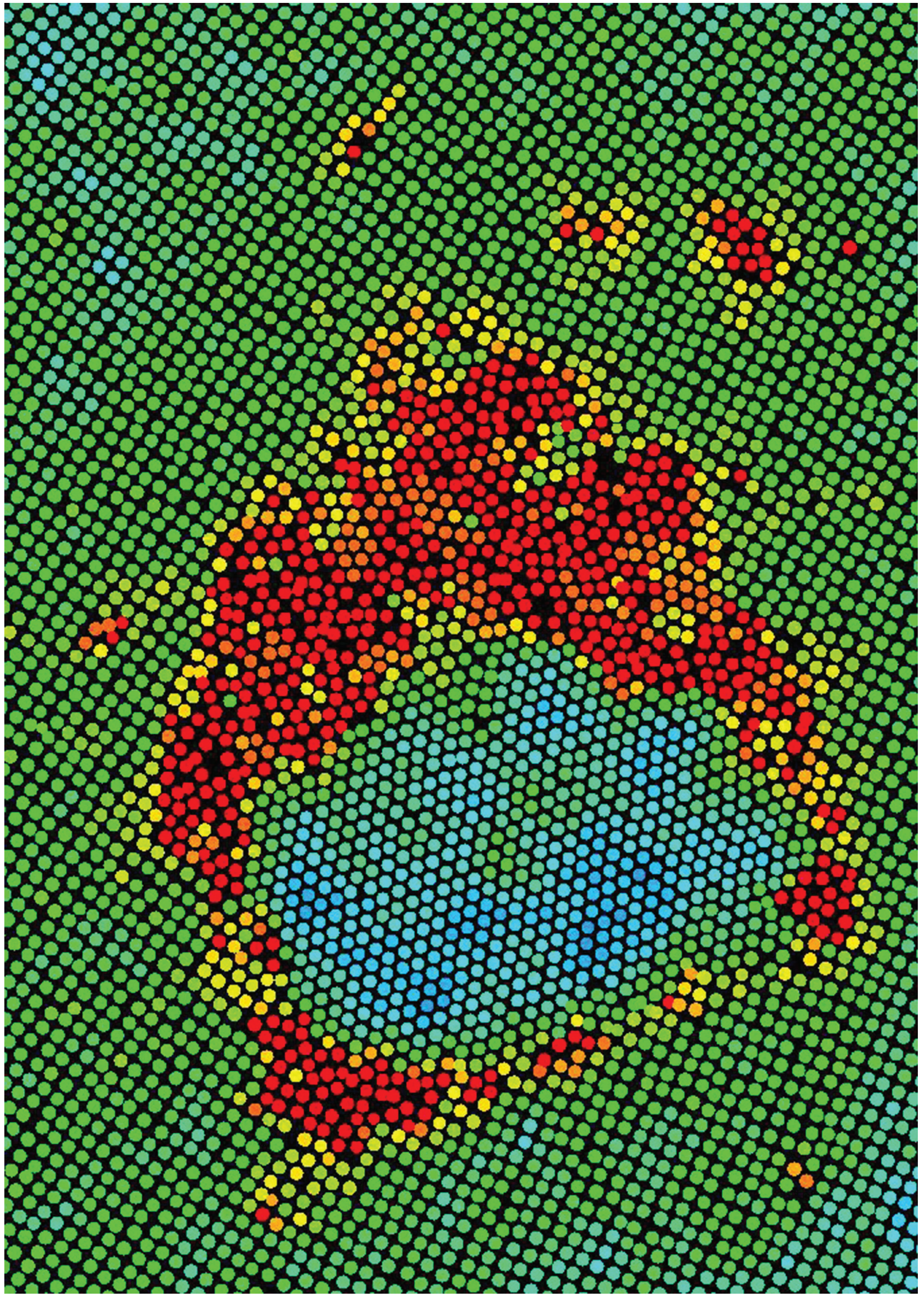


Cover feature, *Nature Materials, Vol 14*, 2015

VISUALIZING CHANGE

Diverse as they may seem, polymers, gels, liquid crystals, sand, and living cells all form part of one fascinating field – soft condensed matter, a recent interdisciplinary arrival at the cutting edge of scientific exploration spanning physics, chemical engineering, mechanical engineering, biophysics, and food science. And what might be the link between such materials? Many are disordered or partially disordered and viscoelastic – rigid like a solid over a short period of time and flow like a liquid over a long period of time. Now, researchers at HKUST are delivering fresh insights to phase transitions – when a material transitions from one form to another – while an innovative HKUST methodology, under development, is helping scientists probe further into the properties of living cells.

UNFOLDING THE MYSTERIES OF MATTER

Phase Transition Dynamics

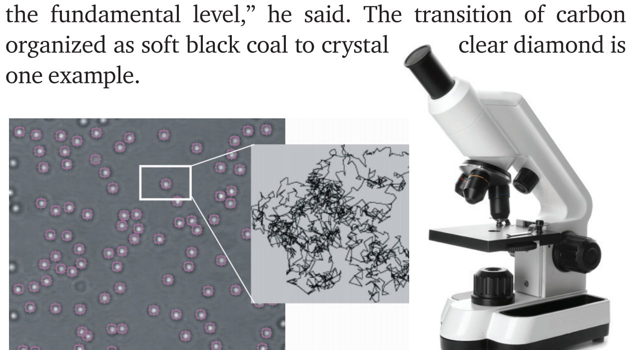
Have you ever looked at an ice cube and wondered how it melted? From the outside, or inside, or a bit of both? Or how atoms rearrange their positions to transform from graphite to diamond, both made of pure carbon but vastly different in their appearances and properties? If you have, you are considering one of the fundamental questions of physics – how matter changes from one state to another.

These questions have piqued the curiosity of soft condensed matter physicist Prof Yilong Han and his team for the past decade, with their findings attracting the attention of physicists globally. In particular, Prof Han has been intrigued by: when transition occurs; how the embryo of the new phase is formed from the parent phase; and what the microscopic kinetic pathway of a phase transition might be.

Such phenomena are "spectacularly difficult" to study, Prof Han said, because it is hard to even observe individual atoms and molecules buried inside a bulk solid or liquid, let alone track their trajectories.

"These phase transitions exist widely in nature and are important in daily life and applications. They are usually first-order transitions, which lack a theory at the fundamental level," he said. The transition of carbon organized as soft black coal to crystal clear diamond is one example.

An opal gemstone is a naturally occurring colloidal crystal. The periodicity of its crystalline lattice is comparable to the wavelength of visible light, supplying the jewel's iridescent colors. Micrometer colloidal spheres are like "big atoms", which can be used to mimic real atomic crystals.



Micrometer-sized colloidal particles dispersed in liquids can mimic large atoms and serve as powerful model systems for studying phase transitions. They have the dual advantage of being large enough to be directly observed under an optical microscope, but small enough to possess strong Brownian motion to form crystal, liquid, gas, and glassy phases. From the trajectories of particles, various physical quantities can be calculated, enabling quantitative measurement of phase transitions *(Nature Reviews Materials, 1, 15011*, 2016*)*.

Solid-to-Solid

It is common for the same type of atoms to form several different crystal structures. Under specific temperature and pressure regimes, these structures can undergo phase transitions from one solid state to another. Such transitions are widely observed in metallurgy and in the earth's mantle, altering mineral properties through structural changes. While the different phases of solids have been known to exist for a long time, their kinetic pathways and the mechanisms by which they transition from one phase to another are an ongoing area of study.

Using novel diameter-tunable colloidal microspheres provided by project collaborator Prof Arjun Yodh and his group at the University of Pennsylvania, the HKUST team was able to drive phase transitions by "tuning" the particle size – that is, to tune the density or effective temperature of the system. Furthermore, the micrometer-spherical gel particles could even be visualized inside the bulk of a crystal. Thus, by beaming a heating light into the colloidal crystal, causing the contraction of microspheres, it then becomes possible to directly observe, for the first time, homogenous nucleation in solid-solid transition.

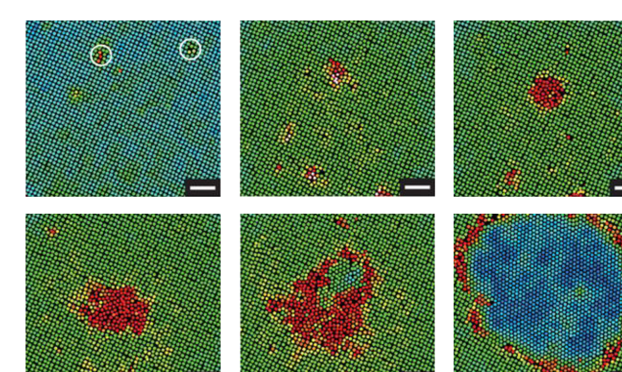
Surprisingly, the researchers found the crystal did not directly form nuclei of the final lattice structure, as conventionally expected, but liquid nuclei, which grew larger and larger, and then crystallized into the final lattice. "Such a two-step nucleation process is caused by a lower liquid-crystal interfacial energy, in comparison with crystal-crystal interfacial energy," Prof Han explained.

The novel transition pathway identified by Prof Han and his collaborators was later confirmed in metals by another research group, lending credence to colloidal systems as an apt methodology for modeling phase transitions of atomic systems. The resulting paper on solid-solid phase transition appeared on the cover of *Nature Materials, 14, 101,* 2015.

Prof Han's group further discovered that the intermediate liquid state disappears when a small amount of pressure is applied. The initial square lattice firstly generated a pair of defects called dislocations, which oscillated and triggered a few more pairs, and produced a nucleus with the final triangular lattice. Then, the nuclei grew by random diffusion of nearby particles. Such early-stage collective motions of particles (martensitic transformation) and the later-stage diffusive nucleation represent a novel type of transition pathway. This result and other pathways were published in *Nature Communications, 8, 14978,* 2017*)*.

> "No one could visualize how a perfect crystal transforms into another crystal at the single-particle level in bulk before. We were the first to see the transient liquid state during such transition"

PROF YILONG HAN
Professor of Physics



A defect-free crystal (square lattice) transforms to a new phase (triangular lattice) through the generation of nuclei with equal probability in space, otherwise known as homogenous nucleation. By directly observing the homogenous nucleation process, the research team found that the crystal does not transform to the final lattice structure as conventionally expected, but forms intermediate liquid nuclei that first grow and then crystallize into the final lattice structure in a two-step nucleation process.

Solid-to-Liquid

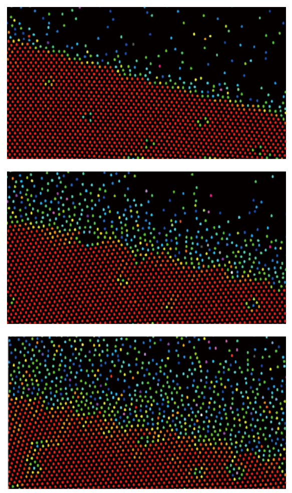
Prof Han's group has also used colloids as model systems to study crystal melting, or solid-to-liquid phase transition, achieving the first microscopic observations of surface pre-melting and internal homogenous melting.

Pre-melting

The surface of a solid often melts into a thin layer of liquid below the melting point, a phenomenon known as pre-melting. For example, two pieces of ice can fuse together below 0 °C because pre-melted surface water freezes into ice at the contact point, when not on the surface. By adding novel attractive forces between colloidal spheres, Prof Han's group was able to study pre-melting and other surface behaviors. They revealed that dimensionality is important for pre-melting, as monolayer and bilayer crystals can have distinct pre-melting behaviors. This work was published in *Nature, 531, 485,* 2016. Surface pre-melting is important in skating, glacial movement, and snowflake formation.

Melting from Within

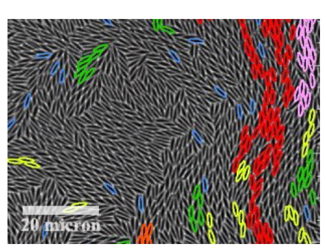
Prof Han's group also realized melting from within a defect-free crystal. In doing so, they found the transition process was initiated via particle swapping, where several adjacent particles switched places in a looping motion before baby liquid nuclei were formed. This contrasted with normal melting, triggered by the formation of crystalline defects. The findings appeared in *Science, 338, 87,* 2012.



The colloidal crystal provides a single-particle resolution for surface pre-melting. The crystal dissociates from the solid part to become liquid.

Liquid-to-Glass

In contrast to the well-understood crystal, disordered glass is poorly comprehended, with the nature of glass transition ranked as one of the 125 major scientific open questions by *Science*. Take, for example, a supercooled liquid frozen to a glass. While its structure hardly alters, why does its dynamics slow down about 10 - 15 times (viscosity increases by 10 - 15 times)? Are there little-known structural changes responsible for this? Seeking the correlation between structure and dynamics is a major area of endeavor in the search for greater knowledge of glass.



Fast-moving particles are shown in color, demonstrating dynamic heterogeneity (non-uniform dynamics)

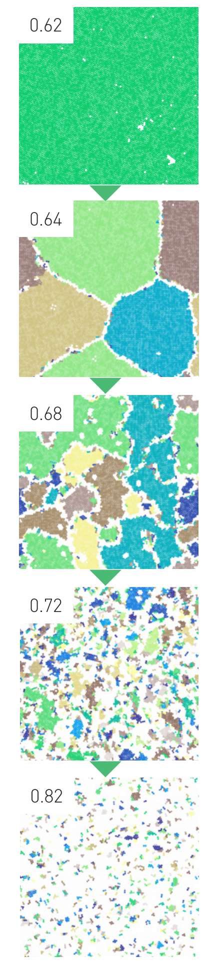
Prof Han's group got off to an early start on this, performing the first experiment on colloidal glass composed of non-spherical particles and discovering a novel glass transition for anisotropic particles, whereby rotational motion jams into the glass first, and translational motion jams into the glass afterward, increasing the density (*Phys. Rev. Lett. 107, 065702,* 2011). In addition, they found various structure-dynamics correlations (*Nature Communications, 5, 3829,* 2014).

Prof Han's group produced colloidal glass by vapor deposition, and explored glass behaviors near the glass-vapor interface with single-particle dynamics for the first time. They resolved different types of collective motions of particles near the surface, reflecting two surface layers (*Nature Communications 8, 362,* 2017).

Crystal-to-Glass

Most crystals, such as metals, are polycrystals composed of billions of randomly-oriented crystalline grains. Each grain is a small single crystal, made up of billions of atoms or molecules on a periodic lattice. If the typical grain size is reduced to just a few atoms, the polycrystal will become an amorphous solid, i.e. glass. How, then, would one distinguish ultrafine-grained polycrystals from glass? Is it just a matter of terminology? Surprisingly, these questions have rarely been asked.

Prof Han's and his group ventured into unexplored scientific territory by being the first to answer this basic question – ultrafine-grained polycrystals are notoriously difficult to fabricate due to their instability, and as a result, have rarely been studied. They compressed crystals into polycrstyals, and further into glass, using simple models by simulations. Their findings revealed that there is, indeed, a point of differentiation between fine-grained polycrystals and glass – at a surprisingly large grain diameter of around 15 particles. Many physical quantities feature a signature sharp polycrystal-glass transition at this size, as opposed to a continuous crossover. These behaviors were shown to be robust in different models in 2D and 3D. It also provides a novel angle to study glass formation from a crystal, instead of the conventional and well-studied process of forming glass by quenching a supercooled liquid. This work was published in *Physical Review X, 8, 041023*, 2018.



Polycrystal or Glass?
A single crystal at area fraction 0.62 is compressed to polycrystals (0.64, 0.68) and then to glass (0.72,0.82). White regions show disorder.

Prof Han, who joined HKUST in 2007 after completing his doctorate and post-doctoral research at the University of Chicago and University of Pennsylvania respectively, has been fascinated by the beauty of physics since his high school days in Mainland China. He is driven to solve basic problems, first and foremost out of deep interest and curiosity. That his work is providing insights, which could assist in the development of new materials and optimization of existing ones, adds a further exciting order of magnitude to the matter.

Prof Han received the International Organization of Chinese Physicists and Astronomers Achievement in Asia Award (2014) and the Chinese Young Scientist Award (2016), for his research contribution to the understanding of phase transitions.

THE PHYSICS OF LIVING MATTER

DNA, proteins, lipids, as well as living cells and tissues, are other forms of soft matter. Understanding the mechanics and physical properties of these squishy materials adds further insights into the physics of living matter.

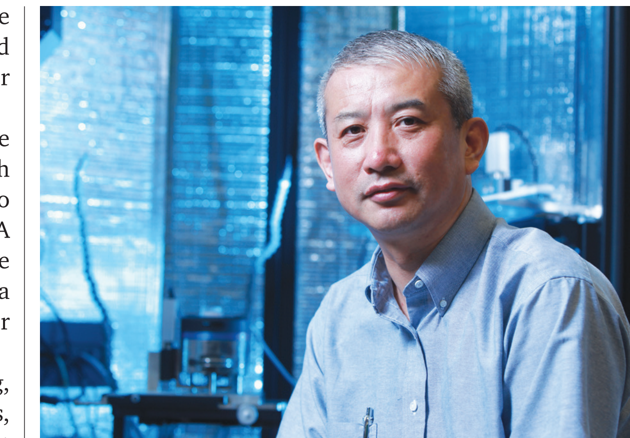
However, living cells are not only delicate, but their Jello-like consistency also poses a major challenge for researchers. Touch the cell with a probe and an adhesive force is generated, due to the cell's "stickiness", leading to inaccurate measurements. A cell's elasticity is also not constant (imagine trying to measure the "hardness" of a drop of liquid). Innovation is, therefore, a must to find methods to map cellular properties without either destroying the cell or making contact with it.

This is the quest of experimental physicist Prof Penger Tong, who works at the interdisciplinary interface between physics, biology, and chemistry. Prof Tong and his collaborators have set out to overcome both of these difficulties by developing a novel way to measure viscoelasticity and other mechanical properties of living cells, by engineering a new type of atomic force microscope (AFM) probe that operates in air rather than liquid.

To create the probe, they glued a tiny glass fiber needle – approximately one micrometer in diameter and 100 micrometers in length – to an AFM cantilever. The needle was covered with a special coating that prevented proteins from sticking to the probe. Then, with the needle tip placed a few nanometers above the cell surface, the tool was pressed to the living cell, creating a contactless method of measuring mechanical properties of a cell while allowing its integrity and activities to remain undisturbed. "Everything is in the air except the tip, which is placed in a thin liquid layer above the cell's surface," Prof Tong explained.

The team worked experimentally on refining the accuracy of the device, alongside working out the hydrodynamic theory needed for the AFM setup in collaboration with theoretical physicist Prof Elisabeth Charlaix at the Université Grenoble Alpes in France.

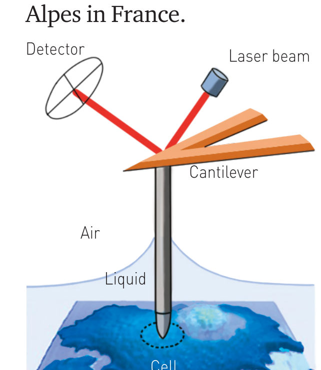
> "I want to understand the mechanical properties of cells and the physics of living matter"
>
> **PROF PENGER TONG**
> Chair Professor and Head, Department of Physics

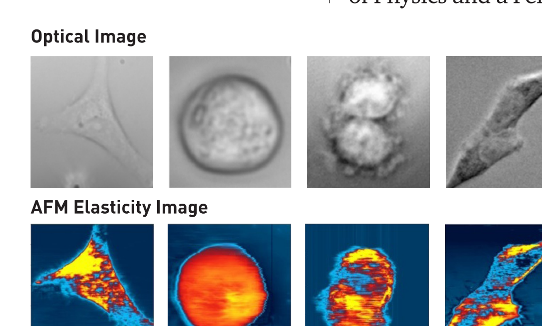


Using the newly-engineered AFM probe, they measured the mechanical properties of HeLa cells, epithelial cysts, neurons, and postsynaptic density droplets in collaboration with HKUST's Division of Life Science faculty, including Prof Robert Qi, Prof Pingbo Huang, and Prof Mingjie Zhang. Comparisons were made to assess whether the cells had distinct functions, or were healthy or diseased, providing new knowledge related to the roles played by the cell's volumetric and elastic properties.

"The hard thing in biology is you have large cell-to-cell variations," Prof Tong noted. "But, that is what life is," he added. "Cellular diversity is tremendous, between different types of cells and within the same kind of cells, even though they are made of similar molecular building blocks." Prof Tong and his team remain undaunted by the demanding task of systematically quantifying and theorizing these many variations. Indeed, in advancing their biological physics research, they hope to uncover the mechanobiological differences between healthy and cancerous cells. They would also like to explore the differences between living and dead cells, an endeavor that would take them to a truly amazing frontier of science – the interface of life and death.

Prof Tong is Head and Chair Professor of the Department of Physics and a Fellow of the American Physical Society.





Elasticity of a Dividing HeLa Cell
A long needle AFM probe is lowered toward the upper surface of a live HeLa cell in water and set for vibration in two frequencies to measure the cell's height and mechanical response, respectively. Water flowing between the needle tip and cell surface cannot keep up with the fast vibrations, creating a drum-like effect that causes cell deformation. Measuring the force required to deform the cell surface, locally, provides the elasticity map. Yellow/red/blue show areas of high/medium/low stiffness, respectively (Reprinted with permission from *Guan et al., Phys. Rev. Applied, 8, 044010,* 2017).