# Bijels: a new class of soft materials

Michael E. Cates and Paul S. Clegg

DOI: 10.1039/b807312k

Bicontinuous interfacially jammed emulsion gels ('bijels') were proposed in 2005 as a hypothetical new class of soft materials in which interpenetrating, continuous domains of two immiscible fluids are maintained in a rigid state, by a jammed layer of colloidal particles at their interface. Such gels should have unusual material properties relevant to catalysis and other applications. Although initially proposed on the basis of computer simulation, the existence of bijels has since been confirmed in the laboratory. However, a wide gap remains between the simulated and the experimental systems. This leaves room for continuing debate on the cause of stability in these materials; in particular, it is not known whether an attraction between the colloidal particles is essential for stability.

### 1 Introduction

Under conditions where they are not completely wet by either phase, colloidal particles immersed in a biphasic fluidfluid mixture tend to sequester at the interface between the two immiscible fluids. This has been known since the early 20th century when Pickering<sup>1</sup> and Ramsden<sup>2</sup> used colloids to stabilize droplet emulsions. Our understanding of the formation of such particle-stabilized emulsions has advanced considerably in recent years.3 Given the increasing availability of colloidal particles and/or nanoparticles with tunable surface chemistry,3,4 this has led to growing use of liquid-liquid interfaces in directing the self-assembly of such particles.4-6 The

liquid-liquid interface is often created by agitation (by ultrasound or mechanically) of the demixed fluids.<sup>3,4</sup> This generally leads to formation of particle-stabilized emulsion droplets; but unlike conventional surfactant-based emulsions, these droplets can exhibit frozen aspherical shapes.<sup>7</sup> In such cases, the particle layer solidified, clearly presumably has imparting mechanical rigidity to each droplet. (Similar phenomena are seen in particle-stabilized gas bubbles.8) This solidification could be promoted by attractive colloidal interactions, but might also stem from the jamming of particles into repulsive contact under the influence of interfacial tension alone.

Clearly, agitation is not the only way to create a large interfacial area between immiscible fluids. For instance, if a binary mixture of simple fluids, initially in a single phase and with no particles present, is quenched deep into a biphasic region, the process of spinodal decomposition initially creates an enormous interfacial area.9 This area then decreases continuously with time, at a rate set by the balance of interfacial tension (which is the driving force) against either viscous dissipation or inertia within the fluid phases. For roughly symmetric quenches (equal phase volumes), the spinodal structure is bicontinuous, *i.e.*, each of the new phases connects one side of the sample to another *via* a fluid labyrinth. For strongly asymmetric quenches, an initially bicontinuous structure can fragment into droplets later in the demixing process.

Several years ago, we began asking whether this fluid-bicontinuous structure, normally present only transiently *en-route* to bulk phase separation, could become permanently frozen in place by adsorption of a layer of colloids onto the fluid– fluid interface. The resulting



Michael Cates

Mike Cates is known for his theoretical studies of polymers, emulsions, colloids, surfactant solutions, and granular matter. He is currently interested in the flow of materials which do not reach equilibrium even at rest. Cates has held the Chair of Natural Philosophy at the University of Edinburgh since 1995 and was made a fellow of the Royal Society in 2007.



Paul Clegg received his DPhil from the University of Oxford, following which he held positions at MIT and the University of Toronto. He then moved to the University of Edinburgh where he is currently a lecturer. His experimental studies involve creating and understanding novel arrested states which emerge when particles are dispersed in complex fluids.

Paul Clegg

SUPA, School of Physics, University of Edinburgh, Kings Buildings, Mayfield Road, Edinburgh, Scotland, UK EH9 3JZ



Fig. 1 Bijel structure found by simulation. Both fluids are transparent; the interface between them is shown blue on one side and yellow on the other. In the second frame the particles are shown translucent to make the interfacial structure more visible. This example has slight (55 : 45) asymmetry between the phase volumes of the two fluids. After ref. 16; image courtesy of E. Kim.

'bicontinuous interfacially jammed emulsion gel' (or 'bijel' for short; Fig. 1) could be of interest for several reasons, as follows.

First, a material formed this way should, if the particle layer truly solidifies, become a three-dimensionally solid gel with a finite elastic modulus and a yield stress. This is somewhat different from particle-stabilized droplet emulsions, although a suspension of the latter certainly can solidify macroscopically if compressed.10 sufficiently Solid-like mechanical properties would starkly contrast with the case of microemulsions, in which a similarly bicontinuous fluid morphology is thermodynamically stabilized by a monolayer of amphiphiles.<sup>11</sup> In the microemulsion state, such a fluid interface is not frozen, but labile: the local topology of the domains is endlessly changing in a manner that readily admits fluid flow, with the effect that microemulsions are not much more viscous than their component fluids.

Second, the nonlinear mechanics of bijels might prove unusual, particularly if they could be formed using purely repulsive colloids. In this case, solidification of the particle layer stems solely from compression by interfacial tension, which acts to reduce the surface area available to the adsorbed colloids. A large enough (order unity) mechanical strain might increase the area enough to unjam the particles, allowing fluid-like rearrangement before rejamming in a partially relaxed configuration. This transient fluidization contrasts conventional yielding mechanisms, which usually proceed via an accumulation of local plastic events.

Third, and perhaps the most significant from an applications viewpoint, is that bijels should be able to serve as a crossflow microreaction medium. or 'membrane contactor', in which the two fluids are made to flow in opposite directions through the solid gel, allowing intimate contact between mutually insoluble reagents (Fig. 2). These reagents can meet at the exposed fluid-fluid interstices of the particle layer; any reaction product that is soluble in either phase can be swept out continuously. (Note that in a jammed colloidal monolayer, around ten percent of the fluid-fluid interface remains exposed at interstices. Thus the colloids pose a significant obstacle to interfacial reactions only when reagents or products are of comparable size to the colloids themselves.) This continuous mode of operation contrasts with microreactor designs based on droplet emulsions,12 in which the dispersed phase can only be emptied of products (or replenished with reagents) by breaking the emulsion. Intriguingly, a bijel device would 'plumb in' automatically to adjacent bulk phases of the two fluids: a bulk phase of either fluid should connect, without interface or other obstruction, to the matching bicontinuous domain.

Finally, all these properties of a bijel should be controllable by varying the radius *a* and volume fraction  $\phi$  of the particles. Presuming all the particles to reside on the fluid-fluid interface, the typical pore-size *L* of the bicontinous domains scales as  $a/\phi$ , while the shear modulus and yield stress scale as  $\sigma/L$  with  $\sigma$  the fluid-fluid tension. Since *a* can be



Fig. 2 Schematic geometry of a cross-flow microreactor. The bicontinuous morphology of the bijel should allow two immiscible fluids to be passed through the material in opposite directions via a continuous process.14 First panel: possible macroscopic geometry of microreactor. Blue: aqueous phase; yellow: oil phase; green: bijel phase. Arrows denote fluid motion; in a simple gravity-driven flow as shown, the denser fluid (water) is injected at the top of the sample and sinks through the gel before being extracted at the bottom, vice-versa for oil. Note that in practice, to achieve a reasonable flow rate, pumping under pressure rather than merely gravity is likely required. Second panel: internal flow within the bijel microstructure. Blue: aqueous domain; yellow: oil domain; white: particles. Note that fluid in neighbouring domains flows in opposite directions (arrows).

varied from nanometres to microns, while  $\phi$  might vary from 10<sup>-3</sup> to 10<sup>-1</sup>, this gives about 5 decades of tuning range for the modulus. Comparing the yield stress with the viscous stresses generated locally in a crossflow geometry, one finds that a bijel should be able to support a velocity difference between the two fluids of order  $\sigma/\eta$  without disruption. Even allowing for a small numerical prefactor in this expression as suggested by simulation work,<sup>13</sup> the result is of order centimetres

per second; remarkably the criterion is independent of the pore-size L. By making this small, intimate mixing at high flow rate should be possible—although small L does require large pressure gradients to force the fluids through the gel.

The claims listed above were made in 2005,<sup>14</sup> with supporting evidence based on computer simulations.<sup>13</sup> A bijel with these properties would fall within a novel class of materials defined by three criteria: (i) an amorphous structure; (ii) fluid bicontinuity; and (iii) a yield stress. Few other members of this class are known; most analogous materials (bicontinuous microemulsions, ternary lipid cubic phases, dense Pickering emulsions, and conventional colloidal gels) lack one of these three features.

The rest of this article reviews data not only from the initial and subsequent simulations,<sup>13,15,16</sup> but also from laboratory experiments.<sup>17,18</sup> The experimental evidence leaves little doubt that bijels are indeed realizable. However, several questions remain open on their likely material properties, and also the microscopic origin of their stability.

For space reasons, in this article we exclude discussion of related work involving stabilization of polymeric rather than simple fluids (*e.g.*, ref. 19). Clegg<sup>20</sup> gives a more detailed survey, addressing this and other links to the wider literature, including that on Pickering emulsions.

# 2 Simulation evidence

Simulations were done in ref. 13 using a mesoscopic algorithm known as lattice Boltzmann (LB). The method simulates spherical colloidal particles of radius *a*, at volume fraction  $\phi$ , with near-hard-sphere interactions, undergoing Brownian motion at temperature *T* in a binary fluid solvent that can undergo demixing to form two fluids separated by a sharp interface of known interfacial tension  $\sigma$ .

A detailed description of the LB algorithm is beyond our scope; see, *e.g.* ref. 21 for a recent review. While it is arguably the best method available for simulating Brownian colloids in binary solvents,<sup>21</sup> it is important to recognize that LB is operating right at its limits when studying this problem. This would also be true of any alternative simulation method, for a simple reason: in a putative bijel structure one must resolve inter-colloid forces in the jammed layer (at surface separations a fraction of a), and simultaneously resolve a domain structure on scales of order  $L \sim a/\phi \sim 10a$ . Moreover, a simulation must contain many domains for boundary effects to become convincingly small. Thus the bijel structure is sensitive to physics across about 2.5 decades of length. To resolve this in d dimensions, one must simulate around 10<sup>2.5d</sup> degrees of freedom, which is around 30 million in three dimensions. Likewise, several decades separate the timescale for macroscopic arrest from that of microscopic colloidal motion; also, one must resolve interfacial motion which, early in the quench protocol, is rapid compared to that of the colloids. In practice, for 5 nm colloids in a pair of fluids with interfacial tension and viscosity appropriate to an oil-water system ( $\sigma = 6 \times 10^{-2}$  N m<sup>-1</sup>,  $\eta =$  $9 \times 10^{-4}$  N m<sup>-2</sup> s), the maximum time scale reached by simulation approaches, but does not exceed, the Brownian time  $\tau_{\rm B}$  $\simeq 6\pi \eta a^3/k_{\rm B}T \approx 1 \,\mu {\rm s}$ , which is the time for a free particle to diffuse its own radius.

Even to reach this time scale, we are forced to operate LB in a regime of discernible numerical error from several different sources.<sup>13,21,22</sup> It is therefore reassuring that an alternative mesoscopic simulation method, called dissipative particle dynamics (DPD), has very recently been used<sup>15</sup> to confirm in some detail the findings of our initial LB studies,<sup>13</sup> whose results we now outline.

In the simplest simulated protocol,13 one starts with a sample in the singlephase region of a symmetric (50 : 50 by volume) binary fluid, in which are suspended colloidal particles having equal affinity for the two fluids. (The mixed and unmixed fluids all have equal viscosity.) There follows a quench into the twophase region so that the fluids demix by spinodal decomposition. As demixing proceeds, colloidal particles are swept onto the fluid-fluid interface; since the two solid-liquid interfacial tensions are equal, the colloids adopt a 90° contact angle (neutral wetting). As the interface reduces its area by the usual coarsening process, the colloids become forced into close proximity, and growth of the domain size L(t) is dramatically curtailed.13

Subsequent simulations<sup>16</sup> have shown this scenario to be robust to modest

variations in the phase volumes, whereas for large asymmetry droplets (of aspherical shapes) are formed instead. We have not simulated wetting asymmetry, and the wetting angle is difficult to verify quantitatively although experiments with varying surface treatments suggest a significant window of tolerance.<sup>17</sup>

The results summarized so far are encouraging in that they show the spontaneous formation of a jammed colloidal layer during spinodal decomposition. However, such simulations cannot currently establish whether this layer is permanently jammed and therefore capable of imparting macroscopic rigidity to the material. In all the bijel simulations so far reported, the domain size L(t)continues to slowly increase throughout the simulation. To establish eventual saturation, which is a pre-requisite for a fully frozen structure, one needs to access time scales longer than  $\tau_{\rm B}$  which, as explained above, are not easily accessible in LB when fluid-fluid interfaces are also present.

Although our simulations cannot be run for long enough to determine the ultimate fate of the resulting structure, arguments were given in ref. 13 for its permanent arrest. Specifically, there is an energy barrier  $\alpha \varepsilon$ , where  $\varepsilon = \sigma \pi a^2$ , to detachment of a particle of radius a from a fluid-fluid interface of tension  $\sigma$ . We may write  $\varepsilon/k_{\rm B}T = (a/a_0)^2$  where  $a_0^2 = k_{\rm B}T/a_0^2$  $\pi\sigma$ ; then for T = 300 K and typical  $\sigma$  of order 0.01 N m<sup>-1</sup> or larger,  $a_0$  is 0.4 nm or less. The geometry-dependent parameter  $\alpha$  is of order unity for a single particle on a flat surface, and arguably should be similar in a dense particle layer; if so,  $\alpha \varepsilon / k_{\rm B} T \ge 10$  even for a particle of 1 nm radius, and thermally activated detachment can be safely neglected for, say,  $a \ge$ 3 nm. On the other hand, due to the complicated energy landscape involved, we cannot quantitatively estimate  $\alpha$  for a crowded curved monolayer with any precision. The possibility remains that such a layer might have pathways allowing sequential particle expulsions while continuously decreasing the fluid-fluid interfacial area, so that  $\alpha = 0$ . In ref. 13, LB studies of structural motifs were reported, giving some evidence for  $\alpha \geq$ 0 for jammed particle layers on cylinders and rippled sheets. These simplified structures could be simulated to higher resolution than bijels within LB; to access

 $t \ge \tau_{\rm B}$  an enhanced temperature  $T \gg 300$ K was also used. Nonetheless, the latetime regime,  $t \gg \tau_{\rm B}$ , was not achieved for these curved monolayer motifs.

Our recent simulation efforts<sup>16</sup> have taken a different but related approach. This is to directly estimate the activation energy to particle detachment by starting with a bijel structure (formed with 5 nm colloids at T = 300 K) and monitoring the rate r of detachment of particles from the interface during the late stages of the simulation where L(t) is barely increasing. This was done for a range of enhanced temperatures spanning one decade, allowing  $t \geq \tau_{\rm B}$  to be accessed. It was found for each temperature T that r(T,t)approached a constant (per particle) only at late times,  $t \ge 3.5\tau_{\rm B}$ . This late time data r(T) was then used to construct an Arrhenius plot, which could be used to estimate the activation barrier  $\alpha \varepsilon$  (Fig. 3). This was done allowing for either a constant or a linear dependence of the pre-exponential rate factor on temperature. There was a noticably better fit for the first of these (which might suggest a barrier-crossing attempt rate set by coarsening dynamics rather than colloid diffusion). The best estimate for the geometrical barrier factor  $\alpha$  emerging from this study was  $\alpha \leq 8 \times 10^{-3}$ ; however a value of  $\alpha = 0$  could not be ruled out.<sup>16</sup>

Our LB simulations thus leave unsettled an important question concerning the ultimate fate of bijels formed by interfacial jamming of particles with purely repulsive colloidal interactions. For an arrested solid structure to be sustained at  $t \gg \tau_{\rm B}$ , we presumably require  $\alpha \varepsilon \gg k_{\rm B}T$ . If  $\alpha$  is indeed around  $10^{-2}$ , then the minimum radius of colloids required for



Fig. 3 Arrhenius plot of late-time interfacial detachment rate per particle r(T) versus inverse temperature (in lattice Boltzmann units). From the slope of this plot, an estimate of the activation barrier  $\alpha \varepsilon$  is found. After ref. 16; image courtesy of E. Kim.

such stability (in a fluid mixture with  $\sigma \simeq 0.01$  N m<sup>-1</sup> or larger) is raised from a few nanometres to ten times that. This is still much smaller than the colloids used in the laboratory experiments discussed below, and represents only a quantitative, not a qualitative, change to the claims made in the introduction concerning the putative material properties of bijels.

Alternatively, if  $\alpha$  is strictly zero, for repulsive colloids the jammed layer can continuously reduce its area by ejecting particles. The interfacial film is then ultimately viscous, not solid, and coarsening will continue indefinitely. Moreover, the mechanical properties of the three dimensional bijel material will also be ultimately viscous rather than solidlike. In that case, any experimental observation of bijels with the previously predicted properties of permanent mechanical rigidity<sup>13,14</sup> would have to be attributed to the presence of strong attractive bonding between the colloidal particles. Such bonding could provide an additional barrier to particle detachment that might well be enough to create a quasi-permanent structure. Indeed, many conventional colloidal gels maintain a long-lived mechanical integrity in precisely this way.23 If so, the bijel could be seen as a structurally templated but ultimately conventional gel with peculiar properties stemming from the binary-fluid route to its formation.

#### 3 Experimental evidence

Investigating bijels in the laboratory is challenging, partly due to the differences between the idealized protocol used in the simulations and the conditions that are practically achievable. For instance, it is not possible in practice to perform an instantaneous quench to a state point, well within the two-phase region, with high interfacial tension between the two phases. Instead, our studies begin with the particles dispersed in the single-fluid phase, followed by quenching at some finite rate, eventually arriving deep into the demixed region. As the sample passes through the intervening temperatures, pre-transitional effects can occur, nucleation can be seeded and phase compositions will smoothly change. All of these factors can complicate the observed behaviour.

Despite this, we have recently been able to produce fully three-dimensional bijels that are stable for many months.<sup>18</sup> So far we have made use of colloidal silica of a size that aids visualization of the resulting structures (a > 200 nm); this gives a high barrier energy scale  $\varepsilon$  for interfacial detachment, and limits the role of Brownian motion to a level well below that seen in the simulations (which were geared towards nanoparticles<sup>13</sup>).

Our initial explorations<sup>17</sup> targeted the alcohol-alkane combinations methanolhexane and ethanol-dodecane, both of which phase-separate on cooling (with  $\sigma \approx 1 \text{ mN m}^{-1}$  at the observation temperatures). The chosen composition of the two fluids represents a compromise between ensuring spinodal decomposition (requiring a quench close enough to the critical composition) and maintaining a bicontinuous domain configuration (requiring near-equal volumes of the two new phases). As described above, we first dispersed colloids (with  $a = 220 \pm 7$  nm, modified surfaces giving  $\varepsilon \approx 10^4 k_{\rm B}T$ , and typically  $\phi = 0.02$ ) at a temperature where the two solvents are fully miscible. We employed a thin (200 µm) capillary of rectangular cross-section to hold the sample while it was quenched deep into the demixed regime by submersion in a bath of cryogens. Our confocal microscopy studies revealed both convoluted domain arrangements and long cylinders each stabilized by interfacial colloids. (Similar thin bijel structures have also been created starting from spun-cast polymer blends.19)

There are significant differences between these results for alcohol-alkane systems and the computer simulations.<sup>13</sup> Firstly, the capillary is barely thicker than the domain scale, L, making the overall structure quasi-two-dimensional. This leaves open the possibility that the samples are stabilized by the confining walls. Indeed, subsequent experiments in capillaries which were twice as thick led to convoluted bijel-like domains only near the boundaries, with a spatial evolution towards a colloid-stabilized droplet emulsion at the centre of the sample. Secondly, the interfacial layers of colloids were 'fluffy' and more than a monolayer thick. Since the actual fluid-fluid interface is very thin on the scale of a particle, many of the particles in this fluffy layer could not be physically attached to the fluid-

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fluid interface but were presumably attached to other particles instead. The required attractions between particles could arise at different stages during the quench and from a variety of origins.<sup>17</sup>

Our second set of experiments18 instead involved quenches, taken through the critical point, for a system with a lower critical solution temperature: water and 2,6-lutidine. (Since this system is phase separated at high temperatures, the "quench" is now upward in temperature.) We again used colloidal silica ( $a = 290 \pm 7$ nm), this time tagged with fluorophore FITC which, when combined with appropriate drying conditions, leads to colloids exhibiting neutral wettability with these two solvents. (The interfacial tension is estimated<sup>18</sup> as  $\sigma \approx 0.22$  mN m<sup>-1</sup>, again giving  $\varepsilon \approx 10^4 k_{\rm B} T$ .) This time we used a thick (1 mm) cuvette to hold the sample ( $\phi = 0.02$ ). To carry out the quench we inserted this in a preheated aluminium block (313 K giving a warming rate of 17 K min<sup>-1</sup>) located on a confocal microscope. The block also served to reduce spatial temperature gradients which can be problematic close to demixing. The formation process is sufficiently slow that we could record it from the earliest time that L was resolvable by microscopy. We found that the initial spinodal decomposition continues to occur in the presence of the particles. However, as phase separation proceeds, there is an increasingly large population of particles on the interface between the two phases, and this slows down the separation process.

By employing particles with well-tuned wettability, we were able to arrest our

fully three-dimensional bijels for seven months at least (Fig. 4). During this time there was no noticeable ageing on resolvable scales, although we cannot exclude local changes in the packing of the colloids within the monolayer. Using fluorescence confocal microscopy we were able to resolve the particle-coated fluidfluid interface at depths into the sample of up to 0.5 mm, and hence we demonstrated integrity of the bicontinuous fluid domains right through to the centre of the sample.18 Numerous fluid domains are encountered on passing from one side to the other, with the typical distance between these (which is roughly the domain scale, L) smaller by at least twenty-fold than the thickness of the cuvette. We also used high resolution confocal microscopy to show that the interfaces are roughly one monolayer thick (Fig. 5).



Fig. 5 High-resolution confocal image of colloid packing at the interface between waterrich and lutidine-rich phases. The interface is stabilized by little more than a monolayer of particles. Scale bar; 1  $\mu$ m. After ref. 18; image courtesy of K. White.



**Fig. 4** Bijel structure as seen using fluorescence confocal microscopy. Both fluids are dark with the interface bright. In the left frame a sample is shown one week after formation; the right frame is a different sample seven months after formation. The samples are water–2,6-lutidine at critical composition with  $\phi = 0.02$  silica colloids quenched from room temperature to 313 K at 17 K min<sup>-1</sup>. The scale bars are 100 µm. After ref. 18; images courtesy of E. Herzig.

and also for Pickering emulsion droplets (both systems of much simpler geometry than the bijel), work is well advanced on studying the viscoelastic properties that arise from the presence of jammed colloidal layers.3,10,20 As yet we have only just begun to probe this aspect of the bijel. So far, we demonstrated the existence of a yield stress by dropping a 200 µm diameter copper wire weighing 1.9 mg into a bijel and comparing the trajectory with that of a wire in a droplet emulsion of identical composition. For the droplet emulsion the wire sunk directly to the bottom of the cuvette in a fraction of a second whereas, for the bijel, the wire slowed to a stop after descending a short distance. The wire continued to make intermittent drops and eventually reached the bottom of the cuvette after several days. This demonstrates that the bijel does have some sort of yield stress but suggests that its frozen interfacial structure can slowly reorganize in response to the heavy object. To follow up this preliminary work, we are now planning quantitative rheological studies using a cone-and-plate rheometer.

For colloid-coated planar interfaces,

To test the claim of scalability reported in the introduction, we have varied particle volume fraction ( $\phi$ ), warming rate, and liquid composition and observed the resulting changes in the bijel structure.18 We measured the domain size, L, for  $0.005 \leq \phi \leq 0.04$  in critical quenches with warming at a rate of 17 K min<sup>-1</sup> to 313 K, confirming the expected scaling behaviour,  $L \sim a/\phi$ , at least for the higher  $\phi$  values explored. For  $\phi \leq 0.01$  we found that there were some large droplets within the samples, suggesting either that the bicontinuous structure was not stable, or that the particles were inducing a preferred curvature in the interfaces. The warming rate we typically use (17 K  $min^{-1}$ ) is the fastest possible with this set-up; approaching this rate is important for successful bijel formation (see Fig. 4). Indeed, at 1 K min<sup>-1</sup> substantial secondary phase separation occurs suggesting that the two initial domains are beginning to behave as separate subsystems. Warming still more slowly (0.1 K min<sup>-1</sup>) leads to a structure which collapses on itself during the wide time window of low tension  $\sigma$ , which then arises near the critical temperature.

By varying the proportions of the two solvents to explore off-critical quenches as well as the critical ones just described, we found that the bijel can be thought of as the structure formed by an emulsion at precisely the point where it undergoes phase inversion by variation of fluid composition. In such a phase inversion, the dispersed and continuous phases of an emulsion switch identities without change to the properties of the particles.<sup>3</sup> Phase inversion is known to be affected by the viscosity ratio of the two phases; this could provide another avenue to control the resulting structure.<sup>9</sup>

# 4 Discussion

The bijels we created experimentally from particles in water-lutidine silica mixtures<sup>18</sup> closely resemble the structures predicted in our earlier computer simulations:13 compare Fig. 4 and 1. They are fluid bicontinuous, fully three dimensional, and are stabilized by a monolayer (more or less) of jammed particles at the fluid-fluid interface. However these particles are large compared to the nanoparticles used in the simulations and have more complex interactions. While it would be simple to perform simulations for larger colloidal particles,13,16 in practice this is done by rescaling the fluid parameters and temperature in the simulation. The main effect of doing so is then to increase  $\tau_{\rm B}$ , making it even harder to approach the long-time regime ( $\tau \gg \tau_{\rm B}$ ) which controls the ultimate fate of the bijel. Of course, for extremely large colloids ( $a \gg 1 \mu m$ ),  $\tau_B$  can itself exceed experimental time scales, so that the question of whether Brownian detachment of interfacial particles continues on such time scales itself becomes academic. Nonetheless, this currently frustrates any attempt to perform simulations that are matched closely to the conditions prevailing in the experiments reported above.

For our experimental systems, once the particles become jammed together by the coarsening of the domains, it may be possible for van der Waals attractions or siloxane bond formation to create permanent bonding within the jammed particle layers. There is some evidence that this is indeed what happens,<sup>17</sup> but currently no indication that such bond formation is instantaneous. Indeed, significant particle motion on the interface appears to continue well after the initial jamming has occurred. For

instance, careful inspection of the bijel slices shown in Fig. 4 reveals peninsulas with circular cross-sections protruding out from the interfaces. These appear to be where droplets have coalesced with flat interfaces, and suggest that not only particle rearrangements, but also frozen cusps with long-term stability, are possible.

An important question concerns the yielding mechanism. It is known that, in two dimensions, shear deformation of order ten percent causes particle rearrangements within a dense colloidal monolayer.8 However, this does not translate simply into a yield strain estimate for the bulk bijel. Moreover, for repulsive particles, the yield mechanism is more likely to involve dilation of the interface, as a result of bulk shear deformation, than interfacial shear as such. (The increase in interfacial area can allow the colloids to unjam.13) An area increase of ten or twenty percent is likely to be sufficient, suggestive of a yield strain that is also around ten percent. However a more precise estimate would require detailed simulation of the bijel geometry under shear, and could also depend on the precise strain configuration (simple shear versus uniaxial elongation, etc.).

Although our simulations have mainly addressed bijel formation with purely repulsive particles, we have not yet achieved this limiting case with our experimental bijels. To do so would require switching off both of the sources of attractive bonding interaction just mentioned. On the other hand, purely repulsive interactions, such as the Coulomb interaction between likecharged colloids, have been well studied for droplet and crumpled plane configurations.24 If charged particles repel through a low dielectric constant medium, equilibrium separations of many times the particle radius are often seen. Such particles can stabilize emulsion droplets even when these are pressed into close enough contact to actually share the particles (which then bridge between the two fluid-fluid interfaces).24 Additionally, such particles have been trapped at a flat interface and forced together using an applied surface pressure. The interface crumples at a surface pressure for which the interparticle repulsion balances the interfacial tension; however, no particles detach from the corrugated interface. For

all these experiments  $a > 1.3 \,\mu\text{m}$  and the fluids are fully immiscible so that  $\varepsilon > 10^7 k_\text{B} T.^{24}$  Under these conditions, Brownian motion is unlikely to be a major factor in the evolution of the interfacial structure.

Similar remarks should apply to bijel experiments for particles at the upper end of the colloidal size range, even under idealized conditions where the particle interactions remain purely repulsive. Indeed, unless the geometrical barrier parameter  $\alpha$  defined in Section 2 is strictly zero, then the possibility of Brownian detachment of particles from the interface ceases to be relevant, once the colloids used are large enough. However, for large and small particles alike, the presence and nature of any attractive interactionsparticularly covalent ones such as siloxane bonding-could have strong effects on the material properties of bijels. We hope to clarify this connection in future work. The planned use of bijels as membrane contactors does not require repulsive particles; in fact, attraction or permanent bonding between the colloids could be of some assistance at high flow rates. An ongoing experimental effort is in place to create the counterflow of opposing fluids, within the bijel medium, required for such applications.

# Acknowledgements

The work reviewed was funded by EPSRC GR/S10377 and EP/030173, and by SE /POC/8-CHM-002. MEC holds a Royal Society Research Professorship.

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