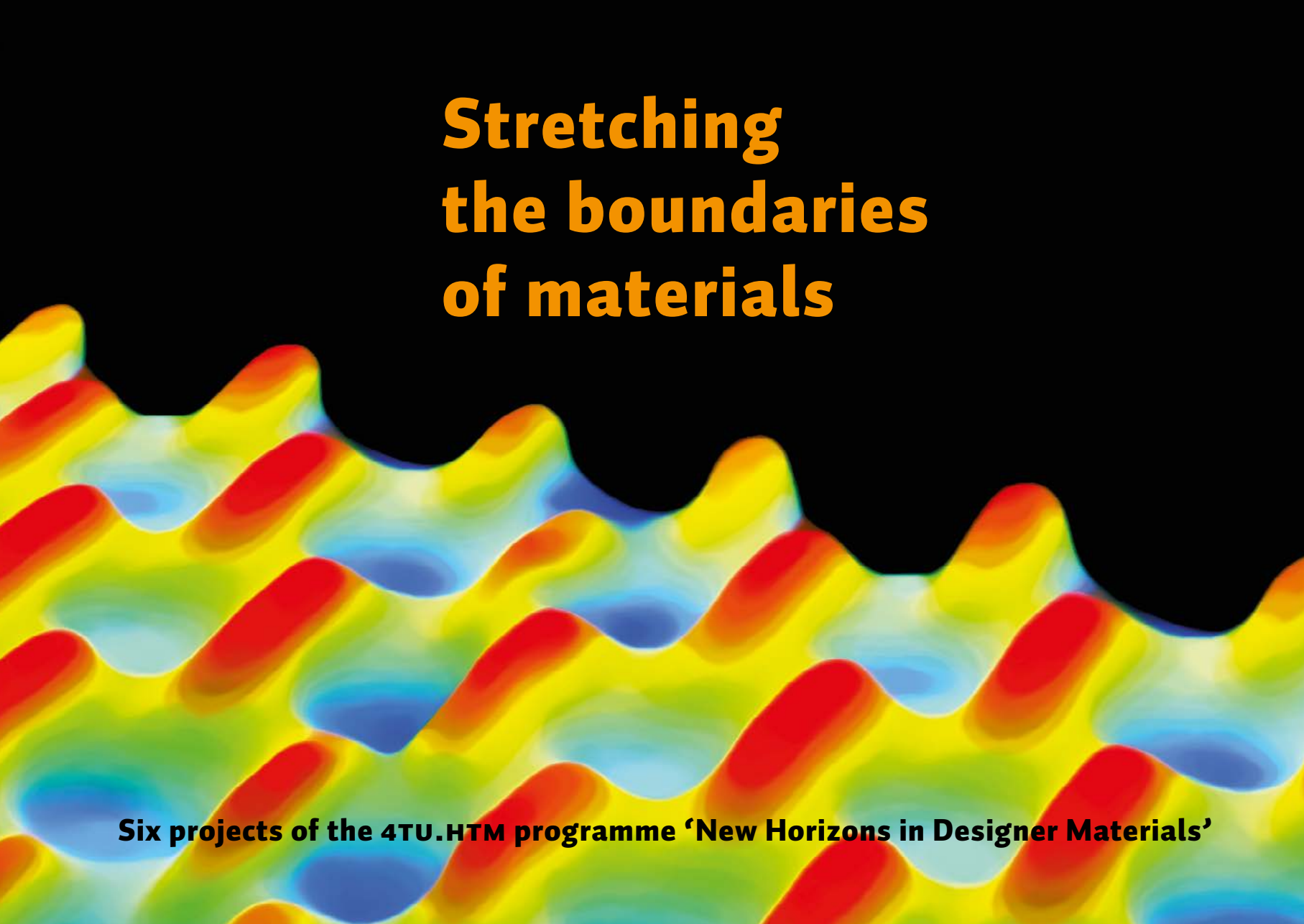
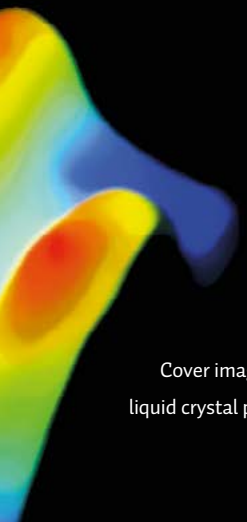
Stretching the boundaries of materials



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]

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

4TU.Research Centre
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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.

We 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,

As we enter into the second century of our co-existence

We are still to reach the sophistication of nature;

A macromolecular nirvana where

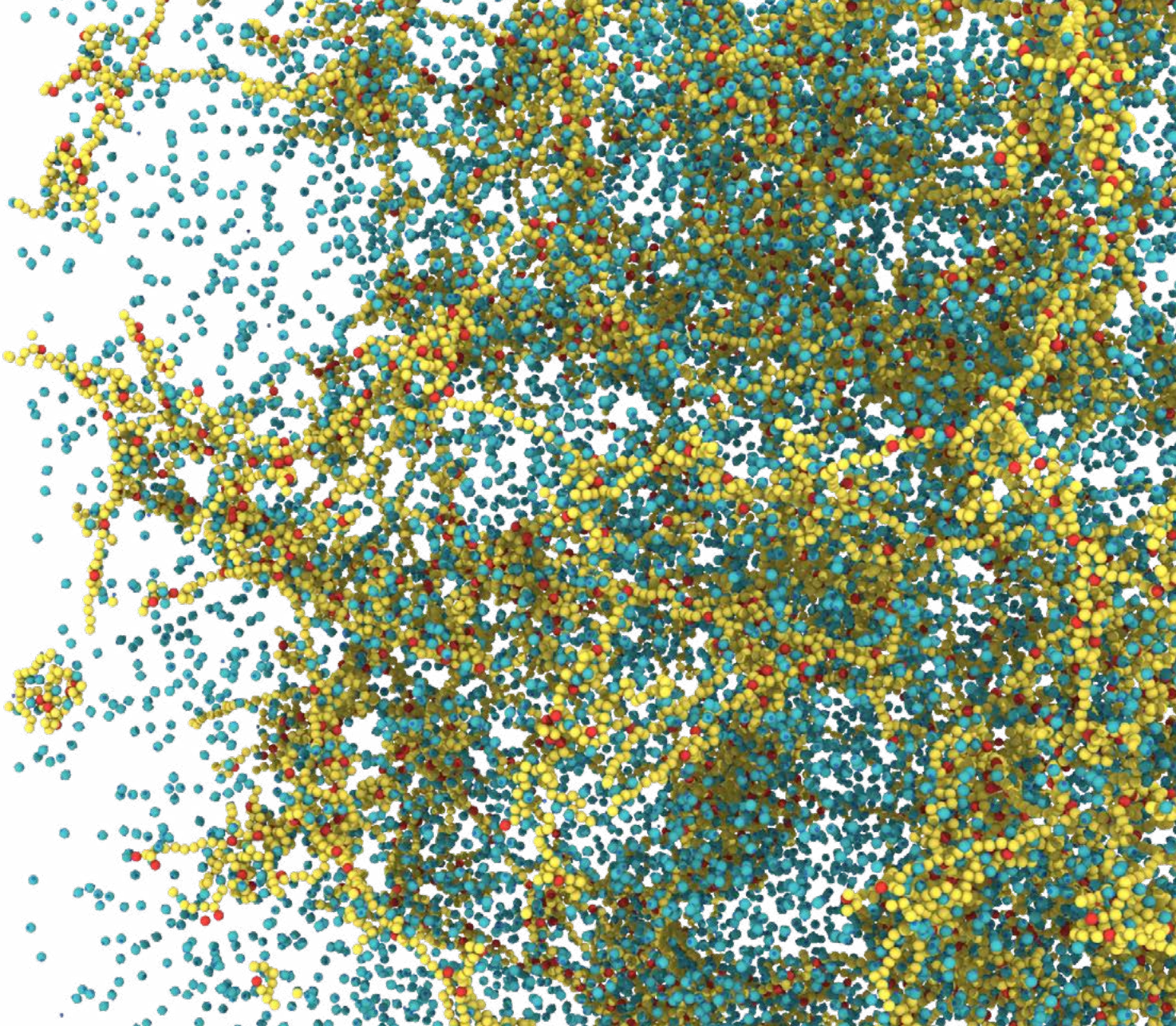
Environmentally friendly, oxygen-tolerant,

And easier to use materials cast off the

Diabolical characteristics of their surfaces,

To finally embrace their borders

With our external world.



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

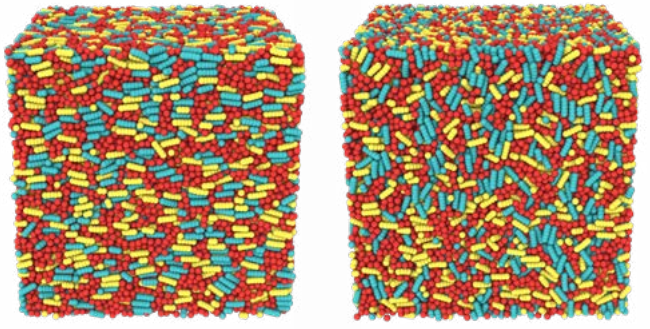
design at the molecular scale? Nicholas explains: "From the thermodynamic point of view, entropy goes into the free energy of the material, just like the enthalpy. A system does not want to minimise its energy, but its *free* energy. Entropy therefore plays an equally important role in guiding how molecules 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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