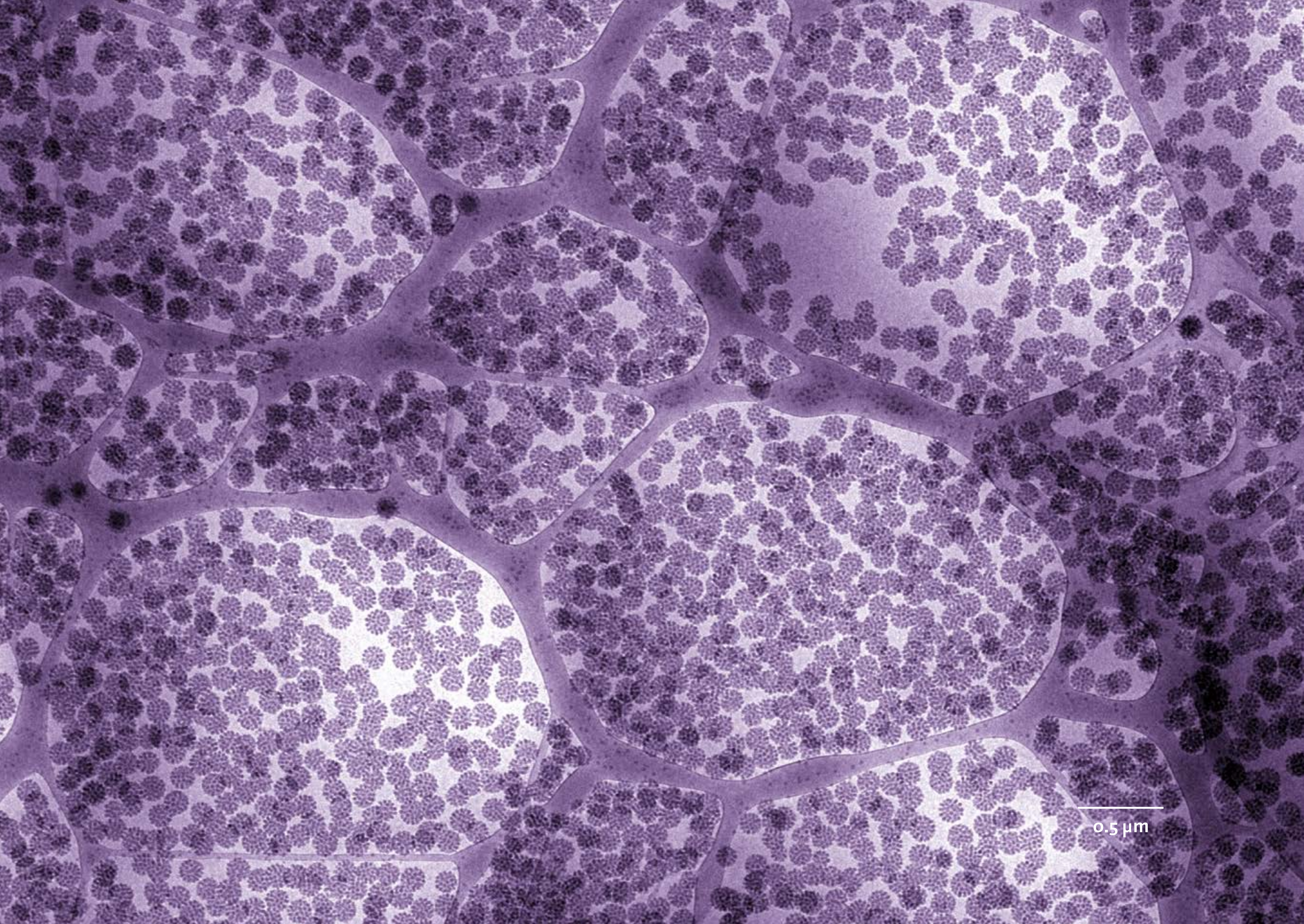
Surface protrusions emerging in a thermally responsive liquid crystal polymer network when the temperature is raised (from top to bottom picture).



International expert:
Prof. Peter Palffy-Muhoray

Prof. Peter Palffy-Muhoray is Professor of Chemical Physics at Kent State University (USA) and an internationally recognised expert in the field of liquid crystals.

"The work in the 4TU.HTM project is part of a larger community effort working on robotics based on soft materials. Although many breakthroughs are needed to realise viable devices, the hope is that the materials, as investigated by Dr. Danqing Liu, will evolve in self-sustaining constructs that can perform pre-set functions by deforming in complex, but pre-designed, manner. One of the topics that I often discussed with the researchers at Eindhoven University of Technology concerns materials that can communicate information by their deformation. The idea is that they can effectively relay the sense of touch over large distances, so that a remote person can feel the touch of another person, for example, which would be of interest in the world of augmented reality."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Project title: Understanding structure formation in hierarchical hybrid materials through in situ liquid phase microscopies
Postdocs: Dr. Joe Patterson, Dr. Mohammad-Amin Moradi
Supervisor: Prof. Nico Sommerdijk
University: Eindhoven University of Technology
International expert: Prof. James De Yoreo (University of Washington / Pacific Northwest National Laboratory, USA)

Shedding electrons on the formation of hybrid designer materials

The materials of the future are constructed from cleverly designed building blocks that come together in exactly the right way to form the desired material structure. These building blocks in turn consist of elementary components that must first be assembled from raw materials. In short, multiple levels of order are needed. To complicate matters further, it is desirable that the materials consist of both organic and inorganic components. The 4TU.HTM project 'Structure Formation' by Dr. Joe Patterson and later continued by Dr. Mohammad-Amin Moradi was about establishing the expertise and tools needed to realise hybrid materials *a la carte*. Joe: "I previously worked on the synthesis of next-generation materials. Despite great progress in this area, I was constantly faced with the same challenge: how do we design a new material if we do not understand the mechanisms by which it is formed? What drew me to the 4TU.HTM project was that we would be synthesising materials and analysing their formation processes synchronously. From my perspective, this is the big step forward that we need to take in materials science research."

Postdoc:
Dr. Mohammad Moradi

Dr. Mohammad Moradi studied chemical engineering and polymer nanomaterials at the Universities of Tehran and Sahand in Iran. He obtained his Ph.D. at Eindhoven University of Technology with research in the field of polymer chemistry. “My interest in nanotechnology was aroused by the books of K. Eric Drexler. He described a future in which tiny nanoscale robots build larger systems, a bit like we’re turning small building blocks into larger building blocks and ultimately into complete materials.” Will those nanorobots ever become reality? “That depends on how much we are willing to pay for it. It’s no coincidence that the first applications of nanotechnology are taking place in highly funded areas such as those of pharmaceuticals and electronics.” Moradi is currently working as a postdoc in the field of electron microscopy at the Department of Chemical Engineering at Eindhoven University of Technology.

"We wanted to use and further develop LP-EM for the development of new materials."

Microscopy inside liquids An important element in the project was the use of advanced microscopy techniques. Mohammad: "The standard techniques with which materials scientists examine small particles, such as dynamic light scattering, provide information about the average of large numbers of particles. They leave many questions unanswered. That is why I turned to advanced microscopy techniques that can zoom in on individual particles. But even with these techniques, I ran into limits." Whether it is electron microscopy (EM) or atomic force microscopy (AFM), materials are generally examined in an abstract test environment. This means that not much can be said about the dynamic behaviour of those materials in a realistic environment. What happens, for example, when building blocks in a liquid organise into a final material structure? Electron microscopes that can uncover processes going on in a liquid are technically a step more complex than microscopes for the solid state. Fortunately, Eindhoven University of Technology is the centre of expertise of the Netherlands for liquid-phase electron microscopy (LP-EM). "We wanted to use and further develop LP-EM for the development of new materials," says Mohammad.

Prestigious result During the first phase of the project, Joe applied LP-EM to a notorious mystery surrounding the growth of spherical vesicles from amphiphilic molecules, organic compounds with both hydrophobic and hydrophilic properties. Two liquids are involved in this process: firstly, a solvent in which the molecules dissolve well, followed, secondly, by water slowly taking the place of the solvent. As a result, the molecules are forced out of the solvent and cluster in the shape of a sphere. How does this process work? Conventional electron microscopy requires that the process be stopped, frozen and the material be introduced into the microscope. In this way it is not possible to fully oversee the dynamics. A new material system must be created for each snapshot and the process must be stopped at the right moment. This introduces a level of uncertainty, despite the fantastic ability of electron microscopy to image the molecules down to the atomic level. That is why the new microscopy technique for liquid environments was →

“Our results can be applied to any amphiphilic system, so the potential impact is huge. Think of medicine, energy, catalysis.”

used. Joe: “The LP-EM study was originally intended to be a good benchmark, something to demonstrate that LP-EM could be used for understanding soft matter self-assembly, but not something that would bring up anything surprising.” But it did produce a surprise: one that concerned the process by which the molecules form a vesicle. “Do they first form a small cluster that then grows into a vesicle? Or do the molecules cluster around the perimeter of what ultimately becomes a vesicle? Scientists have disagreed for years.” It was Joe’s LP-EM measurements that provided the answer. He discovered that actually both growth assumptions are correct: small clusters grow and together form the circumference of a larger vesicle. Mohammad: “A prestigious result!”

Amphiphile self-assembly Why did these results attract so much attention? “The importance of amphiphilic molecules cannot be overestimated,” Mohammad explains. “The building blocks of all life on earth, the cells, consist of amphiphilic molecules. Future drugs homing in on their targets will be made from this type of molecule. Other materials produced on an industrial scale, such as food and chemicals, cannot do without these molecules.” According to Joe, the 4TU.HTM project has provided fundamental insights that can be used to control the thermodynamics and kinetics of amphiphilic self-assembly. “Our results can be applied to any amphiphilic system, so the potential impact is huge. Think of medicine, energy, catalysis. In addition, the interplay between self-assembly and liquid-liquid phase separation has become a hot topic in biology in recent years. Although we did not study a biological polymer in this project, the physical chemistry is the same. I think our breakthrough also has important implications for understanding materials in living systems.” Mohammad adds: “LP-EM is a game changer in the study of vesicles and the design of new materials of medical importance.”

A serendipitous discovery To study the self-assembly of inorganic and organic components into a hybrid material system, the researchers next chose a model system consisting of polystyrene (organic) and silica (inorganic). To help the process of self-assembly, the polystyrene was

Postdoc:
Dr. Joe Patterson

Dr. Joe Patterson studied chemistry at the University of York, after which he obtained his Ph.D. at the University of Warwick (UK). He currently is an Assistant Professor at the Department of Chemistry of the University of California, Irvine (USA). Prior to the 4TU.HTM project, Joe worked as a postdoc at the University of California San Diego (USA) and the Center for Aerosol Impacts on Climate and Environment (CAICE).

"The 4TU.HTM project was an amazing opportunity for me. It allowed me to try out new ideas. Some worked well, others didn't. It also gave me great exposure in the electron microscopy community, expanded my research network, and ultimately helped me get to where I am today."

“Our son was born and I completely forgot about the experiment.”

given a negative charge and the silica a positive charge. Mohammad: “We tried to make an ordered material from these building blocks. We searched for the right temperature, the right concentration. But we were unsuccessful. It remained a disorderly system. This was during the time that my wife and I were expecting our first child. In the middle of an experiment I received a call: I had to come to the hospital urgently. Our son was born there, and I completely forgot about the experiment. About three weeks later I came back. I was about to chuck my old test materials away; I put them under the microscope one last time. And look! There was the hybrid order that we had been looking for, for so long. Apparently, the building blocks needed more time to find their ideal ordering. For the next step, which was to extend the order to a larger volume, we again made a serendipitous discovery. After drying the droplet full of the hybrid components, in a ‘quick and dirty’ experiment, exactly the desired crystal structure emerged. The binary colloids, which normally do not form a crystal structure but form random clusters, arranged in a co-crystalline manner under the influence of the functionalised silica. This is a breakthrough: colloidal crystals are used for different kinds of applications and we now have added a whole new approach to the library of techniques to make such co-crystals.”

Hybrid approach What does Mohammad think is the next step? “We want to produce colloidal quasi-crystals next. We will calculate the geometry of different hybrid particles, prepare them experimentally and analyse the output material through electron microscopy. So, we are talking about multiple levels of assembly and ordering, where the structure of the final material is determined by an interplay of organic and inorganic raw materials. I expect big surprises. We are already further than we could have imagined at the start of the project.” Mohammad is convinced that the hybrid approach, with a combination of organic and inorganic materials, opens the door to a new generation of designer materials. “Ordering rigid materials is a bit ‘all or nothing’: a single defect in the crystal lattice structure can ruin the local order, resulting in openings and disruptions. The presence of softer materials, on the other hand, ensures that there is a margin of error, which increases

Electron microscopy for materials science

Electron microscopy has become an indispensable technique for studying material structures down to the molecular level. In this technique an object or surface is examined not with light but with a beam of electrons. Since the work of the French physicist De Broglie in 1924, we know that particles, like light, have a wavelength. The smaller that wavelength, the higher the resolution of the microscope.

The advantage of electrons is that their wavelength is much smaller than that of light. This is the basis for the two main electron microscopy techniques: in the first, the electron beam scans the surface (scanning electron microscopy, SEM), whereby the interaction between electron beam and atoms releases secondary electrons, which are detected by sensors. The second variant drives the electron beam right through a thin object (transmission electron microscopy, TEM).

The disadvantage of electrons is that their small wavelength is accompanied by a high energy. Some materials, especially in biological systems, are easily damaged by it. In the commonly used cryo-electron microscopy technique (cryo-EM), a thin layer of liquid containing the system under investigation is rapidly frozen using liquid nitrogen (–196°C). At this temperature, the molecules are much less mobile and less sensitive to the electron bombardment of an SEM or TEM. The development of cryo-EM caused a revolution in the study of biological systems. In 2017, it was rewarded with a Nobel Prize.

The advantage of the liquid-phase electron microscopy (LP-EM) technique as used in the 4TU.HTM project is that dynamic processes in liquids can be followed at room temperature. This is at the expense of the imaging resolution. The design of the sample holders or nanoreactors, which are the containers in which the liquid and the experiment are packed, is crucial to limit this disadvantage. Nanoreactor development was part of the 4TU.HTM project and continues full force at Eindhoven University of Technology.

"A big shift is currently taking place in all scientific fields."

the chance of successful crystallisation. This is particularly important if we want to make complex materials through several consecutive assembly steps."

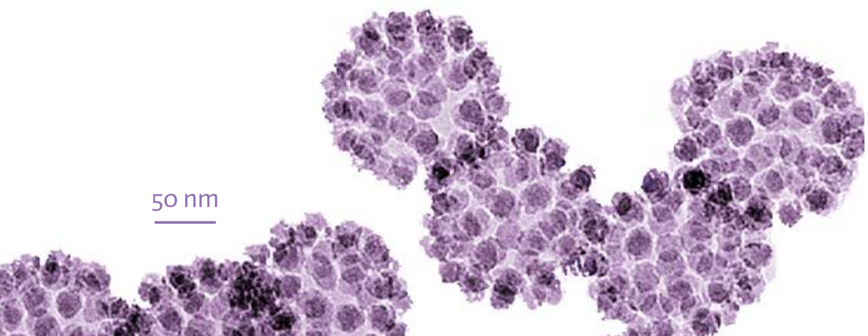
Central understanding Joe is impressed by Mohammad's work: "His analysis of the assembly mechanism of supracolloids shows again that the interplay between thermodynamics and kinetics is essential in determining the final structure of the material. In this case it is controlled by the environment and surface chemistry of the colloids and the kinetics of the drying process. This general approach can be extended to essentially any type of colloid. So, the impact can be far-reaching." Joe's work on polymeric vesicles and Mohammad's work on hierarchically organised hybrid materials support a central understanding: "If we understand the mechanism and know what governs both the thermodynamics and kinetics of the assembly process, we can design materials in a much more effective way. In both examples, experts in the field of theory and simulations were key to generalising what we learned in our detailed experiments."

Microscopy for biology Achieving new fundamental insight goes hand in hand with technology developments. Mohammad: "LP-EM has made a slow but sure rise. Special sample holders are now available with which standard electron microscopes can be turned into LP-EMs. These containers hold the liquid in which the material processes take place in a 50-nanometre thick layer of silicon nitride (SiN). We need this layer to safely hold the liquid, but the disadvantage is that it reduces the resolution of the electron beams. As a result, we are no longer able to study the essential details of biological processes in liquids." With the 4TU.HTM project as a springboard, Mohammad is now preparing a new research proposal to develop LP-EM graphene containers based on ultra-thin composite layers. "These layers are electron-transparent so that hopefully, in a few years, we can study the behaviour of complex biological molecules such as proteins in their natural environment."

Material design supported by artificial intelligence How does Joe see the future of designer materials? "A big shift is currently taking place in all scientific fields. In the

Building blocks for hierarchical hybrid materials, containing silica nanoparticles distributed over the surface of polystyrene latex structures. As shown, the resulting blocks cluster into chains, with the reorganising silica particles at the interfaces, into a single packed layer. This mechanism is to be avoided if truly co-crystalline materials are to be achieved.

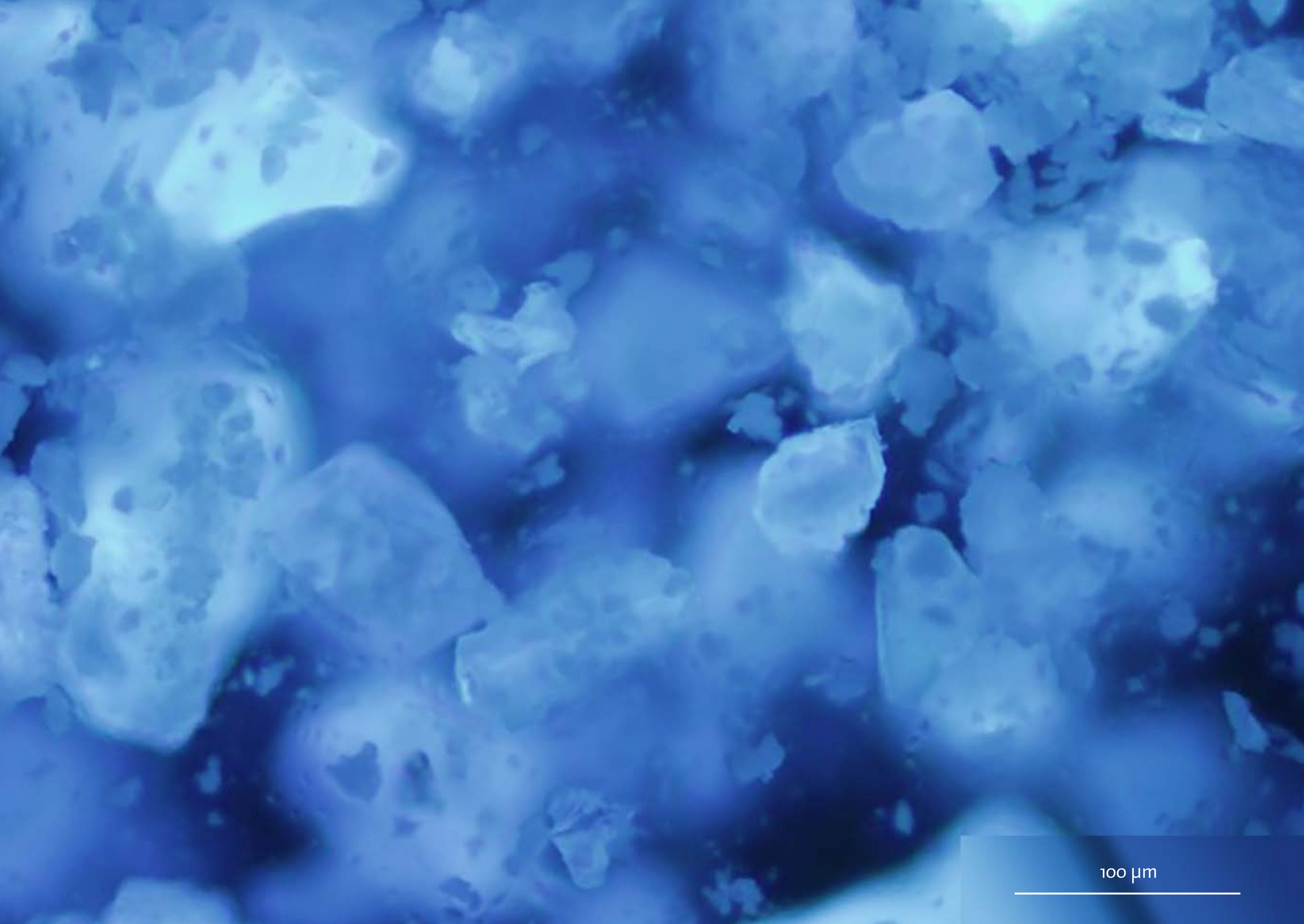
future, much more use will be made of machine learning and artificial intelligence. Apart from the hype, it is true to say that all fields will benefit from these techniques. From a simple engineering perspective, it is relatively easy to integrate machine learning and artificial intelligence into our work because they will help us process large amounts of data and make predictions that can be verified. From a fundamental scientific perspective, it is more challenging because it is often difficult to extract the 'why' from these algorithms. I think that the future will be a combination of automation, high-throughput experiments, large-scale simulations and machine learning / artificial intelligence that show us the way for labour-intensive but highly detailed experiments into the how and why of the materials."



International expert:
Prof. James J. De Yoreo

Prof. James J. De Yoreo is Chief Scientist, Materials Synthesis and Simulation across Scales at Pacific Northwest National Laboratory, and Affiliate Professor in both Materials Science & Engineering and in Chemistry at the University of Washington (USA). Trained as a physicist, he pioneered the use of *in situ* force microscopy to understand the physical principles underlying the formation of biominerals and protein assemblies. More recently, he has undertaken the use of *in situ* liquid-phase electron microscopy (LP-EM), providing fascinating new insights into the mechanisms of crystallisation in solution.

Dr. Mohammad Moradi: "Prof. De Yoreo came to Delft, Eindhoven and Twente and gave some fascinating lectures. He has a very long track record in both atomic force microscopy and electron microscopy and offered very helpful advice throughout the project."


100 µm

Project title: **From Flatland to Spaceland: Towards advanced, three-dimensional materials bottom-up, from polymer decorated nano- and microstructures**
Postdoc: **Dr. Maciek Kopeć**
Supervisor: **Prof. Julius Vancso**
University: **University of Twente**
International expert: **Prof. Krzysztof Matyjaszewski** (Carnegie Mellon University, USA)

Brushing up on functional polymer coatings

We demand a lot from the materials we use every day. They must be reliable, reproducible, affordable and, with more and more emphasis, environmentally friendly. Each material must perform one or more functions, and for that reason it should have specific mechanical, optical, electronic and/or thermal properties. It can come as no surprise that some materials simply fail to meet all simultaneous requirements. In such cases, materials scientists are asked whether functionalisation is possible, for example by applying a surface coating to introduce the required properties. The 4TU.HTM project 'From Flatland to Spaceland' zoomed in on one such coating material, consisting of long, densely packed polymer molecules. Prof. Julius Vancso devised the project as part of his mission to achieve molecular-scale control of functional polymer platforms, and to utilise them in advanced applications. Julius: "What I mean by 'advanced' is that without such molecular scale control, the swiftly growing need for new material functions cannot be met or is notoriously difficult to meet by other approaches. Challenges standing in the way of efficient 'designer' materials for applications related to energy supply, environmental clean-up or in the biomedical domain need to be addressed now."

Postdoc: Dr. Maciek Kopeć

Dr. Maciek Kopeć obtained his Ph.D. at the Institute for Metallurgy and Materials Science (Polish Academy of Sciences) and the Department of Chemistry of the Jagiellonian University in Krakow, Poland. His Master's degree was in the field of polymer chemistry and technology.

Prior to the 4TU.HTM project, he worked as a postdoc at Carnegie Mellon University in the USA. "Both my parents studied chemistry, so I always naturally liked it and decided to study chemistry and chemical engineering. Although I picked polymers by accident, it turned out to be a good decision as I'm still fascinated by these materials." After completing the 4TU.HTM project, he briefly worked as a Research Associate at the University of Bristol and is now a Lecturer at the University of Bath in the UK. "I am busy with new topics, but I will certainly continue with the research line of the 4TU.HTM project in the future."

“We went looking for a viable alternative to heavy metals.”

Functional coating “Take, for example, the lubrication of pipes that drill for oil,” continues Dr. Maciek Kopeć, postdoc on the project. “These so-called pipe dopes are mixtures of an organic lubricant with fine metal particles. They are also used as a sealant to make connections in pipelines leak-tight and pressure-tight.” Why use metals as lubricants? “Metal particles, such as copper or zinc, find and fill the smallest irregularities and can be deformed under pressure. But because of their toxicity, the oil industry is looking for alternatives. Titanium oxide nanoparticles are an option, but mix poorly with the organic lubricants. So, we went looking for a thin organic coating to make these nanoparticles a viable alternative to heavy metals.” To apply a functional layer on a surface, the researchers turned to a technique called Atom Transfer Radical Polymerisation (ATRP).

Hairs in a toothbrush ATRP is a precision synthesis technique developed in the 1990s by Prof. Krzysztof Matyjaszewski, not coincidently associated with the 4TU.HTM project as its international expert. ATRP has since become one of the most effective and widely used methods to form long organic molecules - polymers - from smaller components. It has been successfully used in a wide range of every-day applications such as adhesives, sealants and pigments for printer inks and cosmetics. Future developments are foreseen for biomedical coatings, biodegradable plastics and in the optoelectronic and automotive industries. “What makes this controlled polymerisation technique so attractive for functionalising surfaces is that it yields ultra-thin polymer layers with well-defined properties such as molecular weight, thickness and functionality”, Maciek explains. “In our case, we grew polymers on an inorganic surface. Using the ATRP technique, this results in a forest of long parallel molecules that are packed so closely together that they form a brush-like structure, like the hairs in a toothbrush.”

Moving beyond hit-and-hope In the Netherlands, it was mostly Julius and his Materials Science and Technology of Polymers (MTP) group at the University of Twente who worked on ATRP, albeit mainly to characterise the thin polymer layers grown with the technique, for example

"These environmentally friendly TiO_2-based lubricants could replace lubricants currently used in the oil and gas industry."

by scanning it with atomic force microscopy to reveal the surface structure. The idea behind the 4TU.HTM project was to apply the ATRP technique, specifically the polymer brush layers, to a number of promising systems. In addition, it was an excellent opportunity for Julius' group to broaden their ATRP expertise by mastering the design and synthesis of the polymers. Teaching staff and students formed an important part of the project, Maciek emphasises. "The synthesis of the building blocks for ATRP technology is often copied from recipes in the literature in the hope that it works right away: hit-and-hope. By knowing more about the polymerisation mechanism, the MTP group will be better equipped to design materials as desired. This will speed up their research and increase its quality." Since he had just done a postdoc project in the Matyjaszewski group and was eager to work in the Netherlands, the project seemed made for Maciek. "I was in the right place at the right time."

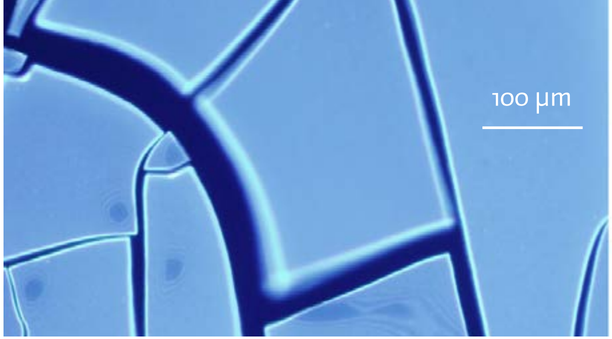
Brushing away friction and wear Returning to the search for pipe doping materials without toxic metals, Maciek and co-workers were successful beyond their expectations: "ATRP provided excellent polymerisation control and a well-defined polymer brush layer around the particles. We compared the polymer-covered TiO_2 particles with bare ones and with commercially available greases. As expected, the organic coating decreases friction and wear. In fact, the coated particles performed on par with commercial metal particles-containing dopes, although the TiO_2 is still not as soft and malleable as heavy metals. These environmentally friendly TiO_2-based lubricants could replace lubricants currently used in the oil and gas industry. Furthermore, the versatility of our approach and popularity of TiO_2 in all kinds of applications make for a powerful combination."

Stimuli-sensitive surfaces Next, Maciek set to work growing polymer brushes from poly(methyl methacrylate) (PMMA), an organic material better known as plexiglass. The resulting surface coatings were ultrathin, less than 50 nanometre thick. "We know that this polymer does not dissolve in water or alcohols but does in a mixture of these liquids. After growing the polymers on a silicon substrate, we saw that the polymer brush structure extends in a water/alcohol mixture, and collapses when brought into contact with pure solvent. We used this behaviour to test a new sensor-like functionality: by means of 'click' chemistry, we attached fluorescent end groups to the polymers. When the polymers collapse in water or alcohol their end groups cluster, resulting in the loss of their fluorescent capacity, which can be reversibly switched back on by changing the solvent. Our experiments showed how both the fluorescence and thickness of the modified PMMA brush layers can be controlled by the solvent. In this way, we demonstrated the principle of stimuli-sensitive ultrathin surface layers."

Mysterious fluorescence In a similar project, Maciek opted for a polymer that does the exact opposite: fluorescence only arises when the polymers cluster together. "Polyacrylonitrile (PAN) is a material that is commonly used in the mass production of carbon fibres. Only a few years ago, researchers found that the material displays a mysterious fluorescence when it aggregates. We have now shown that this effect also occurs in thin polymer layers on →

"There is no such land. The very idea of it is utterly inconceivable."

The title of the project, 'From Flatland to Spaceland', comes from Prof. Julius Vansco. It was inspired by a book for children dating back from 1884. In "Flatland: A Romance of Many Dimensions", English schoolmaster and theologian Edwin Abbott Abbott explains the mathematical concept of dimensions. He does so by describing several parallel worlds in delicious detail: Pointland (0D), Lineland (1D), Flatland (2D) and Spaceland (3D). The protagonist of the story, living happily in Flatland, gets to experience them all: *"In Flatland thou hast lived; of Lineland thou hast received a vision; thou hast soared with me to the heights of Spaceland; now, in order to complete the range of thy experience, I conduct thee downward to the lowest depth of existence, even to the realm of Pointland, the abyss of no dimensions."*
But more, the book describes the sheer impossibility of explaining to any of these worlds the existence of a world with a higher dimensionality, up to the inconceivable and unspeakable suggestion of a world with four dimensions. Julius: "I consider this book as one of the most thought-provoking pieces of science fiction literature with a mathematical flavour. It is a fitting title for the 4TU.HTM project, as we aimed to create a new class of 2D materials platforms and use them to construct 3D systems across the length scales. When we design and build systems with 3D control, we must start the process of building up the material from a molecular platform usually anchored to a surface. These surfaces look a little bit like the foundations of a multipurpose building. Surface-initiated, controlled polymerisations provide such platforms for molecular constructions."



Aggregation-induced blue fluorescence from polyacrylonitrile (PAN) films observed under a fluorescence microscope.

a solid surface, no more than 15 nanometres thick, created using the ATRP technique.” Since polymer brush layers are very dense, it leads to inevitable aggregation of individual polymer chains. In the case of PAN, this resulted in blue fluorescence observed in the solid state. Getting this result was not easy: the material proved difficult to polymerise, the samples difficult to handle. “Not at all a material system with robust applicability, but still a very interesting result,” according to Maciek. “This is fundamental research. Which applications it will have is not yet clear. But I would like to investigate it further.”

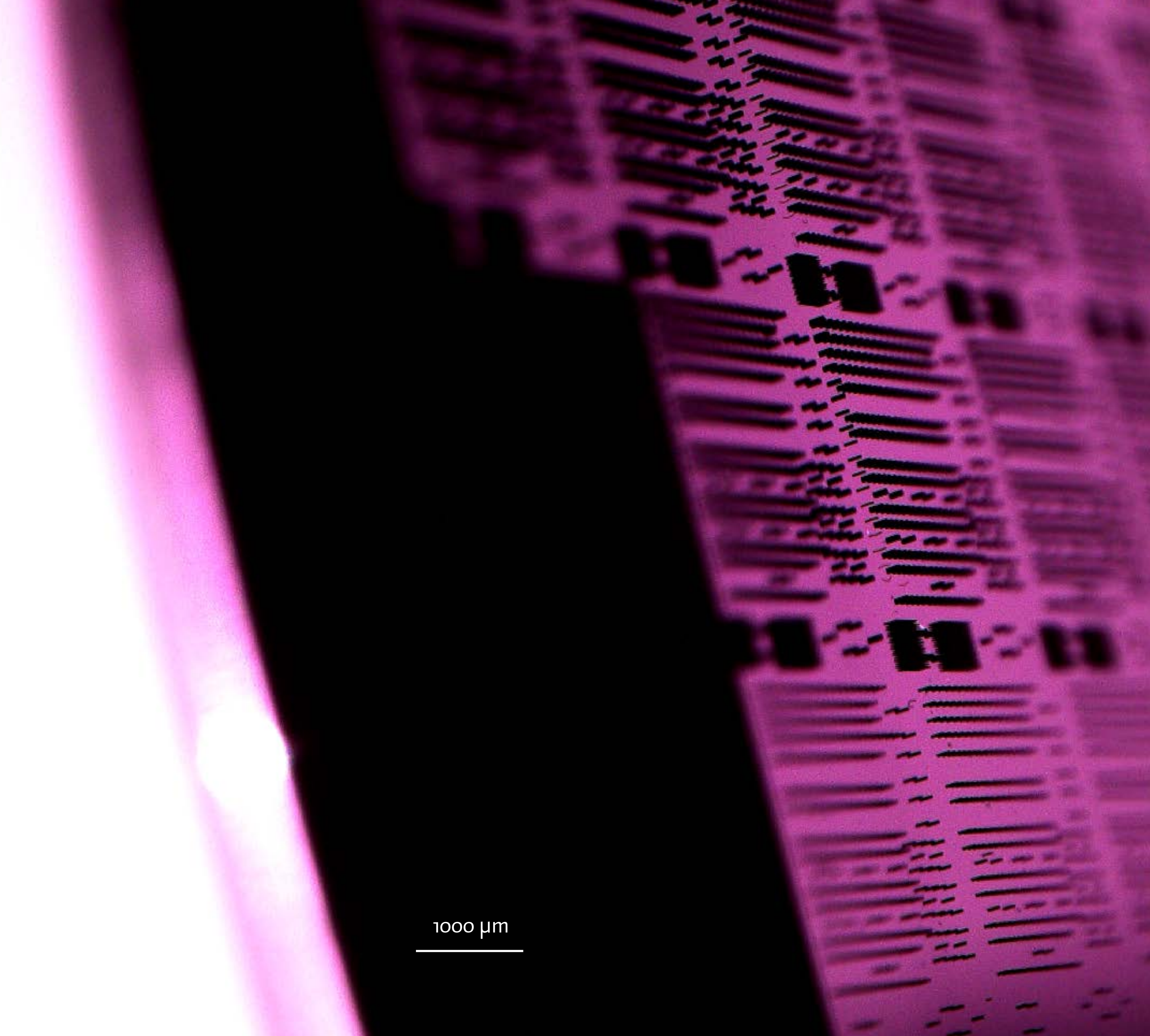
Painting patterns Using ATRP, polymers can either be grown directly on the surface (‘grafting from’) or in a liquid and then deposited on the surface (‘grafting to’). Maciek followed both routes to create his stimuli-sensitive smart surfaces. “The advantage of the second method is that it allows to use lithographic techniques from the microelectronics industry or an inkjet printer to draw a micrometre-sized geometrical pattern of a primer on the surface. The polymers attach only to that pattern and not to areas outside of it, so that the surface pattern becomes a patterned microstructure.” Alternatively, the polymerisation step of the ATRP technique can be designed to be triggered by light. “Using photopolymerisation, we can define a patterned polymer coating by shining light onto the surface through a shadow mask in which an opening has been created in the shape of the intended structure - a super-straightforward technique commonly used in the microelectronics industry as well. The combination of fluorescence signalling in response to an external impulse and easy ‘patternability’ have attracted much attention. Patterned functional surfaces can find applications in sensing, light harvesting or organic electronics.”

Applications waiting to be explored Julius is keen to mention other examples of material structures explored as part of the 4TU.HTM project: “One example is in polymer scaffolds engineered for regenerative medicine. We achieved breakthrough developments due to the application of surface-initiated ATRP to functionalise the scaffolds. We also made cellular ‘spongy’ microstructures for thermal insulation foams, starting from functionalised nanoparticle surfaces. The surface-engineered nanoparticles in this case provided a foam-cell nucleating component. For these, and similar, developments one indeed needs controlled, surface-initiated polymerisations, often in sequential chemical reactions, for which ATRP is very well suited." Maciek agrees that the ATRP technique has many more applications in store for us. "Think of nanoparticles that are added to plastics to improve the overall material properties. Polymer brushes around those nanoparticles can prevent them from clustering so that they get nicely distributed over the organic host material. Another area of application is in antifouling surfaces, where the polymer coating makes the material less susceptible to caking of dirt, which is essential for applications in biological environments." It is clear that the ATRP technique has a bright future ahead. Through the 4TU.HTM programme, the Netherlands has strengthened its position in this exciting area of polymer chemistry for designer materials.

International expert:
Prof. Krzysztof Matyjaszewski

Prof. Krzysztof Matyjaszewski is Professor of Natural Sciences at Carnegie Mellon University in Pittsburgh, USA. He leads the Polymer Group and is director of the Center for Macromolecular Engineering. In 1994 he developed the Atom Transfer Radical Polymerisation (ATRP) process, one of the most effective and widely used methods for carrying out a controlled radical polymerisation.

Supervisor of the 4TU.HTM project Prof. Julius Vansco was thrilled to have Prof. Matyjaszewski on board: "He made a very strong impact on the ongoing Dutch developments in this area during his visits to the universities that participated in the 4TU.HTM programme, and also beyond. Applications of controlled free radical polymerisations to prepare designer materials have been brought to the next level of development in many places within the Netherlands as a result." Matyjaszewski was happy to meet his colleagues in the Netherlands: "Polymer research in the Netherlands is very strong, with many creative and motivated scientists. In terms of designer materials, the four universities of technology of the Netherlands are leading, not only in Europe but worldwide." As to the future of the field, Matyjaszewski explains: "The field is relatively new, barely ten years old, yet it provides access to materials that were not available before with extremely densely grafted polymer brushes that can dramatically change material properties, even for very thin films with thicknesses less than a micrometre. The result is materials with very exciting properties, such as antifouling surfaces or super-lubricating materials with essentially no friction."



Photograph of a wafer onto which a pattern of vertically aligned multi-walled carbon nanotube arrays coated with super-conductor material has been created.

Project title: **Superconducting carbon nanotubes composite as vertical interconnect for qubit integration at cryogenic temperature**
Postdoc: **Dr. Amir Mirza Gheytaghi**
Supervisor: **Prof. Kouchi Zhang**
University: **Delft University of Technology**
International expert: **Prof. C.P. Wong** (Georgia Institute of Technology, Atlanta, USA)

Familiar techniques, new materials: preparing for the quantum revolution

It is a busy day in the cleanroom, the dust-free laboratory of the Faculty of Electrical Engineering, Mathematics and Computer Science at Delft University of Technology. As sealed off as possible from potential contamination and even daylight, scientists dressed from head to toe in protective clothing are operating machines for the manufacturing and study of microelectronics. For decades, cleanrooms around the world have been at the basis of the electronics infrastructure that the modern world can no longer do without. During that time, the manufacturing processes and associated equipment have been accurately tuned in order to sculpt microchip structures with a precision down to the sub-micrometre level. But this success is fragile: any change in process setting or choice of material requires lengthy re-optimisation, with the risk that the original quality level will be lost. No surprise, therefore, that there is some reluctance to introduce a new material or process. "This is what my project was aimed at: exploring whether an exciting application in the quantum domain was worth introducing a new material into the cleanroom," Dr. Amir Mirza Gheytaghi says about his 4TU.HTM project 'Superconducting Nanotubes'.

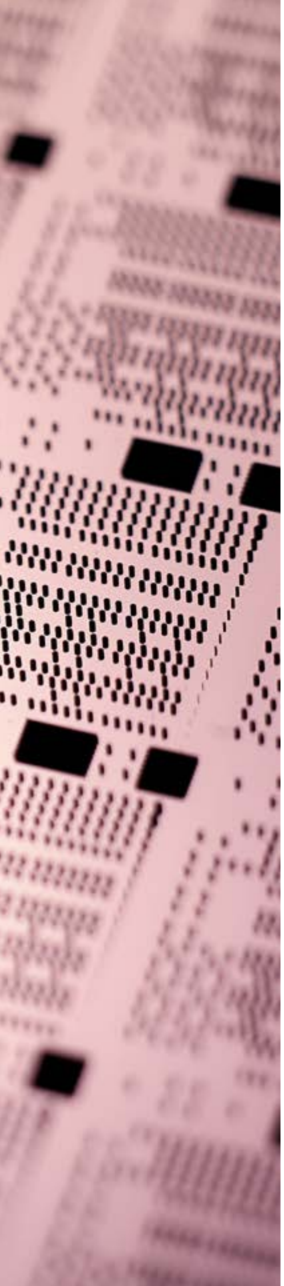
Postdoc: Dr. Amir Mirza Gheytaghi

Dr. Amir Mirza Gheytaghy has a Master's in thermal engineering and a Ph.D. in mechanical engineering from Iran University of Science and Technology. During his Ph.D. research, he already spent ten months at Delft University of Technology, as a guest researcher in the microelectronics department. "The great thing about engineering subjects such as mechanical engineering and electrical engineering is that they are very practical, tangible topics and at the same time based on fundamental theories. I owe my choice for heat engineering to the enthusiasm of my teacher." When Amir started working for the 4TU.HTM project, he had limited experience with materials. "It was a wonderful moment to see my very first bundle of carbon nanotubes. I made that! I have learned a lot in the cleanroom, and I continue to benefit from the experience. In fact, a lot of disciplines come together in the field of microelectronics; in addition to electrical engineering, it is also about heat engineering, mechanical engineering and materials science. All these fields work closely together in the cleanroom. I learned that it's all about making connections between people and between disciplines." Amir is now pursuing a new postdoc project in Delft, on the electronics that turn cars into self-driving cars.

> *“Large companies such as Google and Microsoft are working hard to upscale and commercialise quantum technologies.”*

Bringing together two worlds Successive generations of electronics have been and are still being developed and produced on the basis of the proven production lines known under the collective name CMOS (complementary metal-oxide semiconductor). Yet very occasionally a development comes along that requires new technological solutions. Quantum electronics is such a development. This new type of electronics revolves around the laws of quantum mechanics that enable radically different types of functionalities, leading to, for example, extremely powerful computers or infallible digital encryption. However, the electronic circuits involved are so small and fragile and require such extreme (cold) conditions to operate that the proven CMOS materials and production lines may be insufficient. Amir: “So far, quantum innovations have only been developed at the laboratory scale. But large companies such as Google and Microsoft are working hard to upscale and commercialise quantum technologies. So, it is high time to bring together the worlds of proven CMOS techniques on the one hand and quantum electronics on the other.”

Looking for an alternative A wide grin appears on Amir’s face when the quantum field comes up in the interview. “It is such an exciting new area of research. Prof. Zhang, the professor who supervised me in this project, asked me if I knew how many groups in the world were working on the large-scale introduction of quantum electronics. There are just a few. He said: you are now one of them.” It is the task of materials scientists such as Amir to develop the materials and production processes for the quantum systems of the future. To what extent can CMOS techniques be used for large-scale production? Amir explains the differences between today’s electronics and the upcoming quantum generation: “Where traditional computers have bits, quantum computers work on the basis of quantum bits, or qubits for short. A lot of research has already gone into the development of various types of qubits. For example, there are qubits based on superconductors, which are materials that conduct electrical currents without resistance provided the temperature is low enough.” The next challenge is to combine multiple qubits in an integrated quantum chip. “How do



"Although a single carbon nanotube can be superconducting, superconductivity in a bundle of carbon nanotubes is more difficult to realise."

you connect qubits in two and in three dimensions? The electrical connections across the silicon substrate – called through-silicon vias or TSVs – must be superconductive, just like the qubits themselves, to prevent them from heating up the system and disrupting the quantum magic. Their manufacture must be compatible with that of the qubits, and any contamination can be a fatal. Traditional TSV materials cannot satisfy all these requirements, so we went searching for an alternative."

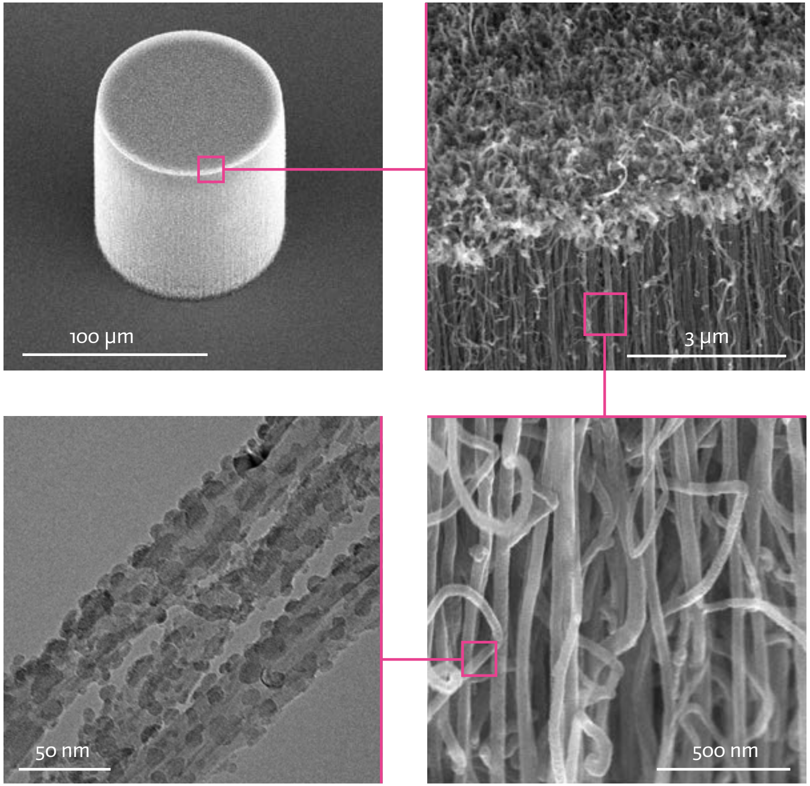
Carbon nanotube bundles "We decided to look at carbon nanotubes. These elongated material systems, a few nanometres in diameter, were discovered in 1991 and caused a bona-fide hope. The properties of a single carbon nanotube are amazing: stronger than steel, more conductive than copper, lightweight, more light absorbing than black paint – the list goes on and on. But on a larger scale, where you bundle hundreds of nanotubes to obtain material structures of micrometres in size, the properties are different. This somewhat dampened the hype, but the hope remained." Initially, Amir wanted to make TSVs based on bundles of nanotubes that would be both strong and highly conductive. Unfortunately, the bundles did not offer the features that he was looking for. "Although a single carbon nanotube can be superconducting, superconductivity in a bundle of carbon nanotubes is more difficult to realise. We then decided to use the bundles as scaffolding material for a proven superconducting material. In the end, we even discovered that these coatings functioned perfectly well even without being filled with nanotubes."

A labyrinth of parameters This research meant that Amir went on an adventure in the labyrinth of materials and process parameters, an adventure that was already started by Amir's predecessor in the 4TU.HTM project, Dr. René Poelma. By coating and infiltrating carbon nanotube bundles with amorphous silicon carbide (SiC), René tuned their mechanical properties over a wide range, from foam-like softness to ceramic-like hardness. Along the way, the team provided proofs of concept of carbon nanotube-based thermoacoustic and thermal applications. "We also developed a synthesis recipe to lower the temperature needed to grow the nanotubes," says Amir. "They're most often grown at 800°C. This temperature is too high to be compatible with the CMOS production line. Other materials start diffusing all over the place at that temperature. To introduce carbon nanotubes into the world of CMOS, that temperature had to go down, to at least below 400°C. Our group succeeded in reducing it to a record-low temperature of 350°C." To do so, the scientists used a cobalt-based catalyst that is brought into contact with acetylene gas (C_2H_2). The reaction that subsequently takes place causes the carbon tubes to grow. This was not the only outcome of the project, Amir explains. "We also mapped the optical and mechanical properties of the bundles with and without superconducting coating and the diffusion of coating material into the carbon nanotube bundle. We built a 'forest' of carbon nanotube bundles on a surface, that together absorb more than 99% of the incoming light." Such light-absorbing surfaces can be used in so-called Fresnel lenses to eliminate unwanted reflections. "By growing patterned carbon nanotube layers combined with an optically transparent polymer, we can create Fresnel lenses of which

Carbon hypes

Carbon is one of the most abundant elements in our universe. What is more, new forms are constantly being discovered. In the last century it happened three times: in 1985, a round molecule consisting of 60 carbon atoms in the shape of a football was discovered: the 'buckyball'. In 1991, an elongated version thereof: the carbon nanotube. More recently, the scientific world went crazy for the extraordinary properties of one-atom-thick layers of carbon, called graphene.
Dutch scientists played an important role in the string of discoveries triggered by the new carbon nanotubes: in 1998, they created a transistor on the basis of a single nanotube. The results were seen as a breakthrough in molecular electronics, the field that aims to miniaturise electronics to the smallest possible scale. Carbon nanotubes would unleash a revolution in solar cells, batteries, filters, electrical cables and many more applications. However, the step from a single molecule to a manageable material on the macroscale proved to be difficult. The most recent setback was the discovery that single nanotubes can be a health hazard. Yet, all the excitement has not been in vain: the material is now being used, albeit in the form of composites, with the carbon enhancing the mechanical or electrical properties of a host material. Nanotubes are currently ingredients of batteries, rust-resistant paint and mechanical parts of aircraft and bicycles.

“It was a wonderful moment to see my very first bundle of carbon nanotubes. I made that!”



the focal point can be changed by stretching the substrate. The simple manufacturing process could be cheap enough to make disposable microscopes, which are valuable for health diagnostics.”

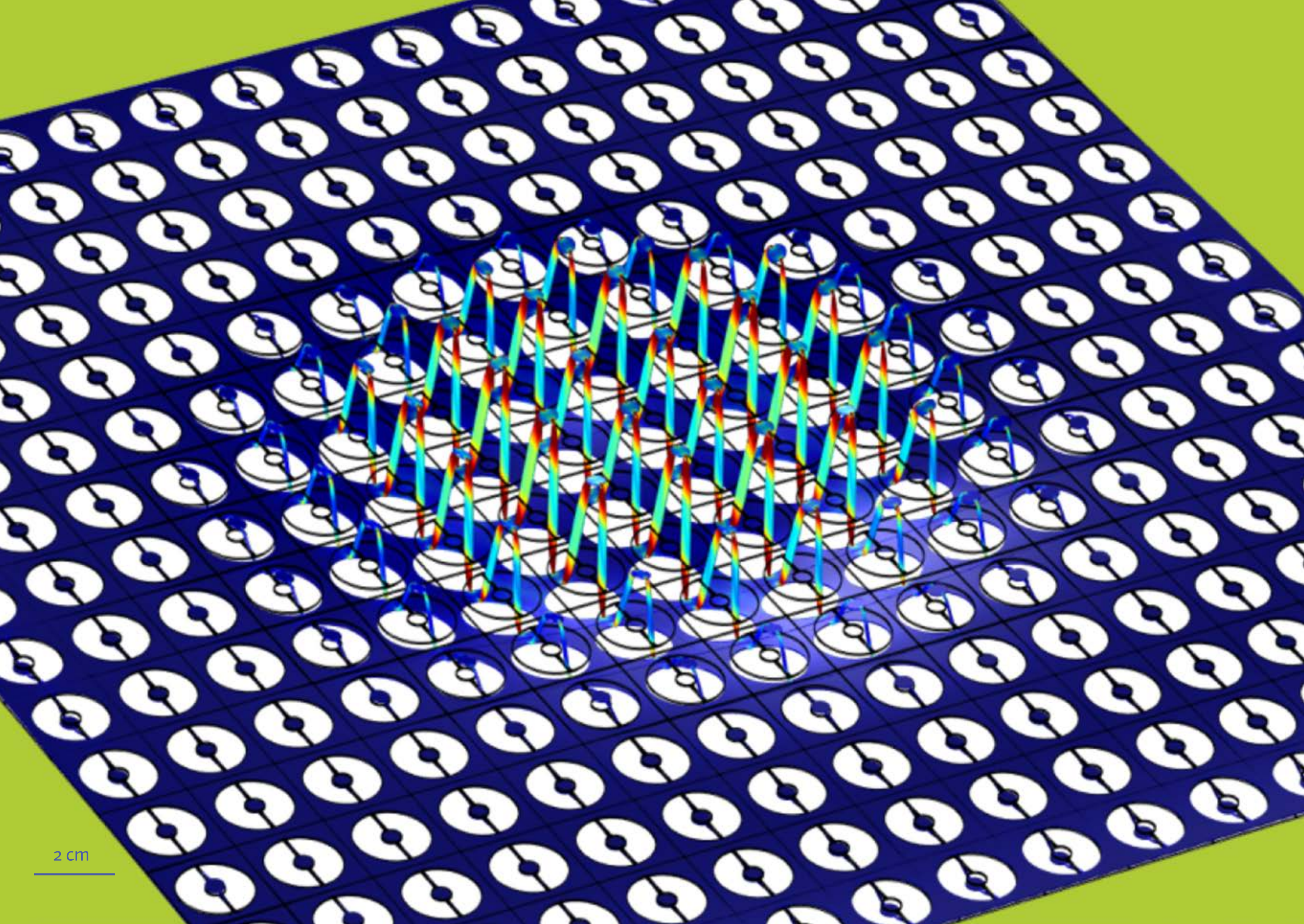
Building a bridge Returning to the original challenge of developing vias for quantum chips, and building on René Poelma’s work on SiC-coated carbon nanotube bundles, Amir and his team came up with carbon nanotube scaffolding covered with a niobium titanium nitride (NbTiN) coating to electrically connect two levels of qubits. “This material is the optimum coating material because it is superconducting at a sufficiently high temperature.” However, as Amir stresses, the most important outcome is that his project built a bridge between the world of the quantum technologists at QuTech and the CMOS world at his faculty. QuTech is the advanced research centre that was founded in 2014 by Delft University of Technology and TNO to conduct research into the quantum computers and quantum internet of the future. “The equipment needed to test these quantum systems is highly complex. Think of cryostats that can reach temperatures as low as 0.02 K or -273.13°C, close to absolute zero. Electrical measurements at these temperatures take a lot of time. While I was lucky that there was some time available to use a cryostat at QuTech, a systematic investigation would require much more measuring time. Perhaps the four universities of technology can purchase cryostat equipment together to facilitate this type of materials research," Amir suggests. "A lot of work is still needed to make quantum technology fully compatible with CMOS techniques, and vice versa, but we have taken a first step."

"It's all about making connections between people and between disciplines."

International expert:
Prof. C.P. Wong

Prof. C.P. Wong was the international expert within the 'Superconducting Nanotubes' project. At the Georgia Institute of Technology in the USA, Wong leads the Microelectronic and Photonic Packaging Materials group.

"His many years of experience in the field of nanotubes was very useful for the project. We also strengthened our ties on other projects," explains Amir. Wong: "I gave yearly lectures for Ph.D. and postdoc researchers at Delft University of Technology. Our discussions about both fundamental aspects and technological ideas related to this project were useful, both for the team in Delft and for me. The use of carbon nanotubes in superconducting electronics is novel, and Delft University of Technology has excellent knowledge and advanced equipment to conduct experiments on carbon nanotube composite structures at cryogenic temperatures. There are still many challenges and opportunities for both scientific advances and technologic breakthroughs."
How does Wong see the future of the designer materials that the 4TU.HTM programme revolved around? "There should be more collaboration between scientists in the fields of experiments and simulations. I also expect artificial intelligence to play an important role." Recently, scientists in the Netherlands made the news by doing exactly that: using artificial intelligence to design a new metamaterial, instead of following the usual trial-and-error approach.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Project title: Metamaterials with tunable dynamical properties
Postdoc: Dr. Priscilla Brandão Silva
Supervisors: Prof. Marc Geers and Dr. Varvara Kouznetsova
University: Eindhoven University of Technology
International expert: Prof. Michael J. Leamy (Georgia Institute of Technology, USA)

Embracing non-linear dynamics to create mechanical metamaterials

Over the past centuries we have succeeded in taming the phenomenon of light. From the exceptional lenses with which Antoni van Leeuwenhoek uncovered the micrometre scale to photonic crystals designed to manipulate light down to the nanometre scale. "Now it's the turn of sound," Dr. Priscilla Brandão Silva says resolutely. In fact, light and sound are both wave phenomena: light travels by means of electromagnetic waves, while sound involves mechanical vibrations. And yet, the step from technological innovations in the field of light to similar advances for sound is a difficult one. How to manipulate sound in such a way that, for example, it is fully transmitted in one direction but completely stopped in the opposite direction? For light, this has been achieved in the form of optical diodes, but for sound it has proven very challenging indeed. What is needed to realise this and other acoustic functionalities is *metamaterials* - and therefore *metamaterials scientists*.

Postdoc: **Dr. Priscilla Brandão Silva**

Dr. Priscilla Brandão Silva studied mechanical engineering at the University of Campinas in Brazil, where she also obtained her Ph.D. in 2015. “It has always been my ambition to model material processes on the micro-scale in such a way that we can use the outcomes to develop new technologies.” After her Ph.D. graduation, Priscilla worked as an Assistant Professor at the Federal University of Ceará (Brazil), followed by the postdoc project in the 4TU.HTM programme. “This project fitted well with my Ph.D. research on metamaterials with a linear response. Thanks to the New Horizons in Designer Materials programme, I was able to move to non-linear phenomena. That was quite new for me, but exactly the path that I wanted to follow.” At Eindhoven University of Technology, there was a lot of expertise waiting for her. “Dr. Varvara Kouznetsova and Prof. Marc Geers have an excellent reputation in the field of computational mechanics. But more than that, what attracted me to the 4TU.HTM project was the collaboration with international partners. Such a collaboration provides access to multiple points of view and the opportunity to learn and develop breakthrough research by combining multiple expertises and insights.” After the 4TU.HTM project, Priscilla found a new research challenge at electronics company Philips. “I wanted to convert my knowledge into innovative technology that people can use to improve their lives. My dream is to apply my knowledge of non-linear metamaterials in industry.”

"For a long time, non-linearity has been seen as complex behaviour, not well understood and therefore difficult to control."

Acoustic pinball machine What is a metamaterial? Priscilla: "The properties of a material are determined by its building blocks –atoms or molecules– and their mutual interactions. If we are aiming for completely different properties, we will have to create innovative material structures." This can be done by designing alternative, often periodic, structures. Wave phenomena are very sensitive to periodicities, but most natural and conventional engineering materials lack periodicities. The right design can make waves bounce back and forth as if in a pinball machine. All those bouncing waves interfere with each other, with surprising consequences. "It is not the chemical composition and thus the identity of material that has changed, but how the material or a combination of materials is designed to achieve extraordinary overall properties, unachievable with materials from nature."

Embracing the non-linearity The challenge Priscilla took head-on in her 4TU.HTM project 'Dynamic Metamaterials' was the non-linear elasto-acoustic response of some materials. In a linear system, a material bends or stretches to an extent that is proportional to the force exerted. Other material systems show a non-linear response, which is more complicated to model. Priscilla mentions rubber in particular: "This hyper-elastic material is a well-known example of non-linearity. For example, rubber is much easier to stretch than to compress." Although rubber and other non-linear materials are used in countless mechanical systems, their non-linear behaviour is mostly circumvented. "For a long time, non-linearity has been seen as complex behaviour, not well understood and therefore difficult to control. In short, something that is better avoided. By keeping the mechanical vibrations small, the non-linear stress versus strain graph can be approximated as being linear, and the bag of tricks from linear mechanics can be used. But what if we embrace the non-linearity of the material when creating a metamaterial? What properties can we design into it that linear systems cannot offer?"

A second band gap appears Priscilla and her colleagues undertook a journey from a simplified model, via an →

"By using the non-linearity of the material, we can give soft robots completely new programmable capabilities."

analytical approach to experimental verification. "This is what I am most proud of, that we have been able to do a complete analysis including experiments." The first step was a numerical model for the metamaterials, in which the non-linearity was captured by a so-called neo-Hookean material model, which offers an approximation of the strain-dependent elasticity modulus of rubber. "The results of the simulation were exactly as we expected: the system filters out vibrations with frequencies in a certain frequency band, and when we increase the amplitude of the incoming vibrations, this attenuation zone or 'band gap' shifts to higher frequencies. But to our surprise, a second band gap appeared when we increased the amplitude even further. We discovered that frequencies of twice the resonance frequency are also stopped by the metamaterial. This phenomenon was new and we were puzzled by it." Their numerical approach did not provide insight into the origins of the effect, and so the scientists went on to construct a more detailed model.

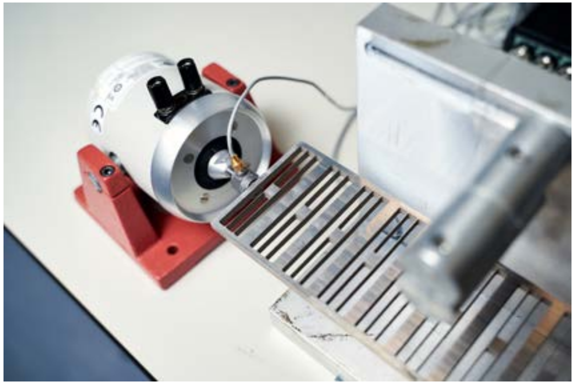
Successful model calculations To realise this model, the input from Prof. Michael J. Leamy at GeorgiaTech, the international expert involved in the project, was essential. Together with his group, Priscilla developed a semi-analytical model that covers various time and spatial scales. While it turned out to be a complex endeavour, Priscilla and her team were successful in their calculations. "Using this new model, we discovered that the system actually becomes unstable in the event of excessive input vibrations. The system solves that problem by itself, by using part of the vibrational energy to excite a second vibration at half the frequency of the input vibration. If the input frequency is set such that this half frequency coincides with the resonance frequency, energy sinks into the local resonators, and the acoustic signal is stopped. "This phenomenon of subharmonic resonance offers new possibilities for wave manipulation, for realising externally controllable functionalities in the metamaterial." And what makes it extra interesting from the point of view of practical applications: hyper-elastic materials such as rubber are already being used pretty much everywhere. "It is also an important ingredient in the soft robotics family. By cleverly using the non-linearity of the material, we can give soft robots completely new programmable capabilities. Similar behaviour cannot easily be obtained using linear mechanics."

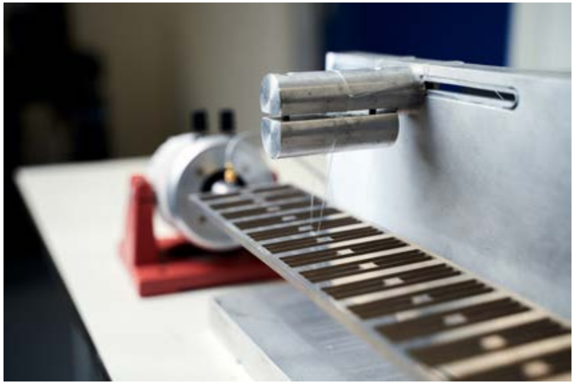
Experimental verification Crowning achievement of Priscilla's project was the experimental verification. "We opted to fabricate a simple model system. So, no epoxy containing rubber-covered metal balls but a microsystem made entirely of aluminium, micromachined into an elongated strip with 50 openings in it. In each of those openings, an aluminium mass was suspended by four arch-shaped beams, mimicking the non-linear behaviour of rubber." The experimental results are hot off the press, and there is a lot of data still to be worked out, but the experiment confirms the existence of a second stop band around the double resonance frequency that took the researchers by surprise in the simulation phase. "We can also see that it takes a while before that band comes into existence. This delay, in practice in the order of milliseconds, is consistent with the model data."

Acoustic metamaterials

The first-ever example of an acoustic metamaterial was realised in 2000. It consisted of a base material (epoxy) containing metal balls encased in a thin layer of rubber. The balls were placed at equal distances from each other, so that a periodic structure of 8 x 8 x 8 unit cells was created, reminiscent of a photonic crystal. If a mechanical vibration moves through this metamaterial, the metal balls resonate. The rubber ensures that these vibrations are almost independent of the surrounding material; they are localised resonances, and provide an additional degree of freedom for the system. The energy for these resonances comes from the mechanical vibrations travelling through the metamaterial, which therefore lose a lot of energy. This made the material an effective type of sound insulator. It insulates better than a conventional material with the same density and thickness. In fact, it mainly stops sound of a certain frequency. That is how the field of acoustic metasystems was born. Next, Prof. Michael J. Leamy went a step further by investigating what would happen if the system went beyond its 'safe' linear regime. He discovered that the filter frequency is dependent on the input amplitude, which is the volume of the incoming sound waves. This creates a programmable metamaterial, the dream of every metamaterial scientist; the sound filtering can be tuned as desired by means of amplitude control, without the material design having to be changed.

“Working with mechanical waves is the future for fast computation.”





Prototype metamaterial consisting of 50 non-linear locally resonant unit cells fabricated from an aluminium alloy sheet.

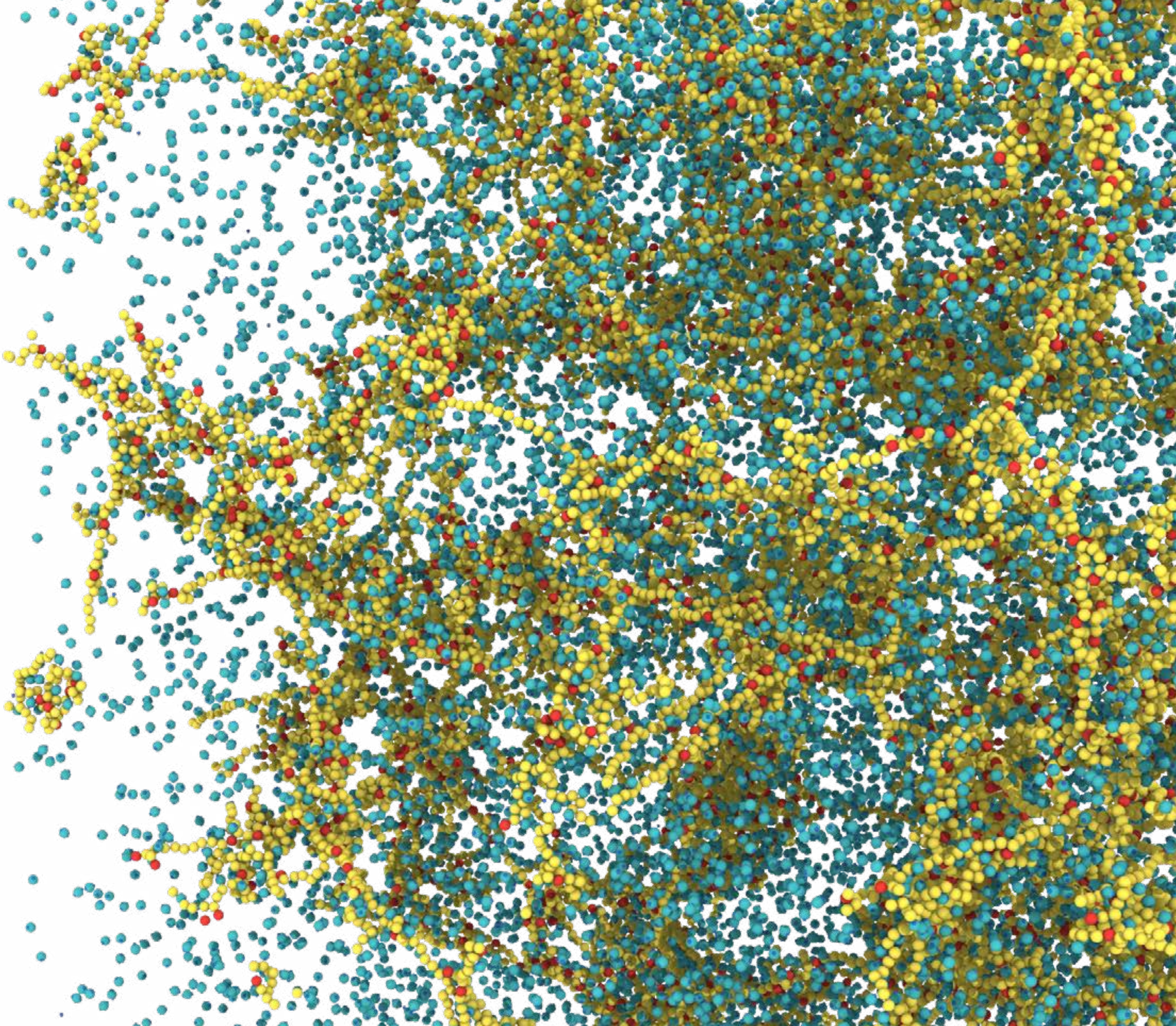
The sound of quantum computation With her semi-analytical model having proven its added value, it can now support the development of new applications. Priscilla hopes that her results will further broaden the research field of non-linear metamaterials. And although she describes her results as very fundamental, she is convinced that in 10 years' time acoustic metamaterials will be used in applications such as acoustic diodes. “The programmability of these systems will be based on the non-linearity of the metamaterials used.” Looking even further forward, Priscilla is excited about the prospects of sound being used in quantum technologies. Qubits, which are the quantum equivalents of computer bits, can be made on the basis of crystal cavities set into motion by means of mechanical vibrations. Recent advances in the fundamental control of phonons, the quanta of mechanical vibration, have inspired researchers to investigate the possibilities of phonon-based quantum computation. Some predict that qubits based on half-sound, half-matter quasi-particles called ‘phonitons’, might even outperform the quantum dot-based qubits that are currently being used to realise the first quantum computers. Priscilla notes that the scale of the current state of the art in phononics is much larger than what would be required for qubits. “Still, working with mechanical waves is the future for fast computation; it is driving a lot of exciting developments. There are also possibilities for acoustic metamaterials in new diagnostic healthcare technologies that make use of (ultra) sound.” Indeed, the era of sound may be upon us!

Page 46: Conceptual scheme of a system of non-linear locally resonant metamaterials enabling exceptional applications such as acoustic signal filtering.

International expert:
Prof. Michael J. Leamy

Prof. Michael J. Leamy leads the Nonlinear Mechanics Research Group in the George W. Woodruff School of Mechanical Engineering at the Georgia Institute of Technology. His research interests are in emerging and multidisciplinary areas of engineering science, with an emphasis on simulating non-linear dynamical behaviour present in structures and materials.

“Eindhoven University of Technology has a very strong programme in computational prediction of material response. They are particularly well-suited to bringing this computational expertise to bear on designing new materials. I have been able to contribute domain-specific expertise on acoustic metamaterials, and modelling and analysis of non-linear metamaterials in particular. My main contribution was guiding Priscilla on the use and development of mathematical tools for predicting their acoustic response. I was most surprised that the analysis developed was able to uncover the underlying mechanism (subharmonic resonance) that enabled the opening of a new, low-frequency band.” Looking forward, Prof. Leamy predicts: “Acoustic metamaterials have not seen widespread deployment in applications yet. I believe it is only a matter of time before their unique ability to passively filter and guide acoustic waves will find use in communication devices, seismic protection, and other sound-shaping applications. Non-linear acoustic metamaterials enrich their behaviour, and will most likely be found in applications at higher power levels.”



Molecular dynamics simulation of a polymer network (yellow), with permanent (red) and reversible (blue) crosslinks.

10 nm

Project title: Reversible crosslinking: a potent paradigm for designer materials
Postdoc: Dr. Nicholas B. Tito
Supervisors: Prof. Kees Storm and Dr. Wouter Ellenbroek
University: Eindhoven University of Technology
International expert: Prof. Costantino Creton (ESPCI Paris, France)

Entropy: friend or foe of the materials scientist?

The properties of materials depend not only on the building blocks from which they are constructed, the atoms, but also to a large extent on the bonds between those building blocks. These bonds come in all shapes and sizes, from weak to strong. For most materials, the breaking of bonds is irreversible, and means end of story. But there are exceptions: an intriguing polymer class contains reversible crosslinks, which are mobile connections that link polymer chains with each other and that can easily be broken, moved and reattached. This type of polymer additive is currently attracting a lot of attention because of prospects of making it into recyclable or self-repairing materials. Dr. Nicholas B. Tito became fascinated by the effects of these crosslinking additives on the overall material properties. It was the starting point for the 4TU.HTM project 'Reversible Crosslinking' that Nicholas carried out at Eindhoven University of Technology.

Postdoc: **Dr. Nicholas B. Tito**

Dr. Nicholas B. Tito studied chemistry and did his Ph.D. in theoretical chemistry at Dartmouth College in the USA. "I was inspired to study physical sciences by the powerful winter cyclones that strike my home town each year. North-eastern snowstorms are a rare example of how physics through a continuum of scales – microscopic to global – act in coincidence to form a beautiful, yet fleeting, natural structure." Building on this inspiration, Nicholas uses computer simulations to solve challenging problems in chemistry and physics. As a postdoc at the University of Cambridge, Nicolas worked with researchers at Eindhoven University of Technology, one of the partners in his research project. "I was very impressed by the collaborative nature of research in the Netherlands." Since finalising his 4TU.HTM project, Nicholas has moved to private-sector research organisation Electric Ant Lab in Amsterdam. "I go where research challenges lead me. At Electric Ant Lab we develop simulation techniques for users who aren't necessarily simulation experts. I used similar techniques for the 4TU.HTM project. What is needed behind the scenes so that these users can do carefree simulations? I love such challenging questions."

"By combining different types of simulations, we get a complete picture of the behaviour of the system."

Recyclable and self-repairing materials "Polymer materials have a disordered, spaghetti-like structure, where the polymer chains hold on to each other via chemical links or through physical entanglement. They are easy to deform and stretch. However, a variety of recent experiments show that the addition of certain kinds of reversible crosslinks lead to a 'tougher' material, yet with few consequences for the intrinsic elasticity of the polymer. The material is stretched just as easily. The only difference that emerges from the measurements is that the polymer material does not break easily when the reversible crosslinks are present, resulting in an increased toughness.
From a microscopic point of view, this is a surprising result. Adding more crosslinks into a polymer network usually causes it to become stiffer, less elastic and more brittle. This result fascinated us, we wanted to understand it."

A toolbox of simulation techniques "In the project, we wanted to see what is generally possible with reversible crosslinks. What materials can we make with it, what range of mechanical properties can we access? It was a very broad question to begin with." To find answers, Nicholas set to work with a toolbox full of computer simulation techniques, including molecular dynamics and Monte Carlo techniques. "This approach avoids the exact quantum-mechanical details of the system. A complete analytical or numerical description is simply too complex. Instead we find analytical approximations of the interactions, and use those as input to the simulations. We optimise the simulations on the aspects that we want to zoom in on, such as the thermodynamics or kinetics. By combining different types of simulations, we get a complete picture of the behaviour of the system."

Hybrid simulation "In particular, molecular dynamics simulations are very time consuming. A detailed simulation with half a million components can easily take around three days. That is why we developed several simulation and numerical modelling techniques, to cover a broader range of time and length scales. For example, we used molecular dynamics to set the coarse network of polymers into motion, occasionally interrupting for Monte Carlo moves →

"Mobile crosslinks are driven to minimize the free energy of the polymer network."

to adjust the connectivity of the reversible crosslinks. We systematically varied the rate at which those connections are broken and how quickly they find places to reattach." And that approach was successful: "Our simulations reveal that the reversible crosslinks roam freely through the material and cluster preferably around permanent crosslinks. At these sites, the polymer chains are already connected to each other, so that the extra crosslinks do not have a major effect on the mechanical properties of the material. The elasticity therefore does not decrease due to the mobile crosslinks. But if the material is pulled hard, the reversible crosslinks act as reinforcements for the permanent ones. In other words, the breaking strength does increase. This is in good agreement with the experimental results with which we started." Of course, the next question was: why do the crosslinks cluster at these specific sites?

A measure of possibility To answer that question, Nicholas came up with an unusual point of view: the entropy of the system. Usually, entropy is attributed as a measure of the randomness and disorder in a molecular system. However, Nicholas explains that entropy is better thought of as a measure of the possible configurations that the system can take; a "measure of possibility", as he calls it. This viewpoint opened the doorway to his theory for this material. "If the reversible crosslinks would be distributed randomly over the polymer material, as you would initially expect, the polymers would be pinned together at many more points, at least temporarily. This would reduce the number of possible polymer configurations and thus the entropy of the system. Fundamentally, every system strives for a state of maximum entropy. In this case, this is the situation in which the mobile crosslinks look for the immobile crosslinks, and thus reduce the entropy of the polymers the least. That is thermodynamically the most favourable from the point of view of entropy." He adds a word of warning: "Of course, the crosslinks do not really seek out specific sites in the material; they don't have a mind of their own. They move in a random fashion fuelled by the thermal energy of the system. Nevertheless, they are driven to minimise the free energy of the system. The free energy is not just enthalpy, the concept that we chemists are most

Liquid crystals
through thick and thin

In a parallel project, Dr. Nicholas B. Tito flexed his simulation muscles by looking at a polymer system that is driven out of equilibrium in a different way. "Here it was not the crosslinks that influenced the dynamics of the polymer material, but an external electric field." For this, Nicholas entered into a collaboration with another 4TU.HTM project, that of Dr. Danqing Liu at Eindhoven University of Technology. "She looks at liquid crystals in a polymer network. The liquid crystals are sensitive to electric fields, so if you put an oscillating voltage across the network, the molecules move back and forth, opening up pockets of nanometre-scale empty space. This results in the material as a whole changing in volume. But under what circumstances are these volume changes largest? In experiments, Danqing saw that this was when the temperature was raised to the so-called glass temperature of the polymer, the temperature at which the material becomes very soft. With our simulations we were able to simulate this behaviour: we too found a temperature at which the volume change was maximal. At lower temperatures the polymers do not have enough energy to make room, at higher temperatures they are so mobile that an empty space opened by a mobile liquid crystal is immediately filled up by another, which reduces the net change in volume. A major achievement was that supporting simulations allowed us to estimate the glass temperature, too; the two temperatures found in the simulations were the same. And so, our qualitative approach had turned quantitative!" Now that the simulations had proven themselves, Nicholas and Danqing apply the same approach to other questions. For example, what is the role of the frequency of the electric field?

"A whole new world will open if we wonder more often how we can exploit the concept of entropy."

familiar with, but also in part entropy. This is where the fun comes in!"

Simulation without prior knowledge What the 4TU.HTM project has delivered in concrete terms is a microscopic design concept for how to build a material that uses its own entropy to achieve a unique functionality. It has also delivered new modelling strategies for reversibly-crosslinked materials. One of these is a lattice model based on self-consistent field theory to predict the configuration of polymer networks that are changing their crosslink connectivity over long timescales. Thanks to a number of clever approximations, it calculates on the one hand the possible polymer conformations and on the other hand spatial probability distributions for the mobile crosslinks through time. "And the best thing is that the calculation requires no prior knowledge about preferred configurations of the polymers or preferred positions of the crosslinks. It is a powerful way to make an estimate for the mechanical properties of a network. This is very exciting from the modelling point of view, and it can help guide more detailed simulations," says Nicholas. For him and his team, the next step was to vary material parameters such as the concentration of crosslinks and make more predictions. "Of course, it is not irrefutable proof of the correctness of our predictions, but so far they all correspond qualitatively with experimental data from the literature. That is a great result."

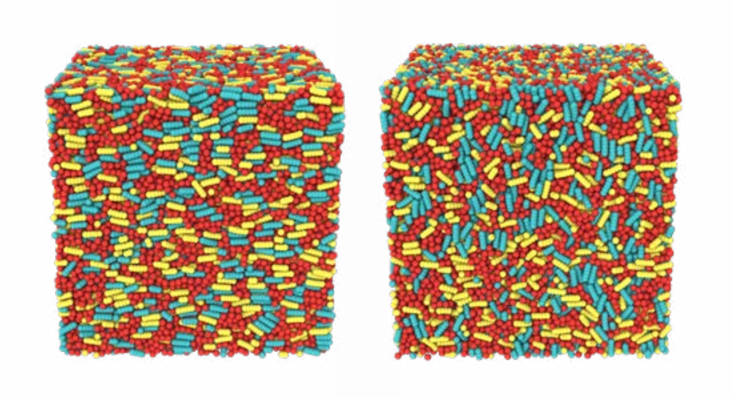
From 'foe' to 'friend' "As chemists, we are mainly concerned with making molecules that connect and bond to each other in a certain way. We tune the coupling strength, the chemical bonds, to ensure that the desired material forms from individual molecules. This chemical approach is strongly based on bonds. It is the enthalpic side of chemistry. Entropy, on the other hand, is often perceived as the 'foe' of complex materials design at the molecular scale. It manifests itself as the 'detours' away from a carefully engineered microscale assembly pathway between the initial ingredients and the final structure. These detours lead the molecules that make up the material to assemble into something other than the desired final structure." How then, can entropy be looked at as a 'friend' for materials design at the molecular scale? Nicholas explains: "From the thermodynamic point of view, entropy goes into the free energy of the material, just like the enthalpy. A system does not want to minimise its energy, but its *free* energy. Entropy therefore plays an equally important role in guiding how molecules in a complex material self-assemble into a final product. It also affects how materials behave when they are driven out of thermodynamic equilibrium, for example when you strain or stretch them. I think that a whole new world will open if we wonder more often how we can exploit the concept of entropy so that a material is, for example, more robust under different circumstances. We should think critically about how we can engineer that entropy itself, like we already do with the enthalpy, in designing the molecular ingredients that make up the core functionality of the material." Materials full of reversible crosslinks are examples of systems where entropy is the driving force behind special material properties.

Discover new materials Nicholas is an enthusiastic supporter of the entropy approach: "Take the vitrimers, →

International expert:
Prof. Costantino Creton

Prof. Costantino Creton is a CNRS research director within the Soft Matter Science and Engineering Laboratory of the ESPCI ParisTech. His expertise is in the mechanical properties, dynamics and structure/properties relationship of soft polymer-based materials, such as soft adhesives, rubbers and hydrogels.

Creton was happy to act as international advisor, having worked with the Eindhoven team before. Dr. Nicholas B. Tito: "Prof. Creton is highly regarded in the polymer physics community. He was a voice of reason from the experimental side, and vital to the 4TU.HTM project. Creton: "The Netherlands are clearly a European leader in materials science and in particular in designer materials. The idea that entropy plays a role in the attachment of dynamic bonds was new to me and a little surprising. Yet I think it is correct." When Nicholas asks whether Creton thought his entropy approach was "crazy", the answer is: "Not at all crazy, but provocative and stimulating."



Molecular dynamics simulation of a polymer network (red) containing liquid crystal molecules (yellow, aqua). By applying an AC electric field to the material, the electrically responsive mesogens (aqua) are torqued, resulting in an increase of the material volume (left to right image).

10 nm

a recently developed class of polymers that has attracted a lot of attention. At low temperatures they are a robust type of plastic with excellent mechanical properties, but at higher temperatures the crosslinks are mobilised, so the material is easily deformed and fractures can be repaired." Here, entropy is at work, Nicholas firmly says. "Entropy ensures that the polymers constantly want to explore new connections. This bond swapping translates into mobile crosslinks. I don't know whether Prof. Leibler, who discovered the material class in 2011, had entropy in mind. But if we look at newly developed materials through the lens of entropy, and extrapolate our findings, I think we can discover a lot of new materials. At least, that is what I hope for as a theoretician."

Bio-materials of the future "In the field of designer materials, I see a trend towards materials that are inspired by nature and towards the smart use of biological compounds", Nicholas says. "Nature makes materials that do cool things. I am very interested in how nature deals with entropy. How does it use or circumvent entropy? It probably does a bit of both." According to Nicholas, simulations can also make a difference in the field of bio-materials. "They teach us how complex ingredients and interactions ultimately lead to systems with all kinds of 'emergent' properties. Modern computer systems and neural networks can mimic this evolution and develop completely new materials. Not so much living materials, but materials that have evolved according to the same laws as life around us." Nicholas is excited by the possibilities: "If we focus on entropy-driven dynamics, much progress can be achieved. It's like making a sculpture. You have to obey physical laws but there are many ways to combine them to see what emerges. That's an art form I really like."

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