

## Engineering Rings in Network Materials

Neophytou, Andreas; Chakrabarti, Dwaipayan

DOI:

[10.1002/apxr.202400007](https://doi.org/10.1002/apxr.202400007)

License:

Creative Commons: Attribution (CC BY)

*Document Version*

Publisher's PDF, also known as Version of record

*Citation for published version (Harvard):*

Neophytou, A & Chakrabarti, D 2024, 'Engineering Rings in Network Materials', *Advanced Physics Research*.  
<https://doi.org/10.1002/apxr.202400007>

[Link to publication on Research at Birmingham portal](#)

### General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

### Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact [UBIRA@lists.bham.ac.uk](mailto:UBIRA@lists.bham.ac.uk) providing details and we will remove access to the work immediately and investigate.

# Engineering Rings in Network Materials

Andreas Neophytou and Dwaipayan Chakrabarti\*

Network materials can be crystalline or amorphous solids, or even liquids, where typically directional interactions link the building blocks together, resulting in a physical representation of a mathematical object, called a graph or equivalently a network. Rings, which correspond to a cyclic path in the underlying network, consisting of a sequence of vertices and edges, are medium-range structural motifs in the physical space. This Perspective presents an overview of recent studies, which showcase the importance of rings in the emergence of crystalline order as well as in phase transitions between two liquid phases for certain network materials, comprised of colloidal or molecular building blocks. These studies demonstrate how the selection of ring sizes can be exploited for programming self-assembly of colloidal open crystals with an underlying network and elucidate rings as a vehicle for entanglement that distinguishes the two liquid phases of different densities involved in liquid–liquid phase transitions of network liquids with local tetrahedral order. In this context, an outlook is presented for engineering rings in network materials composed of colloidal and molecular building blocks, with implications also for metal-organic frameworks, which have been extensively studied as porous crystals, but, more recently, as network-forming liquids and glasses as well.

(e.g., if two people are friends). Networks are, in fact, a hallmark of complex systems,<sup>[1]</sup> which in the realm of materials can be crystalline or amorphous solids, or even liquids.<sup>[2–4]</sup> For instance, in a diamond crystal we can treat each carbon atom as a node that shares an edge with the four atoms to which it is linked via covalent bonds. Due to the tetrahedral symmetry around each carbon atom, we say that diamond is an example of a tetrahedral network. The complexity of liquid water, with its host of anomalous properties (despite its simple molecular structure), is ascribed to its 3D hydrogen-bond network, which is also tetrahedral.<sup>[5]</sup> This network representation of particulate systems is especially powerful when the particles have directional interactions, and forms the basis of the random network theory for glassy systems.<sup>[6,7]</sup> Vitreous silica is the canonical example of a random physical network, comprising a fully connected network of corner-sharing SiO<sub>4</sub> tetrahedra (i.e., every tetrahedron is connected

to four others).<sup>[8]</sup> Within the silica network there are localized geometric distortions to the perfect tetrahedral environment, resulting in an amorphous structure as opposed to the crystalline structures formed in diamond and ice.<sup>[6,7]</sup>

In a network, it is possible to define rings: cyclic paths within the network where the start and end nodes are the same. In network science, rings may also be referred to as cycles or loops. Crystalline networks typically contain rings of a well-defined size; for instance, the diamond crystal contains exclusively six-member rings if only the shortest cycles are considered.<sup>[9]</sup> The presence of rings of different sizes, caused by deviation from the ideal spatial environment at the nodes, frustrates crystallization, thereby producing an amorphous network.<sup>[10]</sup> For example, random tetrahedral networks consist of predominantly five-, six- and seven-member rings.<sup>[11–13]</sup> In recent years, these rings have been recognized as key medium-range structural motifs, playing an important role in the properties of physical networks and their phase transitions.<sup>[14–18]</sup> Additionally, the selective formation of rings of a particular size has been shown to facilitate the colloidal self-assembly of certain network crystals, especially those much sought-after as colloidal photonic crystals.<sup>[19–24]</sup>

In this Perspective, we present an outlook in the context of recent studies that have investigated the role of rings in the self-assembly of network materials. In particular, we focus on two strands of studies, one exploiting ring size selection for

## 1. Introduction

In the current digital age, we frequently encounter networks in our everyday life - telecommunication networks, World Wide Web, and, of course, the ever increasing number of social networks. A network comprises a collection of objects (e.g., people), which can be represented as nodes in a graph, where an edge connects two nodes if they share some kind of interaction

A. Neophytou  
Dipartimento di Fisica  
Sapienza Università di Roma  
Piazzale Aldo Moro 5, Roma 00185, Italy

D. Chakrabarti  
School of Chemistry  
University of Birmingham  
Edgbaston, Birmingham B15 2TT, UK  
E-mail: [d.chakrabarti@bham.ac.uk](mailto:d.chakrabarti@bham.ac.uk)

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/apxr.202400007>

© 2024 The Authors. Advanced Physics Research published by Wiley-VCH GmbH. This is an open access article under the terms of the [Creative Commons Attribution](#) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/apxr.202400007

programmed self-assembly of open crystals from patchy colloidal particles and the other exploring the role of rings, and their geometry and topological properties, in driving the liquid–liquid phase transitions (LLPTs) in tetrahedral networks. By open crystals, we refer to porous crystals, comprising low-coordinated particles, whose maximum density is less than what can be achieved at close packing.<sup>[25]</sup> On the other hand, LLPTs in tetrahedral networks,<sup>[26]</sup> most extensively discussed for water,<sup>[27–30]</sup> involve phase transitions between two liquids of different densities. While these two strands of research may initially appear somewhat disjointed thematically, all these studies fundamentally concern the formation of rings in network materials. Therefore, these studies together should strengthen our understanding of network materials by providing complementary insight.

## 2. Ring Selection for Open Crystals

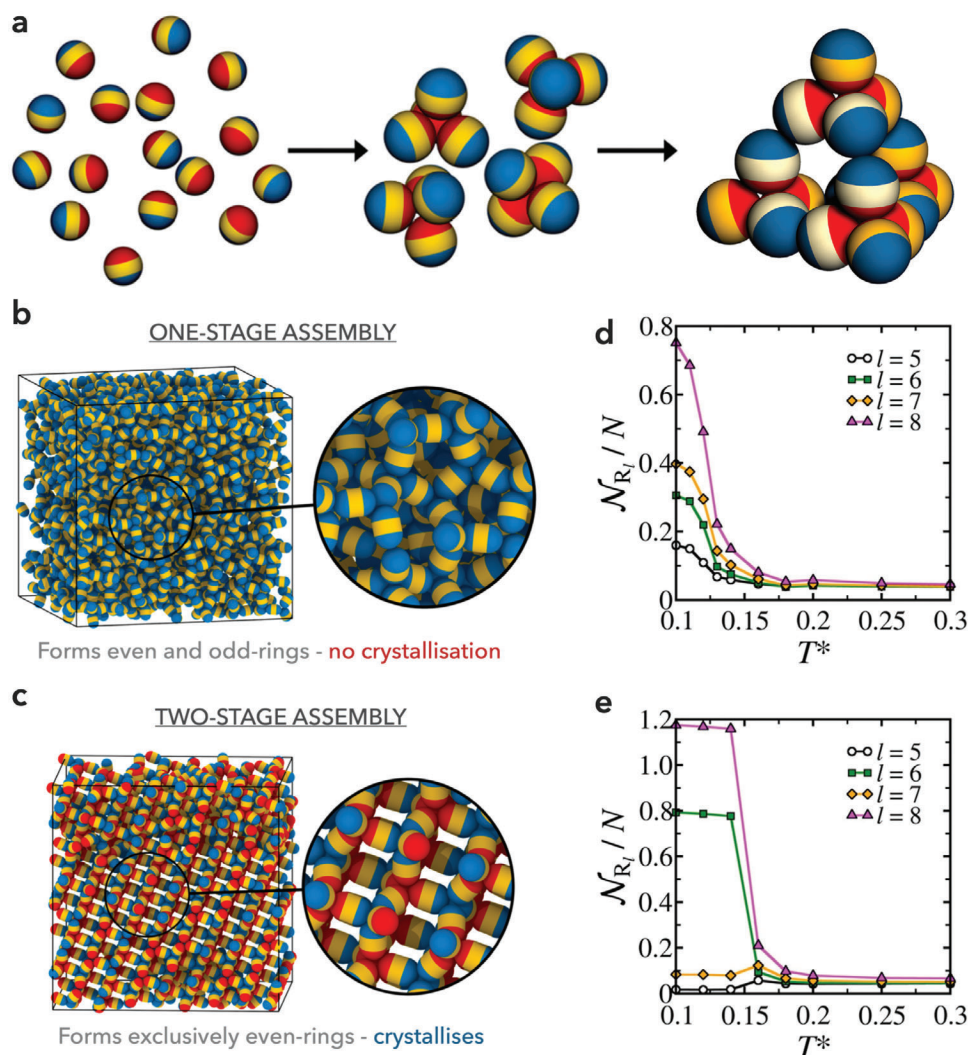
Diamond has become a key fixture in our modern lives. Due to its hardness, it is used in a variety of industries and technologies, but of course, diamond is most well known for its use in jewellery. If we are asked to complete the two-word phrase “diamond...”, many of us would immediately guess the missing word to be ring! While most, when hearing the phrase “diamond ring”, may picture a neatly cut gemstone on a metallic band, those of us who have taken a solid-state physics or chemistry course may also picture six carbon atoms forming a “chair” configuration in the underlying covalent network of diamond.<sup>[31]</sup> At this point, it is important to clarify that by diamond, we are referring to the allotrope of carbon that has cubic symmetry (hereafter referred to as cubic diamond). But this crystal has a polytype with hexagonal symmetry – referred to as hexagonal diamond (also known as Lonsdaleite) – that is an alternative allotrope of carbon.<sup>[32]</sup> The atomic structures of the two diamond polytypes are almost identical since both are formed from  $sp^3$  hybridized carbon atoms that form a tetrahedral network containing six-member rings.<sup>[33,34]</sup> However, while the rings formed by the carbon atoms in cubic diamond are all in a chair configuration, hexagonal diamond has a mixture of rings in chair and boat configurations.<sup>[31,35]</sup> While we are most familiar with the cubic diamond structure of carbon, other atomic, molecular, and colloidal systems are able to form structures identical to that of its hexagonal counterpart. The hydrogen-bond network formed between the water molecules in the ice that we might use to cool a drink on a hot summer day is an example of such a system.<sup>[36]</sup>

For more than three decades now, a cubic diamond crystal structure self-assembled from colloidal particles has been highly coveted in the soft-matter community, even being dubbed the “holy grail” of colloidal self-assembly.<sup>[37,38]</sup> The desire to establish a bottom-up route to “colloidal (cubic) diamond” stems from its ability to support a wide photonic bandgap (PBG), potentially paving the way for a variety of technological applications arising from a photonic crystal operating at optical frequencies.<sup>[39,40]</sup> However, establishing a particle design that is conducive for the self-assembly of a cubic diamond crystal is a deceptively difficult task.<sup>[21,41–44]</sup> Tetrahedral patchy particles – spherical particles with a repulsive core and four attractive patches in a tetrahedral arrangement<sup>[45,46]</sup> – appeared to be an obvious choice for the targeted self-assembly of cubic diamond owing to their clear similarity to a  $sp^3$  hybridized carbon atom.<sup>[46–48]</sup> The self-assembly of

a diamond crystal from tetrahedral patchy particles has, however, proven to be a challenging task, and the requirement of the selection of the cubic polytype for photonic applications adds to this challenge. When the particles possess narrow patches clathrate crystals assemble instead of diamond as five-member rings form faster than six-member rings.<sup>[44]</sup> When the patches are too wide, instead a glassy network that contains a distribution of ring sizes is formed.<sup>[41,42,44,49]</sup>

To successfully program the self-assembly of colloidal particles that yield a desired colloidal open crystal it is not sufficient to simply ensure that the target structure is the global free energy minimum, the crystal structure must also be kinetically accessible via self-assembly pathways.<sup>[50–52]</sup> For instance, triblock patchy particles<sup>[53]</sup> – repulsive spherical particles with two attractive circular patches at opposite poles, as shown in **Figure 1a** – are known to stabilize tetrastack crystals,<sup>[54]</sup> also much sought-after in their cubic form as a colloidal photonic crystal.<sup>[55]</sup> However, AA-triblock patchy particles (where “AA” refers to the fact that the two patches are identical in geometry, as well as in the strength of patch-patch interactions) may get trapped in an amorphous network containing a distribution of ring sizes.<sup>[19]</sup> A recent computational study by Chakrabarti and co-workers demonstrated that the self-assembly of tetrastack crystals can be promoted by making one set of patches (A patches) interact more strongly than the other set (B patches), where the interactions between the two sets are not ruled out but are of intermediate strength (i.e.,  $\epsilon_{AA} > \epsilon_{AB} > \epsilon_{BB}$ , where  $\epsilon_{ij}$  is the depth of the well corresponding to the attractive interaction between patch *i* and patch *j*).<sup>[19]</sup> This hierarchy of interactions, with sufficient separation in their strengths, encodes two-stage self-assembly pathways,<sup>[19,56]</sup> as illustrated schematically in **Figure 1a**. In the first stage, AB-triblock patchy particles form a tetrahedral cluster fluid driven by the strong A-A interactions over a range of temperatures;<sup>[19]</sup> then these tetrahedral clusters behave as meta-particles and come together through the weaker B-B interactions to form a tetrastack crystal upon further cooling. Since each tetrahedral cluster formed in the first stage of assembly can only form chains of particles that are multiples of two, the formation of five- and seven-member rings in the second stage of assembly is suppressed and the emergence of crystalline order is promoted. The two-stage assembly route therefore introduces a ring-selection protocol, whereby the AB-triblock patchy particles only form even-member rings in the second stage. The local minima associated with amorphous structures arising from the formation of five- and seven-member rings are thus effectively avoided, making the global minimum more accessible. For such a two-stage self-assembly scheme to succeed, it is essential to perform gradual cooling, which effectively prohibits A-B interactions by exhausting all A patches through A-A interactions before B-B interactions come into play at lower temperatures. We will return to this point later.

A subsequent computational study implemented this ring selection strategy with AB-triblock patchy rods, modelled as repulsive spherocylinders with attractive circular patches on the two hemispherical caps.<sup>[20]</sup> In this case, two-stage self-assembly is programmed to yield segmented rod-connected diamond, while avoiding being trapped in an amorphous phase (see **Figure 1b–e**).<sup>[20]</sup> This crystal structure is so called because the rods connect the nearest-neighbor sites of the diamond lattice,

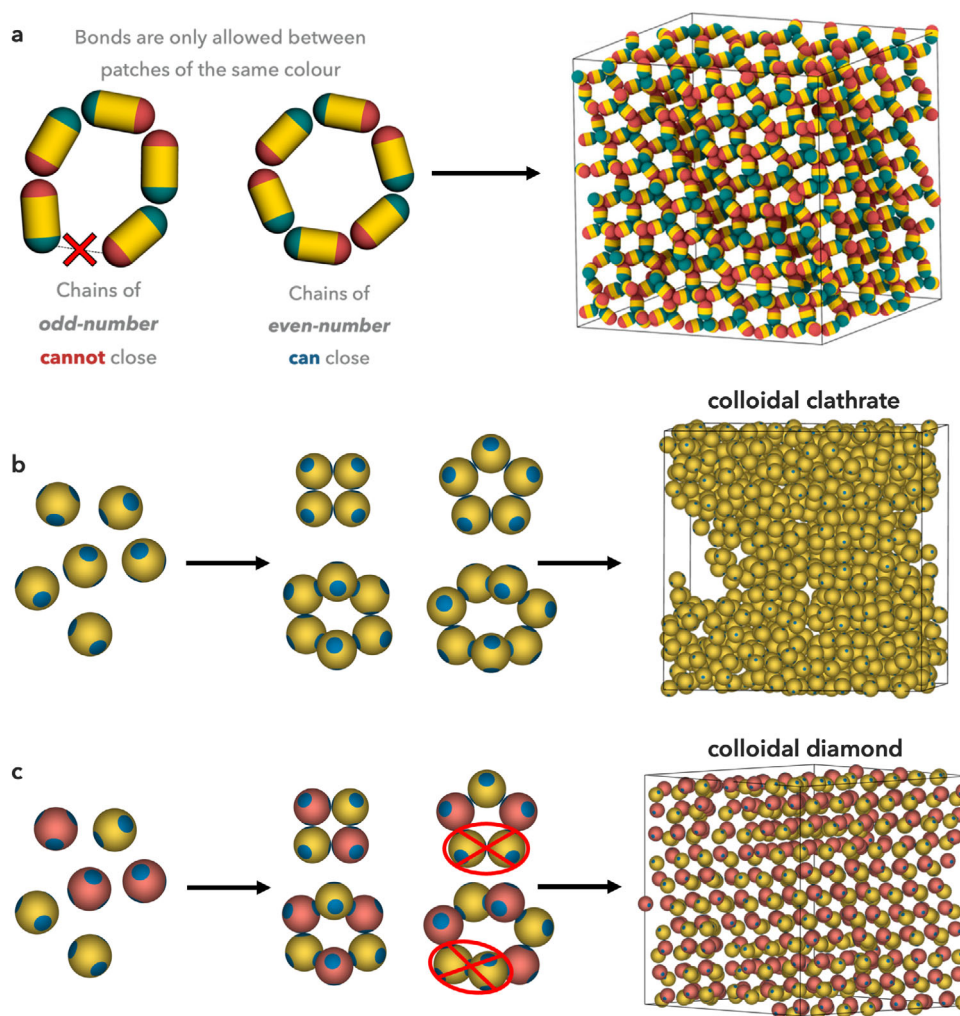


**Figure 1.** Crystallization via ring selection along two-stage self-assembly pathways for triblock patchy particles. a) Schematic illustration of two-stage self-assembly of a tetrastack crystal, comprising corner-shared tetrahedra. Each spherical triblock patchy particle has, on opposite poles, two equal-size attractive patches, which form bonds of different strengths: patch A (colored red) forms stronger bonds with another patch A relative to those formed between patches of type B (colored blue). In this case, the interactions between the two types of patches are not ruled out, but of an intermediate strength. For a sufficient hierarchy of interaction strengths, the particles come together to form a tetrahedral cluster fluid in a first stage of assembly via the interactions between A patches, which are thus exhausted. At lower temperatures, then the patch B-patch B interactions lead to the formation of a network structure, which can only contain even-member rings, such as the six-member ring formed by the particles with off-white middle band.<sup>[19]</sup> b–e) Self-assembly of triblock patchy rods with equal-size patches on opposite hemispherical caps. If the two patches form bonds of equal strengths, then an amorphous network with local tetrahedral order is formed at low temperatures (b), with a distribution of ring sizes evolving with the reduced temperature  $T^*$ , as shown in (d).<sup>[20]</sup> Two-stage self-assembly, encoded by a hierarchy of patch–patch interaction strengths, results in the formation of a segmented rod-connected diamond crystal (c) via the selection of even-member rings (e). In (d,e),  $\mathcal{N}_{R_l}$  is the number of rings containing  $l$  vertices present in a system of  $N = 2000$  particles. The panel (a) is reproduced from ref. [19] under CC BY license. The panels (b–e) are reprinted (adapted) with permission from ref. [20]. Copyright 2021 American Chemical Society.

leaving tetrahedral voids there. Rod-connected diamond, the cubic polytype of which is known to support the widest complete PBG for a given refractive index,<sup>[40]</sup> can be obtained via post-assembly processing. The ring statistics shown in Figure 1d,e highlight that the ring-selection strategy is at work to promote the crystallization.

Understanding the mechanism by which this two-stage assembly protocol promotes crystallization paved the way for an alternative scheme for imposing ring selection rules to achieve the self-assembly of segmented rod-connected diamond, as

shown in Figure 2a. This involves the use of specific interactions to prevent the formation of A-B bonds (i.e.,  $\epsilon_{AA} = \epsilon_{BB}$ ,  $\epsilon_{AB} = 0$ ). To distinguish between these triblock patchy particles with specific interactions and those with a hierarchy of interaction strengths, we hereafter refer to the former as AA'-triblock patchy particles. Such specific interactions between patches on opposite poles can be realised synthetically via DNA-functionalization.<sup>[48,57]</sup> In fact, the ring selection strategy executed with specific interactions has two added advantages over the two-stage self-assembly protocol. First, if the first stage of assembly for the AB-triblock



**Figure 2.** Ring-selection rules encoded in designer patchy particles through specific interactions for programmed self-assembly of colloidal open crystals. a) Self-assembly of a segmented rod-connected diamond crystal from triblock patchy rods with two distinct patches on opposite hemispherical caps (right). Functionalization (“coloring”) of the patches such that bonds are allowed to form only between patches of the same color ensures the formation of even-member rings exclusively (left), thus promoting crystallization via ring selection.<sup>[20]</sup> b) Self-assembly of a clathrate structure from tetrahedral patchy particles with narrow patches in the absence of ring-selection strategy due to the predominant formation of five-member rings.<sup>[21]</sup> c) Self-assembly of colloidal diamond from a binary 1:1 mixture of tetrahedral patchy particles in the presence of specific interactions such that bonds can only form between patches on particles of different types. The selection of even-member rings facilitates the self-assembly of a colloidal diamond crystal.<sup>[21]</sup> The panel (a) is reprinted (adapted) with permission from ref. [20]. Copyright 2021 American Chemical Society. The panels (b,c) are adapted from ref. [21] under CC BY license.

patchy particles is incomplete, then five- and seven-member ring may still form as defects and possibly hinder the formation of the crystal. The AA'-triblock patchy particles do not suffer from this issue, and hence, should produce crystals with fewer defects even with rapid cooling. As such, the kinetic traps are not explicitly removed from the energy landscape of the AB-triblock patchy particles, but are only avoided through the cooling protocol.<sup>[20]</sup> Therefore, defects associated with the formation of five- and seven-member rings are only avoided in the AB-system if the first stage reaches completion. Second, vacancies may form in the growing crystal and for the AB-system a vacancy will be for four particles instead of one. Due to the diameter of the tetrahedral cluster being comparable to that of the crystal voids, diffusion of free tetrahedra through the

voids can be slow and these vacancies are thus less likely to be filled.

Following these studies on triblock patchy particles, ring selection rules were applied to efficiently drive the self-assembly of colloidal diamond from tetrahedral patchy particles, as shown in Figure 2b,c.<sup>[21]</sup> In this case, a system containing two types of tetrahedral patchy particles in a 1:1 mixture is considered, where bond formation could only occur between the two different types of particles (Figure 2c). Specific interactions therefore only allow for the formation of even-member rings, thereby facilitating the self-assembly of colloidal diamond in preference to other competing phases, such as clathrates (shown in Figure 2b) and amorphous structures.<sup>[21]</sup> Importantly, the binary system of tetrahedral patchy particles permits the use of a wider range of patch

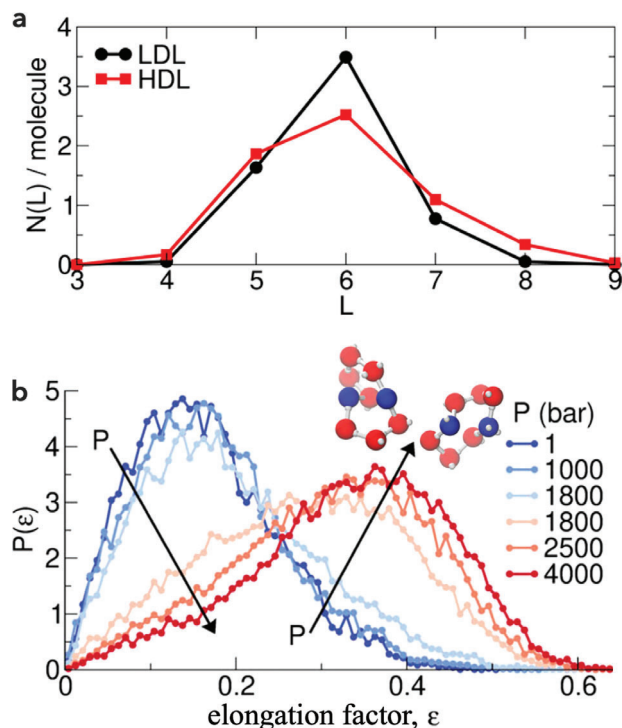
widths, as compared to the corresponding one-component system, for the self-assembly of colloidal diamond, thus facilitating experimental fabrication.

More recently, a computational study has reported on the direct self-assembly of an enantiomorphic pair of single colloidal gyroids, which can function as chiral photonic crystals.<sup>[24]</sup> The single colloidal gyroid structures are chiral networks, containing ten-member rings.<sup>[58]</sup> The networks have threefold connectivity at each node, with successive nodes involving a characteristic dihedral angle that distinguishes the enantiomorphic pair. In the computational study by Flavell et al.,<sup>[24]</sup> these chiral crystals are self-assembled from spherical patchy particles with two staggered rectangular patches on opposite poles. The selection of dihedral angle requires two rectangular patches on opposite poles, as opposed to circular patches typically considered for triblock patchy particles, to prevent unrestricted rotation, and a well-defined non-zero skew angle between these two rectangular patches. The disposition of the patches thus makes the colloidal building blocks chiral. In this study, which has developed an effective pair potential for particles with the rectangular patches, the increase of crystalline order is paralleled by a growing number of ten-member rings, suggesting that the chirality transfer from the single-particle level to an enantiomorphic crystal occurs via the formation of ten-member rings.<sup>[24]</sup>

### 3. Rings in the Liquid–Liquid Phase Transitions

Water, while providing the key to life, is seemingly an ever-evolving enigma and constant source of challenges for condensed matter physicists. Unlike any other chemical compound, water has many anomalous thermophysical properties, which become more pronounced as it is supercooled (cooled below the freezing temperature without crystallizing).<sup>[59–61]</sup> The origin of water's strange behavior has been a topic of great debate over the years, but one leading hypothesis (which has garnered significant attention) suggests that it is a manifestation of a first-order LLPT line in the supercooled region of water's phase diagram.<sup>[26]</sup> Two distinct phases of liquid water – the low-density liquid (LDL) and high-density liquid (HDL) – are separated by this LLPT line that is predicted to terminate at a critical point.<sup>[26]</sup> A growing body of numerical studies has confirmed the hypothesis of the existence of a LLPT in computational models of water, and significant progress has been made towards its experimental validation.<sup>[27,29,30]</sup> However, revealing the microscopic mechanisms governing the LLPT in water, and other tetrahedral liquids, is still an active area of research.<sup>[15,62–68]</sup>

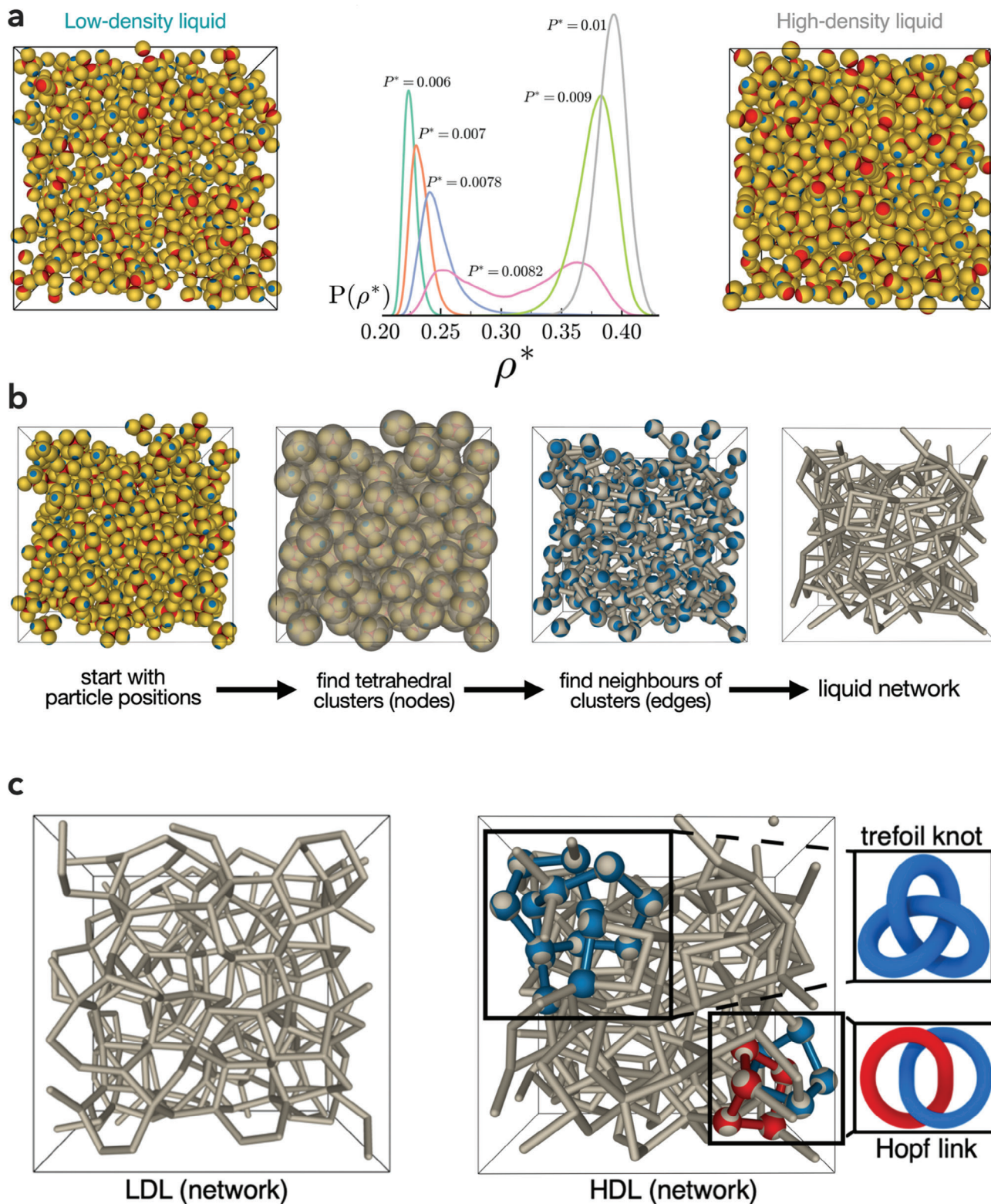
Over the years, it has become apparent that rings play an important role in the properties and phase transitions of these liquid and amorphous network structures.<sup>[15,17,69–73]</sup> The focus has mostly been on enumerating the number of rings of different sizes in the networks, with some arbitrariness in the definition for what constitutes a ring. There have been some studies in the literature also investigating how the geometry and topology of the rings change across the LLPT and related phase transitions. Parinello and coworkers show that with increasing pressure rings in amorphous ice networks deviate from a perfectly circular and planar conformation to become more “elongated”, with larger rings (rings containing more than six molecules) adopting more elongated conformations.<sup>[71]</sup> Foffi et al., have found that this is



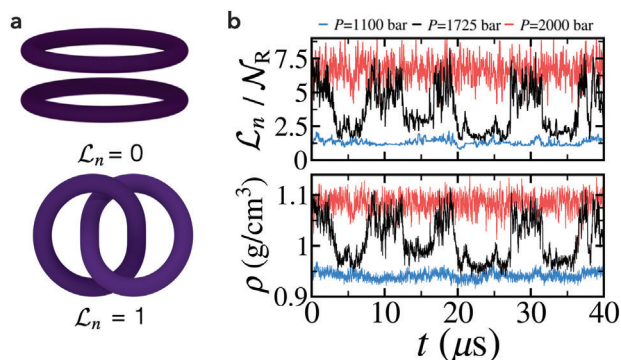
**Figure 3.** Geometric properties of rings in a model supercooled water. a) Ring statistics for the low-density liquid (LDL) and high-density liquid (HDL) networks at  $T = 188$  K and  $P = 1800$  bar, showing a distribution of the number of rings of size  $L$  in the network. b) Distributions of the elongation factor  $\epsilon$  for seven-member rings in the LDL and HDL states at different pressures along the  $T = 188$  K isotherm. The inset shows examples of eight- and nine-member rings that have adopted an elongated configuration in the HDL network. Reprinted from ref. [15], with the permission of AIP Publishing.

also the case for supercooled water, with rings in the HDL being much more elongated than those in the LDL, as shown in Figure 3.<sup>[15]</sup> Again, the morphological change from circular to elongated rings is much more pronounced for larger rings, in particular for seven-member rings (see Figure 3b), presumably due to the fact that larger rings can rearrange into an elongated conformation without introducing too much strain energy into the network.<sup>[71]</sup> This elongation or “folding” of the rings is suggested to control the local interpenetration of the HDL network since particles, which are well separated in terms of chemical bonds, are brought into close spatial proximity.<sup>[43,74–76]</sup> Additionally, the LDL networks are noted to only contain rings having seven or less particles, while the HDL also possess 8-member rings (see Figure 3a). The formation of these larger rings in the HDL networks is understandable since the rings are then able to fold into more compact geometries to facilitate the densification of the network.

In a recent computational study,<sup>[17]</sup> Neophytou et al. have provided a topological perspective of the LLPT in water, first uncovered in a colloidal model of water, as summarised in Figure 4, and then in two molecular models of water,<sup>[77,78]</sup> for which the existence of a LLPT has been confirmed.<sup>[28]</sup> The LLPT between the LDL and HDL is captured in this colloidal model of water as the reduced pressure  $P^*$  is varied at a reduced temperature of  $T^*$



**Figure 4.** Topological aspects of the liquid–liquid phase transition revealed in a colloidal model of water. a) Probability distribution functions for the reduced density ( $\rho^*$ ) for the colloidal water model<sup>[17]</sup> at various reduced pressures ( $P^*$ ) at a reduced temperature of  $T^* = 0.105$ . The probability distributions highlight that two liquids of different densities form at low temperatures (representative configurations of which are shown on either side of the plot) separated by a liquid–liquid phase transition (LLPT) line. b) Deconstruction of a typical configuration of the colloidal water model into a network representation. c) Snapshots of the low-density liquid (LDL) and high-density liquid (HDL) networks, where examples of topologically complex motifs present in the HDL (such as trefoil knots and Hopf links) are highlighted. Adapted from ref. [17] under the CC BY license.



**Figure 5.** The liquid–liquid phase transition in a molecular model of water, captured by the network linking number,  $\mathcal{L}_n$ , which is a topological order parameter. a) Visual representation of a pair of unlinked rings (top), for which  $\mathcal{L}_n = 0$ , and a pair of linked rings (bottom), for which  $\mathcal{L}_n = 1$ . b) Evolution of the density,  $\rho$ , and the network linking number,  $\mathcal{L}_n$ , normalized by the total number of rings,  $\mathcal{N}_R$ , along molecular dynamics trajectories of  $N = 300$  model water molecules interacting via the TIP4P/Ice pair potential at a temperature of  $T = 188$  K and at pressures of  $P = 1100$ , 1725 and 2000 bar. Adapted from ref. [17] under the CC BY license.

$= 0.105$  (see Figure 4a). The colloidal water model is a tetrahedral network formed by AB-triblock patchy particles, with  $\epsilon_{AA} > \epsilon_{BB}$  and  $\epsilon_{AB} = 0$  (see Figure 4b), and is so called because of its ability to capture a number of thermodynamic anomalies known for water.<sup>[17]</sup> In this study, the authors not only probe the formation of rings in the LDL and HDL networks, but also investigate the degree to which the rings are entangled by utilizing concepts from knot theory (see Figure 4c).<sup>[17,79]</sup> In particular, the presence of any knots, theta-curves or links is probed in the liquid networks of colloidal water and two molecular models of water.<sup>[77,78]</sup> A knot corresponds to a ring that is entangled with itself, a theta-curve is formed when two joint rings are entangled with one another, and a link is formed when two disjoint rings are entangled. By computing the network writhe (capturing the presence of knots and theta-curves) and network linking number (capturing the presence of links) for the liquid networks as a function of pressure, it is found that the LDL is unentangled (i.e., knots, theta-curves and links are almost entirely absent), while the HDL is entangled, containing an ensemble of knotted and linked rings (see Figure 5). Figure 5a illustrates the concept of the network linking number,  $\mathcal{L}_n$ , which provides a quantitative measure of the degree of entanglement by summing up the absolute values of the linking number, which, in turn, is defined for a pair of disjoint rings in terms of a double line integral that is proportional to how many times the two rings wind around one another.<sup>[17]</sup> As shown in Figure 5b for a molecular model of water, the network linking number  $\mathcal{L}_n$  correlates remarkably well with the density fluctuations, as configurations belonging to both the LDL and HDL phases are sampled along a molecular dynamics trajectory, shown in black, near the second-order critical point.<sup>[17]</sup>

It is clear that rings represent important structural motifs in these liquid networks, and that the LDL and HDL networks contain populations of rings that have very distinct size, geometry and topology. Upon increasing pressure, there are two mechanisms by which these networks could increase their density while maintaining the bonds in the network – these systems want to

form structures with as many bonds as possible since the LLPT occurs at low temperatures. The first mechanism is to form more rings that are larger in size and more flexible so that they are more “deformable”, as shown in refs. [15] and [71]. However, due to the highly directional nature of the bonds in these systems and their limited flexibility, the degree to which the networks are able to condense by this mechanism alone is limited. Therefore, these systems also form knotted and linked rings, thereby facilitating the densification of the system without needing to introduce highly contorted ring structures into the network (this is especially true for linked rings). Which mechanism is dominant is likely to depend on the flexibility of the bonds formed between the particles, with more rigid bonds favoring the densification of the system through the formation of topologically complex motifs.

#### 4. Outlook

It is clear that rings are important structural motifs of medium-range order in both crystalline and amorphous network materials. There is growing understanding in recent years how rings can be exploited to steer the emergence of crystalline order via self-assembly and drive phase transitions. Here, we have covered two different strands of work, both showcasing the importance of engineering rings: one concerns programming the self-assembly of colloidal open crystals, where the selection of ring sizes has emerged to be a critical design rule; the other elucidates rings as a vehicle for entanglement that distinguishes the two liquid phases of different densities involved in liquid–liquid phase transitions in tetrahedral network liquids. In these cases, rings can be engineered either by the choice of interactions between designer building blocks or using pressure as a control. In the context of these advances in our understanding, there are several curiosity-driven questions, which appear to us well worth exploration. While the focus of imposing ring-selection rules has been, so far, on programming the self-assembly of crystals with diamond symmetry by targeting the selection of even-member rings, this concept can be extended to target network structures with odd-member rings. For example, the so-called SAT-assembly strategy, where the interaction rules between the patches are obtained by transforming the combinatorial problem into a Boolean satisfiability problem, can be employed.<sup>[22,23]</sup> Additionally, patchy particles with two staggered rectangular patches on opposite poles offer a richer design space as compared to triblock patchy particles with circular patches, and the skew angle that defines the relative orientation of the rectangular patches can be used as a parameter to control the size of the rings formed in the self-assembled networks.<sup>[24]</sup>

Although there is yet no consensus about the origin of thermodynamic anomalies in water,<sup>[66,80]</sup> they are found to critically depend on the local tetrahedral order that exists in water’s hydrogen-bonded network. In fact, water-like thermodynamic anomalies are fairly common in tetrahedral liquids.<sup>[81]</sup> It is a pertinent question whether the topological distinction between LDL and HDL that has been recently uncovered in the case of water holds good for other tetrahedral liquids, such as silicon.<sup>[82]</sup> Water is also known to exist in more than one solid amorphous form of different densities, giving rise to polyamorphism – aka amorphous polymorphism.<sup>[66]</sup> The connection between water’s



polyamorphism and a LLPT has been debated.<sup>[80]</sup> It will be of interest to explore this connection from a topological perspective, with the elucidation of the role that rings may play.

Metal-organic frameworks (MOFs) are network materials that have been extensively studied as porous crystals for a variety of applications over the years,<sup>[83]</sup> but a few of them are now known to form network liquids and glasses.<sup>[84–87]</sup> A powerful approach to the rational design of MOFs via reticular chemistry involves the deconstruction of the crystal structures of MOFs into their underlying nets, where the vertices and edges are clusters and linkers, respectively.<sup>[9,88,89]</sup> In this net representation, shortest cycles (closed paths around the net) are called rings, which have well-defined sizes for crystalline nets. We envisage the ring-selection strategies discussed here to underpin novel routes for crystalline MOFs via reticular synthesis, while a distribution of ring sizes to emerge as a universal feature for liquid and glassy MOFs.<sup>[84,90]</sup> It is of interest to note that the zeolitic imidazolate framework, ZIF-4 [Zn(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>], which is composed of tetrahedrally co-ordinated Zn and imidazolate linkers, is known to undergo a LLPT between LDL and HDL, and form low-density amorphous (LDA) and high-density amorphous (HDA) states.<sup>[84]</sup> In the context of recent findings in colloidal and molecular water,<sup>[17]</sup> it is likely that a similar topological distinction between LDL and HDL of ZIF-4 (or between its LDA and HDA states) in terms of entanglement exists. The validity of this hypothesis should establish entanglement as a general mechanism for densification in amorphous tetrahedral network materials, comprised of building blocks from across length scales.

## Acknowledgements

The authors thank Francesco Sciortino, Vinodhan N. Manoharan and Neil R. Champness for stimulating discussions and the Royal Society and the University of Birmingham for funding (the former via International Exchanges Award IES/R3/183166).

## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

colloidal self-assembly, liquid–liquid phase transition, metal-organic frameworks, network materials, rings

Received: January 29, 2024

Revised: April 17, 2024

Published online:

- [1] A.-L. Barabási, *Science* **2009**, 325, 412.
- [2] O. D. Friedrichs, A. W. M. Dress, D. H. Huson, J. Klinowski, A. L. Mackay, *Nature* **1999**, 400, 644.
- [3] A. C. Wright, R. A. Hulme, D. I. Grimley, R. N. Sinclair, S. W. Martin, D. L. Price, F. L. Galeener, *J. Non-Cryst. Solids* **1991**, 129, 213.
- [4] C. S. Dias, N. A. M. Araújo, N. M. Telo da Gama, *Adv. Colloid Interface Sci.* **2017**, 247, 258.
- [5] T. Head-Gordon, G. Hura, *Chem. Rev.* **2002**, 102, 2651.
- [6] W. H. Zachariasen, *J. Am. Chem. Soc.* **1932**, 54, 3841.
- [7] Z.-H. Jiang, Q.-Y. Zhang, *Prog. Mater. Sci.* **2014**, 61, 144.
- [8] R. J. Bell, P. Dean, *Nature* **1966**, 212, 1354.
- [9] O. M. Yaghi, M. O’Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, 423, 705.
- [10] J. P. Doye, A. A. Louis, I.-C. Lin, L. R. Allen, E. G. Noya, A. W. Wilber, H. C. Kok, R. Lyus, *Phys. Chem. Chem. Phys.* **2007**, 9, 2197.
- [11] A. Wright, M. Thorpe, *Phys. Status Solidi B* **2013**, 250, 931.
- [12] R. Mozzi, n. B. Warren, *J. Appl. Crystallogr.* **1969**, 2, 164.
- [13] T. Uchino, Y. Kitagawa, T. Yoko, *Phys. Rev. B* **2000**, 61, 234.
- [14] D. O. Morley, A. L. Goodwin, M. Wilson, *Phys. Rev. E* **2020**, 102, 062308.
- [15] R. Foffi, J. Russo, F. Sciortino, *J. Chem. Phys.* **2021**, 154, 184506.
- [16] Y. Liu, N. Dehmamy, A.-L. Barabási, *Nat. Phys.* **2021**, 17, 216.
- [17] A. Neophytou, D. Chakrabarti, F. Sciortino, *Nat. Phys.* **2022**, 18, 1248.
- [18] M. Pósfai, B. Szegedy, I. Bačić, L. Blagojević, M. Abért, J. Kertész, L. Lovász, A.-L. Barabási, *Nat. Phys.* **2024**, 20, 142.
- [19] A. B. Rao, J. Shaw, A. Neophytou, D. Morphew, F. Sciortino, R. L. Johnston, D. Chakrabarti, *ACS Nano* **2020**, 14, 5348.
- [20] A. Neophytou, V. N. Manoharan, D. Chakrabarti, *ACS Nano* **2021**, 15, 2668.
- [21] A. Neophytou, D. Chakrabarti, F. Sciortino, *Proc. Natl. Acad. Sci. USA* **2021**, 118, e2109776118.
- [22] J. Russo, F. Romano, L. Kroc, F. Sciortino, L. Rovigatti, P. Sulc, *J. Phys.: Condens. Matter* **2022**, 34, 354002.
- [23] L. Rovigatti, J. Russo, F. Romano, M. Matthies, L. Kroc, P. Šulc, *Nanoscale* **2022**, 14, 14268.
- [24] W. Flavell, A. Neophytou, A. Demetriadou, T. Albrecht, D. Chakrabarti, *Adv. Mater.* **2023**, 35, 2211197.
- [25] X. Mao, Q. Chen, S. Granick, *Nature Materials* **2013**, 12, 217.
- [26] P. H. Poole, F. Sciortino, U. Essmann, H. E. Stanley, *Nature* **1992**, 360, 324.
- [27] K. H. Kim, A. Späh, H. Pathak, F. Perakis, D. Mariedahl, K. Amann-Winkel, J. A. Sellberg, J. H. Lee, S. Kim, J. Park, K. H. Nam, T. Katayama, A. Nilsson, *Science* **2017**, 358, 1589.
- [28] P. G. Debenedetti, F. Sciortino, G. H. Zerze, *Science* **2020**, 369, 289.
- [29] K. H. Kim, K. Amann-Winkel, N. Giovambattista, A. Späh, F. Perakis, H. Pathak, M. L. Parada, C. Yang, D. Mariedahl, T. Eklund, T. J. Lane, S. You, S. Jeong, M. Weston, J. H. Lee, I. Eom, M. Kim, J. Park, S. H. Chun, P. H. Poole, A. Nilsson, *Science* **2020**, 370, 978.
- [30] K. Amann-Winkel, K. H. Kim, N. Giovambattista, M. Ladd-Parada, A. Späh, F. Perakis, H. Pathak, C. Yang, T. Eklund, T. J. Lane, S. You, S. Jeong, J. H. Lee, I. Eom, M. Kim, J. Park, S. H. Chun, P. H. Poole, A. Nilsson, *Nat. Commun.* **2023**, 14, 442.
- [31] M. Salehpour, S. Satpathy, *Phys. Rev. B* **1990**, 41, 3048.
- [32] C. Frondel, U. B. Marvin, *Nature* **1967**, 214, 587.
- [33] K. E. Spear, A. W. Phelps, W. B. White, *J. Mater. Res.* **1990**, 5, 2277.
- [34] A. Phelps, W. Howard, D. Smith, *J. Mater. Res.* **1993**, 8, 2835.
- [35] C. G. Salzmann, B. J. Murray, J. J. Shephard, *Diam. Relat. Mater.* **2015**, 59, 69.
- [36] K. Y. Lonsdale, *Proc. R. Soc. A* **1958**, 247, 424.
- [37] W. Liu, M. Tagawa, H. L. Xin, T. Wang, H. Emamy, H. Li, K. G. Yager, F. W. Starr, A. V. Tkachenko, O. Gang, *Science* **2016**, 351, 582.
- [38] M. He, J. P. Gales, E. Ducrot, Z. Gong, G.-R. Yi, S. Sacanna, D. J. Pine, *Nature* **2020**, 585, 524.
- [39] K. M. Ho, C. T. Chan, C. M. Soukoulis, *Phys. Rev. Lett.* **1990**, 65, 3152.
- [40] M. Maldovan, E. L. Thomas, *Nat. Mater.* **2004**, 3, 593.
- [41] F. Romano, E. Sanz, F. Sciortino, *J. Chem. Phys.* **2011**, 134, 174502.
- [42] I. Saika-Voivod, F. Romano, F. Sciortino, *J. Chem. Phys.* **2011**, 135, 124506.
- [43] F. Smalenburg, F. Sciortino, *Nat. Phys.* **2013**, 9, 554.

- [44] E. G. Noya, I. Zubieta, D. J. Pine, F. Sciortino, *J. Chem. Phys.* **2019**, *151*, 094502.
- [45] E. Bianchi, R. Blaak, C. N. Lokos, *Phys. Chem. Chem. Phys.* **2011**, *13*, 6397.
- [46] Z. Gong, T. Hueckel, G.-R. Yi, S. Sacanna, *Nature* **2017**, *550*, 234.
- [47] Z. Zhang, A. S. Keys, T. Chen, S. C. Glotzer, *Langmuir* **2005**, *21*, 11547.
- [48] Y. Wang, Y. Wang, D. R. Breed, V. N. Manoharan, L. Feng, A. D. Hollingsworth, M. Weck, D. J. Pine, *Nature* **2012**, *491*, 51.
- [49] I. Saika-Voivod, F. Smallenburg, F. Sciortino, *J. Chem. Phys.* **2013**, *139*, 234901.
- [50] D. Frenkel, D. J. Wales, *Nat. Mater.* **2011**, *10*, 410.
- [51] S. Whitelam, R. L. Jack, *Annu. Rev. Phys. Chem.* **2015**, *66*, 143.
- [52] D. Morphew, D. Chakrabarti, *Nanoscale* **2018**, *10*, 13875.
- [53] Q. Chen, E. Diesel, J. K. Whitmer, S. C. Bae, E. Luijten, S. Granick, *J. Am. Chem. Soc.* **2011**, *133*, 7725.
- [54] W. F. Reinhart, A. Z. Panagiotopoulos, *J. Chem. Phys.* **2016**, *145*, 094505.
- [55] T. Ngo, C. Liddell, M. Ghebrehrehan, J. Joannopoulos, *Appl. Phys. Lett.* **2006**, *88*, 241920.
- [56] D. Morphew, J. Shaw, C. Avins, D. Chakrabarti, *ACS Nano* **2018**, *12*, 2355.
- [57] T. Hueckel, G. M. Hocky, S. Sacanna, *Nat. Rev. Mater.* **2021**, *6*, 1053.
- [58] S. T. Hyde, M. O'Keeffe, D. M. Proserpio, *Angew. Chem. Int. Ed.* **2008**, *47*, 7996.
- [59] C. A. Angell, *Annu. Rev. Phys. Chem.* **1983**, *34*, 593.
- [60] P. G. Debenedetti, *J. Phys.: Condens. Matter* **2003**, *15*, R1669.
- [61] J. Russo, F. Leoni, F. Martelli, F. Sciortino, *Rep. Prog. Phys.* **2021**, *85*, 016601.
- [62] E. Shiratani, M. Sasai, *J. Chem. Phys.* **1998**, *108*, 3264.
- [63] M. J. Cuthbertson, P. H. Poole, *Phys. Rev. Lett.* **2011**, *106*, 115706.
- [64] J. M. M. de Oca, F. Sciortino, G. A. Appignanesi, *J. Chem. Phys.* **2020**, *152*, 244503.
- [65] H. Tanaka, H. Tong, R. Shi, J. Russo, *Nat. Rev. Phys.* **2019**, *1*, 333.
- [66] H. Tanaka, *J. Chem. Phys.* **2020**, *153*, 130901.
- [67] L. Steinberg, J. Russo, J. Frey, *J. Cheminform.* **2019**, *11*, 1.
- [68] C. Faccio, M. Benzi, L. Zanetti-Polzi, I. Daidone, *J. Mol. Liq.* **2022**, *355*, 118922.
- [69] A. Rahman, F. H. Stillinger, *J. Am. Chem. Soc.* **1973**, *95*, 7943.
- [70] R. J. Speedy, J. D. Madura, W. L. Jorgensen, *J. Phys. Chem.* **1987**, *91*, 909.
- [71] R. Martoňák, D. Donadio, M. Parrinello, *J. Chem. Phys.* **2005**, *122*, 134501.
- [72] G. Camisasca, D. Schlesinger, I. Zhovtobriukh, G. Pitsevich, L. G. Pettersson, *J. Chem. Phys.* **2019**, *151*, 034508.
- [73] M. Formanek, F. Martelli, *AIP Adv.* **2020**, *10*, 055205.
- [74] C. W. Hsu, J. Largo, F. Sciortino, F. W. Starr, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 13711.
- [75] F. Smallenburg, L. Filion, F. Sciortino, *Nat. Phys.* **2014**, *10*, 653.
- [76] S. Ciarella, O. Gang, F. Sciortino, *Eur. Phys. J. E* **2016**, *39*, 1.
- [77] J. L. Abascal, C. Vega, *J. Chem. Phys.* **2005**, *123*, 234505.
- [78] J. Abascal, E. Sanz, R. García Fernández, C. Vega, *J. Chem. Phys.* **2005**, *122*, 234511.
- [79] C. C. Adams, *The knot book*, American Mathematical Society, Rhode Island **1994**.
- [80] P. H. Handle, T. Loerting, F. Sciortino, *Science* **2017**, *114*, 13336.
- [81] J. Russo, K. Akahane, H. Tanaka, *Proc. Natl. Acad. Sci. USA* **2018**, *115*, E3333.
- [82] S. Sastry, C. A. Angell, *Nat. Mater.* **2003**, *2*, 739.
- [83] H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444.
- [84] T. D. Bennett, J.-C. Tan, Y. Yue, E. Baxter, C. Ducati, N. J. Terrill, H. H. M. Yeung, Z. Zhou, W. Chen, S. Henke, A. K. Cheetham, G. N. Greaves, *Nat. Commun.* **2015**, *16*, 8079.
- [85] R. Gaillac, P. Pullumbi, K. A. Beyer, K. W. Chapman, D. A. Keen, T. D. Bennett, F.-X. Coudert, *Nat. Mater.* **2017**, *16*, 1149.
- [86] T. D. Bennett, S. Horike, *Nat. Rev. Mater.* **2018**, *3*, 431.
- [87] N. Ma, S. Horike, *Chem. Rev.* **2022**, *122*, 4163.
- [88] M. O'Keeffe, O. M. Yaghi, *Chem. Rev.* **2012**, *112*, 675.
- [89] H. Jiang, D. Alezi, M. Eddaoudi, *Nat. Rev. Mater.* **2021**, *6*, 466.
- [90] A. Qiao, T. D. Bennett, H. Tao, A. Krajnc, G. Mali, C. M. Doherty, A. W. Thornton, J. C. Mauro, N. Greaves, Y. Yue, *Sci. Adv.* **2018**, *4*, eaao6827.



**Andreas Neophytou** graduated with a BSc degree (2017) in Natural Sciences, and subsequently earned an MSc by Research (2019) and a PhD (2023) at the University of Birmingham, while researching in the Chakrabarti group on computational studies of programmable self-assembly. He was hosted by Professor Vinothan N. Manoharan at Harvard University as a Fellow of the Harvard John A. Paulson School of Engineering and Applied Sciences in 2022. He is currently a postdoctoral researcher at Sapienza Università di Roma in the Sciortino and Russo groups, where he is investigating phase transitions in network-forming systems.



**Dwaipayan Chakrabarti** currently holds the position of Associate Professor in Soft Matter in the School of Chemistry at the University of Birmingham, having earned a PhD from Indian Institute of Science, Bengaluru and subsequently held several research fellowships at the University of Cambridge. With their expertise in computation and theory, the central focus of the Chakrabarti group's research is on the design and development of advanced materials for applications in photonics, phononics, and opto-electronics. The Chakrabarti group has rich experience in programming self-assembly of soft materials, exploiting especially anisotropic interactions between building blocks ranging from molecular to microscale.