

## PHYSICS OF WATER

## Water untangled

Computer simulations have revealed the topological nature of the liquid–liquid phase transition in colloidal water. This finding might lead to an experimental observation of this topological transition with colloids as building blocks.

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Water has a simple chemical composition consisting of two atoms of hydrogen and one atom of oxygen. However, macroscopically water behaves like anything but a simple liquid — for example, unlike other liquids, water expands as it freezes, making it possible for ice to float. The many anomalies of water may be rationalized by the existence of a liquid–liquid phase transition between a high-density and a low-density liquid, but the microscopic origin of this process remains unclear. Now, writing in *Nature Physics*, Andreas Neophytou and colleagues<sup>1</sup> reveal that this transition is marked by a change in the topology of the liquid network.

Curiously, the thermodynamic anomalies of water become more pronounced if one manages to supercool it below its equilibrium freezing point. This year marks the 30th anniversary of the liquid–liquid critical point hypothesis<sup>2</sup>, which attributes water anomalies to the presence of a critical point located at deep supercooling. However, avoiding crystallization of liquid water in experiments is notoriously difficult<sup>3</sup>, leaving the existence of a liquid–liquid critical point in water an open problem.

Computer simulations play a key role in this context as they can probe the behaviour of simple models in conditions that naturally suppress crystallization. With considerable computational effort, the existence of a liquid–liquid critical point in classical water models was demonstrated recently<sup>4</sup> and further confirmed in water models that combine quantum accuracy with machine-learning efficiency<sup>5</sup>.

More generally, computer simulations offer an ideal platform to identify the minimal ingredients that give rise to a particular phenomenon. A key feature of water molecules is the formation of a tetrahedral network via hydrogen bonds (Fig. 1a). Furthermore, network interpenetration — the ability of each tetrahedron to host additional water molecules belonging to other tetrahedra — is known to aid liquid–liquid phase transitions<sup>6</sup>.

Neophytou and colleagues designed a computer model that combined these key

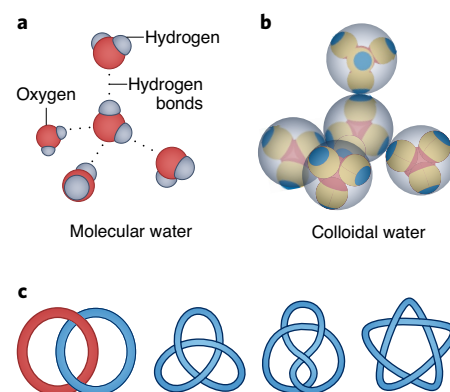
ingredients. It consisted of colloidal particles that self-assembled into a tetrahedral network fluid upon cooling, mimicking the one found in water. In particular, the opposite poles of the colloids were covered with patches of different sizes and attraction strengths. Their design forced the large patches to only attract other large patches and the small ones to only attract other small ones.

On cooling, the more strongly attractive large patches stuck the colloids together. Their large size ensured tetrahedrality of the resulting clusters but prevented cluster interpenetration because of the lack of free volume. The clusters bound to each other via weaker small patches upon further cooling, forming a tetrahedral network fluid with enough free volume to allow interpenetration (Fig. 1b).

The authors demonstrated that the model was indeed a colloidal analogue of water in the sense that it successfully reproduced its thermodynamic anomalies. In addition, the colloidal water exhibited a liquid–liquid phase transition and corresponding critical point. Crucially, careful tuning of colloidal interactions made the phase transition stable<sup>7</sup>, solving the crystallization problem.

The team focused on the network properties, in particular the geometry of the ‘rings’ formed by connected clusters. Careful inspection revealed that the high-density network was highly entangled in the sense that such rings formed links and knots (Fig. 1c), which could connect up to 15 neighbouring clusters. The low-density network instead contained unknotted and unlinked rings. The folding and linking of the network allowed the system’s volume to be minimized while maximizing the number of bonds. This microscopic picture thus explained the macroscopic density change observed at the transition.

Low- and high-density networks had distinct topological properties. Their degree of entanglement could be measured by counting how many times a ring looped around itself, two rings wound around one another, or a ring pierced the surface enclosed by another ring. The former two contributed to the



**Fig. 1 | A colloidal water model unveils the knots and links that characterize high-density liquids.**

**a**, Molecular water forms tetrahedra via hydrogen bonds. **b**, Neophytou and colleagues designed a water analogue using colloidal particles with attractive patches of different strengths on their poles. These patches enabled self-assembly into a tetrahedral network, which exhibited low-density and high-density liquid phases separated by a discontinuous transition. **c**, The high-density liquid network forms knots and links, whereas the low-density network is untangled.

linking number, and the latter to the writhe of the network — two measures borrowed from knot theory. The unknotted and unlinked rings instead had a zero contribution to both measures.

The authors showed that both the linking number and the writhe jumped discontinuously at the liquid–liquid phase transition and fluctuated widely close to the critical point in colloidal water, as well as in classical water models. This provides a much sought-after generic, structure-based order parameter that fundamentally distinguishes tetrahedral liquid states at the microscopic level.

Colloidal particles have long been used in the lab to gain insight into the statistical mechanics of atoms. By designing synthetically available<sup>8</sup> colloidal building blocks for tetrahedral liquids — such as water, but also silicon and liquid phosphorus — the authors’ findings pave

the way to a new generation of soft-matter experiments that will shed new light on the microscopic origin of liquid–liquid phase transitions.

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#### Competing interests

The author declares no competing interests.