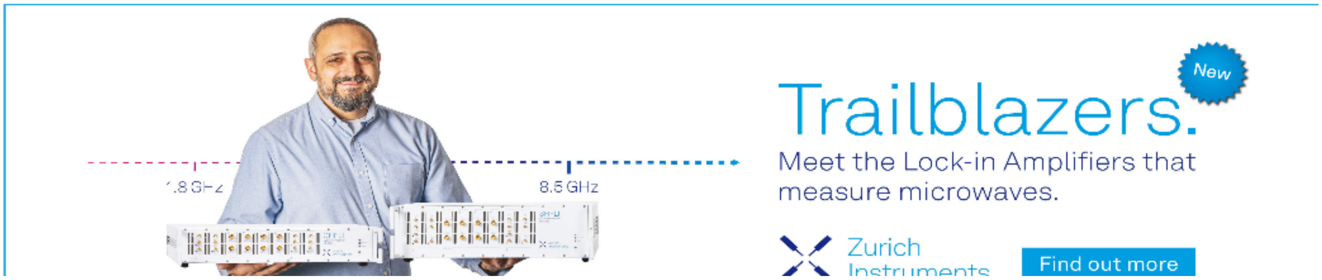
The freedom of confinement in complex fluid

Amy Q. Shen and Perry Cheung

Citation: Physics Today **63**, 9, 30 (2010); doi: 10.1063/1.3490498
View online: https://doi.org/10.1063/1.3490498
View Table of Contents: https://physicstoday.scitation.org/toc/pto/63/9
Published by the American Institute of Physics



feature article

The freedom of confinement in complex fluids

Amy Q. Shen and Perry Cheung

When it comes to self-assembly of photonic, drug-delivery, and biomimetic materials, big opportunities can be found in small spaces.

Amy Shen is an associate professor in the department of mechanical engineering at the University of Washington in Seattle. **Perry Cheung** is a postdoctoral researcher in Shen's soft-matter and microfluidics lab.

Although easily overlooked, complex fluids—non-Newtonian, typically multiphase fluids—are ubiquitous and play an integral role in our daily lives. In nature, examples run the gamut from particle dispersions (such as saps, mud, blood, and lava) to high-molecular-weight polymers (like DNA and proteins), to aggregates of low-molecular-weight surfactants (such as lipids). Complex fluids include such familiar products as shampoo, detergents, shaving cream, chocolate mousse, paint, glue, and liquid-crystal-based displays. Their multiple, coexisting phases give rise to a hierarchy of length and time scales not seen in conventional fluids; the interactions between those phases can yield fascinating properties and behavior. See, for example, reference 1 and previous PHYSICS TODAY articles by Thomas Witten (July 1990, page 21), Alice Gast and William Russel (December 1998, page 24), and Pierre-Gilles de Gennes (June 1983, page 33).

The behavior of a complex fluid depends crucially on the shape, motion, and characteristic length scales of its confining boundaries. When the confining length scale, say the distance between opposing boundaries, becomes comparable to the intrinsic length scale of the fluid, say the size of the particles in the dispersed phase, the confined fluid can behave quite differently from an identical fluid in the bulk. Surface energy, entropy, and commensurability—the compatibility of the intrinsic and confining length scales—become the most important factors affecting material morphology.[2] At the large surface-to-volume ratios typical of confined systems, surface energies often are large enough to alter microstructural orientation and symmetry. Narrow confinement also tends to lower the fluid's entropy, leading to ordered arrangements of particles that would configure randomly in the bulk. So-called supramolecular structures—loosely bound aggregates of molecules—may stretch or compress if their length scale is incommensurate with the boundary dimensions.

Confinement can be classified by dimensionality: A liquid film, though it has two degrees of freedom in the plane, is one-dimensionally constrained along the film depth and thus considered to be under 1D confinement; micro- and nanochannel configurations, typically constrained by the channel depth and width, are said to have 2D confinement; droplets are a canonical example of 3D confinement.

Many naturally occurring complex fluids systems bene-

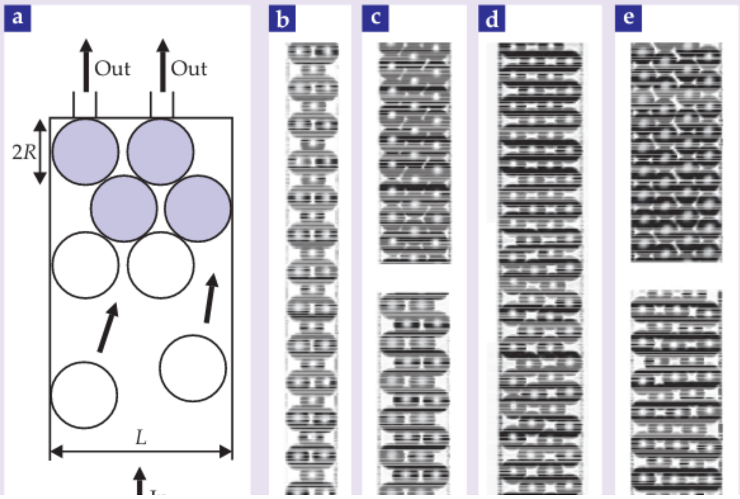


Figure 1. Building colloidal crystals in microchannels. **(a)** A microchannel design developed by George Whitesides and colleagues features small pores at the outlet that let fluid pass but trap colloidal particles, which then arrange into a repeating lattice. By adjusting the relative microchannel width, $L/2R$, where L is the channel width and R is the particle radius, one can produce robust two-dimensional crystalline arrangements. **(b–e)** An assortment of colloidal crystals are generated in channels with $L/2R$ equal to 2.20, 2.65, 3.33, and 3.71, respectively. (Adapted from ref. 6.)

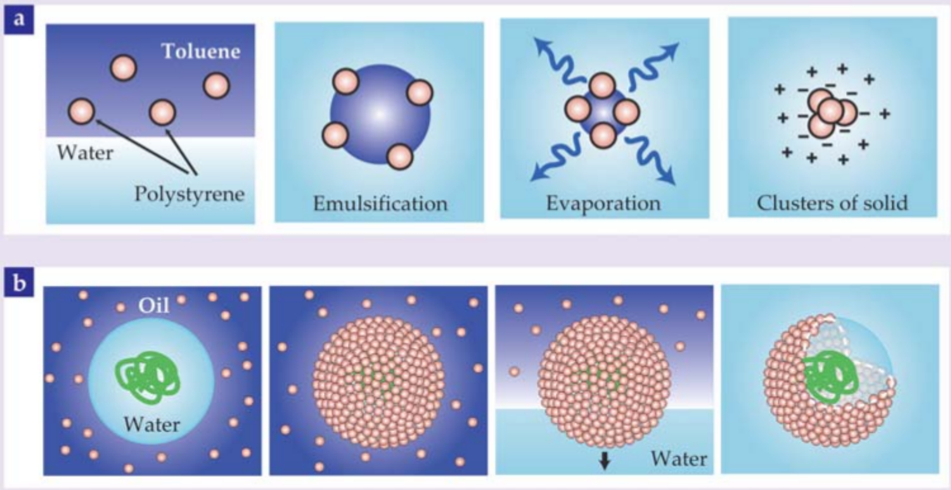


Figure 2. Self-assembly in microdroplets. **(a)** Colloidal clusters are made by mixing a dispersion of polystyrene microspheres in toluene with water to generate an oil-in-water emulsion. The toluene is then evaporated, leaving behind robust particle clusters that have fixed and reproducible symmetry. Surface charges prevent the clusters from aggregating with one another. (Adapted from V. Manoharan, M. Elsesser, D. Pine, *Science* **301**, 483, 2003.) **(b)** In a slightly different procedure, elastic capsules called colloidosomes—whose sizes range from microns to millimeters—can be prepared by emulsifying water droplets that contain a material of interest (green) to make a water-in-oil emulsion. Colloidal particles (tan spheres) assemble at the oil–water interface, in the fashion of a so-called Pickering emulsion, and the resulting colloidosomes are then transferred to water via centrifugation. The material of interest is preserved within the permeable colloidosome shell. Colloidosomes can be adjusted for permeability and elasticity and have potential applications in drug encapsulation and delivery. (Adapted from A. Dinsmore et al., *Science* **298**, 1006, 2002.)

fit from confinement—think of phloem transport in plants or capillary blood flow in humans. In cells, energy-gradient-driven molecular assembly occurs in highly confined environments. Researchers are now learning how to similarly exploit confinement in the lab. By varying the confining length scales, one can control the formation of supramolecular structures—and thus the morphology and orientation of soft materials—to generate a host of interesting new phenomena. Recent studies of molecular fluids, polymer melts, and colloidal suspensions show that the properties of the fluid-to-solid phase transition in a confined fluid are substantially different from those in a bulk fluid. In porous media, qualitatively new behaviors emerge as the pore size shrinks and the morphology of the interface becomes dominant.[1] Intermolecular interactions and reaction kinetics in confined systems can also be tuned to create materials with hierarchical ordering.[2]

The ability to control microstructures in confined complex fluids opens new possibilities for designing soft materials with desired physical behaviors and mechanical properties, an important development for areas such as sensor technology, drug delivery, biotechnology, catalysis, and nanotechnology. Confinement effects are important in a wide variety of complex fluids systems, including liquid crystals,[3] polymers,[4] and block copolymers.[5] We focus here on confinement effects on morphology and self-assembly in two representative systems—colloids and amphiphilic systems.

Colloidal crystals: Photonics and beyond

Colloidal mixtures, or just colloids, are composed of nanometer- to micron-sized particles dispersed in a continuous, usually liquid phase. They include inks, blood, paints, and cosmetics. A technological advantage of colloids is that their dispersed particles can be physically and chemically altered, independent of the surrounding fluid, to achieve desirable material properties. For example, in India ink, it is the colloidal carbon, not the surrounding fluid, that strongly absorbs light, giving the ink its color.

rigid boundary, like particles constrained to the droplets of an emulsion. Both are attractive techniques for developing novel, self-assembled materials such as photonic crystals—periodic structures that can block the propagation of light at certain wavelengths in one or more directions. Opal, whose closely packed silica spheres are responsible for its iridescent color, is essentially a naturally occurring photonic crystal.

In 2003 George Whitesides's group at Harvard University introduced an elegant technique for fabricating photonic crystals from a colloidal flow in a microchannel.[6] The microchannel included small pores at the outlet that let fluid pass but trapped colloidal particles, which would subsequently arrange into an ordered lattice (see figure 1). By adjusting the width of the microchannel, Whitesides's group was able to produce an assortment of 2D crystalline arrangements. Michael Solomon and colleagues at the University of Michigan in Ann Arbor built on that approach, adding a mechanism to actively and programmably feed particles into the microchannel. Their design allowed them to produce anisotropic colloidal chains of fixed length and orientation that, when thermally fused, can act as stable building blocks for photonic materials.

Colloidal crystals can also be formed by gravity- or electric-field-driven sedimentation of colloidal particles on patterned templates. The templates—typically produced by micro- or nanolithography techniques or by reactive-ion etching—can range from simple rectangular wells or channels to periodic holes or grooves. The templating method, compared with growing crystals on a bare substrate, gives improved ordering and increased control over the packing symmetry. Applications for the resulting colloidal crystals include coatings for lenses and mirrors, color-changing paints and inks, and photonic-crystal fibers. They may also potentially be developed for optical computers. A thorough review of the use of patterned templates to engineer colloidal crystals can be found in reference 7.

Although physical confinement can produce long-range

Colloids can be confined either physically—by the walls of a rigid geometry, as in microfluidic channels—or by a non-

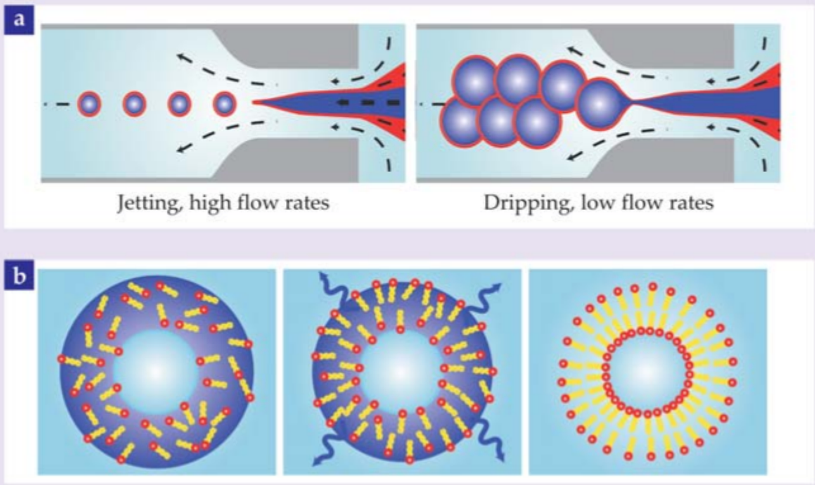


Figure 3. Double emulsions, liquids that contain "bubbles within bubbles," provide a versatile medium for self-assembly. **(a)** A double emulsion can be produced by the coordinated flow of three fluids in a microfluidic device. A high flow rate of the inner fluid (dark blue) combined with a low flow rate of the middle fluid (red) leads to jetting; low flow rates for both the inner and middle fluids result in dripping. The outer, continuous fluid phase is shown in light blue. **(b)** Vesicles can be made by dissolving surfactants in the oil phase of a water-oil-water double emulsion. When the oil is evaporated, it leaves behind the vesicle, a self-assembled, spherical bilayer of surfactants that encapsulates an inner water droplet. If diblock copolymer is used instead of surfactant, the structure is known as a polymersome.

ordered structures, those structures are typically limited to dense arrangements, such as face-centered cubic crystals, since spherical colloidal particles tend to settle into efficient packings. But low-density, low-degree-of-symmetry photonic crystals, such as a diamond lattice, diffract light more efficiently and are often more desirable. New techniques are being explored to engineer building blocks of varying shape and anisotropy that can be used to design unique photonic materials. A group led by David Pine at the University of California, Santa Barbara used an emulsion-evaporation approach to mass-produce robust clusters of colloidal particles with reproducible symmetries (see figure 2a). David Weitz's group at Harvard developed a conceptually similar approach to prepare hollow, elastic capsules called colloidosomes, which have potential applications in drug encapsulation and delivery (see figure 2b).

A colloidal glass transition

If a liquid is cooled rapidly enough and to low enough temperatures, it undergoes a glass transition; that is, it freezes into an amorphous microstructure, with each molecule trapped by its nearest neighbors. Although glassy materials—including drug formulations, polymers, and metallic alloys—are widely produced and used, the processes and forces that govern the glass transition are still not fully understood.[8] An important breakthrough was the 1990s discovery of confinement effects on the glass transition: The glass transition temperature in a small pore or thin film can be either lower or higher than in the bulk, depending on the surface interactions at the boundaries.

The particles in a colloidal mixture undergo an analogous transition when the solid-particle volume fraction increases above some critical value; in that sense, increasing the volume fraction in a colloidal system has the same effect as decreasing the temperature in a molecular system. And although the time and length scales that characterize the colloidal glass transition differ by orders of magnitude from those describing the molecular glass transition, the two processes share remarkably similar qualitative features. Colloids, which are easier to visualize and manipulate than their much smaller molecular counterparts, thus provide an attractive model system with which to study the fundamentals of the glass transition.

A group led by Eric Weeks at Emory University in At-

transition in colloids. The researchers found that much like the thin-film effects on molecular glasses, increased confinement caused the colloidal glass transition to occur at lower volume fractions than in the unconfined bulk. The confinement effects—indicated by a drastic slowdown in the particles' diffusive dynamics—set in roughly when the width between plates was on the order of 10 particle diameters.

The same kind of wedge configuration can be used to induce order among charged colloidal particles. Near a wedge's apex, where the distance between glass plates is about the same as a particle diameter, colloidal particles pack into a single, triangular-lattice monolayer. Moving away from the apex, the triangular monolayer gives way to a cascade of crystalline phases, transitioning first to a buckled bilayer, then to square- and triangular-lattice bilayers, then to a square-lattice trilayer, and so on, as the distance between the glass plates increases.[8]

Confinement can also affect ordering in truly parallel plate geometries. A study by Weitz and colleagues showed that when the distance between plates is narrow and incommensurate with the particle length scale, shearing causes a dense, hexagonally packed colloid to adopt buckled structures not seen in bulk systems.

Self-assembly in microdroplets

Colloidal particles need not be solid. The development of techniques to control the formation and size of dispersed colloidal liquid droplets is an active field with applications for controlled drug delivery, microreactors, and material design.[9] Consider the example of water dripping from a faucet—droplet size is governed by the balance between the interfacial tension forces and the weight of the droplet. The process of forming a microdroplet is similar, except that interfacial tension now competes with the drag of a much more viscous surrounding fluid at length scales small enough to correspond to low Reynolds number flow.

Droplets of uniform size and composition can be formed in microfluidic devices by a carefully designed, continuous flow of two immiscible fluids. Three fluids can yield a double emulsion—an inner droplet, which may contain drugs or another material of interest, encapsulated in a protective outer droplet, immersed in a continuous fluid phase. Imagine an lanta, Georgia, used a quasi-parallel wedge configuration of glass plates to probe the effects of confinement on the glass

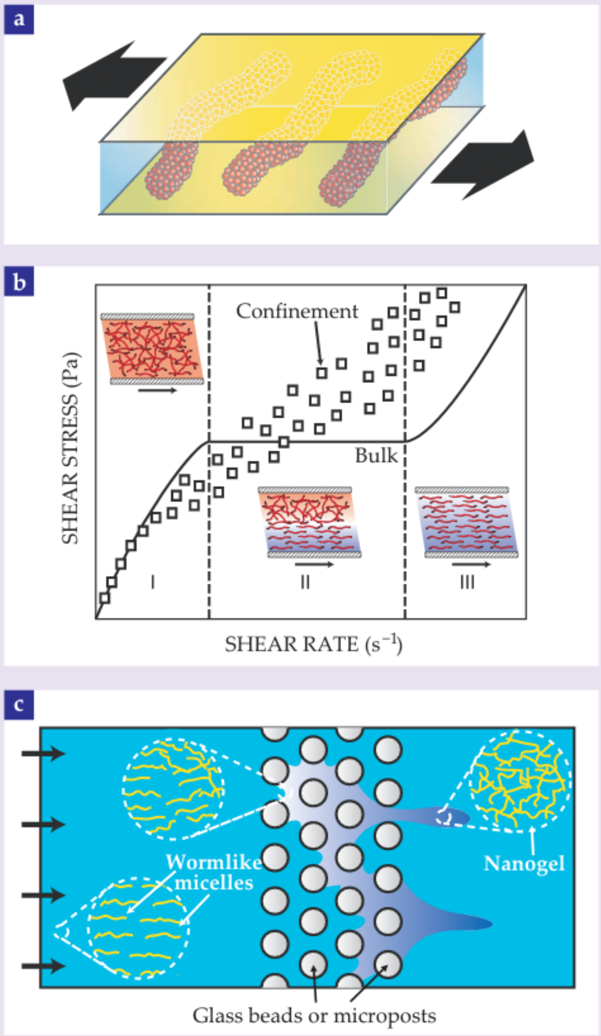


Figure 4. Confinement effects in wormlike micelle solutions. **(a)** Under bulk shear, wormlike micelles tend to align in the shearing direction, but when confined to an ultrathin film like that depicted here, they align perpendicular to the shearing direction and "logroll." (Adapted from ref. 13.) **(b)** The flow curves for bulk (solid line) and confined (squares) wormlike micelle solutions show qualitative differences. The bulk-shear flow curve first increases, corresponding to randomly arranged micelles, then plateaus, indicating the emergence of an oriented phase near the moving wall, and then resumes increasing after all micelles have joined the oriented phase. By contrast, the flow curve of a confined micelle solution grows continually and has no discernable plateau regime. (Adapted from ref. 13.) **(c)** A stable nanogel is formed by feeding a wormlike micelle solution through a microchannel packed with either glass beads or microposts. The micelles, subjected to extreme extensional and shear flow as they move through the restrictions, entangle permanently, forming a gel that could potentially be used as a biocompatible porous scaffold. (Adapted from ref. 15.)

inner droplet of water surrounded by an oil droplet immersed in water. If the oil contains surfactants and is allowed to evaporate, it leaves behind a spherical surfactant bilayer, a versatile structure analogous to the colloidosome. If diblock copolymer is used instead of surfactant, the structure is known as a polymersome (see figure 3).

Diblock copolymers are polymers that contain two chemically different polymer chains, or blocks, joined at their ends (see the article by Frank Bates and Glenn Fredrickson in PHYSICS TODAY, February 1999, page 32). If one of the blocks is hydrophobic and the other hydrophilic, the copolymer acts as a surfactant that can be flexibly engineered to produce polymersomes that fit desired applications. For example, polymersome membrane thickness can be tuned by varying the degree of polymerization of the constituent block molecules; membrane permeability can be adjusted by selecting the hydrophobic block according to glass transition temperature or fluidity. By altering the chemical properties of individual blocks, it is possible to prescribe the specific conditions that would trigger release of an encapsulated fluid, an attractive feature for targeted drug delivery applications.[10] Furthermore, quantum dots can be encapsulated in the hydrophobic region of a polymersome's bilayer shell to produce particles that could be used for in vivo fluorescence imaging.[9]

Microdroplet technology opens possibilities for a host of

by Pierre-Gilles de Gennes in his 1991 Nobel lecture, the classically inspired, eponymous colloidal particles possess different chemical properties on their two hemispheres. If one hemisphere of the Janus particle is engineered to be polar and the other nonpolar, the resulting particles might behave like surfactant molecules, adsorbing at a water–air interface. If, instead, the two hemispheres are given different surface charges, the particles will orient in response to an electric field. The potential applications for Janus particles are numerous (see, for example, the Quick Study tutorial by Steve Granick, Shan Jiang, and Qian Chen, PHYSICS TODAY, July 2009, page 68).

Other amphiphilic phenomena

The block copolymers discussed above, like lipids and other surfactants, are amphiphilic—they contain both hydrophilic and hydrophobic groups. (Those versed in etymology will recognize "amphi" as Greek for "both sides" and "philos" as Greek for "love" or "fondness for.") When dissolved at large concentration in a polar solvent, amphiphilic molecules tend to assemble into spherical aggregates called micelles; the hydrophobic ends orient inward, leaving the hydrophilic ends exposed to the solvent, a formation entropically preferable to unique microgel-derived materials, perhaps the most fascinating of which are monodisperse Janus particles.[11] Named

an unassociated solute. A micelle can be thought of as an oil droplet in a polar coat. The aggregates are constantly breaking up and reforming at millisecond time scales and exchanging individual molecules with the solvent at microsecond time scales. Micelles are good model systems for studying nonequilibrium self-assembly and nonlocal rheology under confinement and flow.

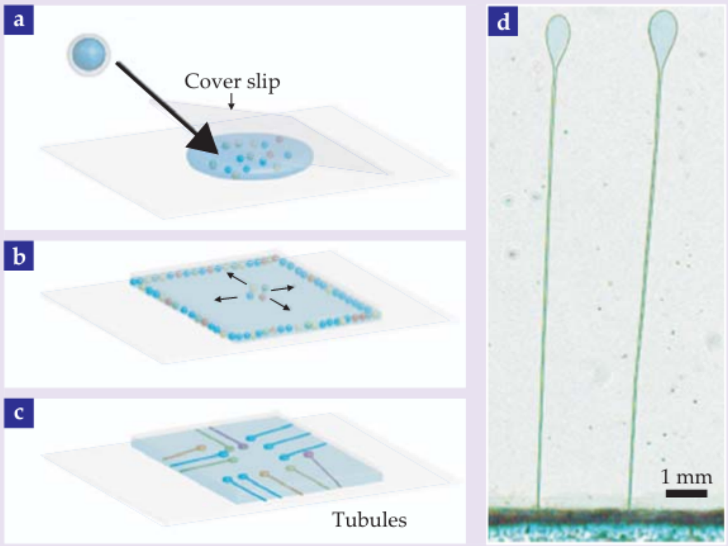


Figure 5. Coaxed by confinement, lipid vesicles assemble into tubules. **(a)** The lipid vesicle solution is first confined to the thin film between a glass plate and a square cover slip. **(b)** In a process similar to coffee-ring formation, evaporation of the confined liquid causes an outward capillary flow, which carries the vesicles toward the edge of the cover slip. **(c)** There, the vesicles organize into inward-protruding tubules of up to 1 cm or more in length, each capped by a compartmentalized head. **(d)** A microscopy image shows lipid tubules entrapping a blue aqueous dye. (Adapted from ref. 16.)

In systems containing charged micelles, the addition of counter-ions causes electrostatic screening, which decreases the Debye screening length—the distance over which a charge can be "felt"—and can lead to the formation of long, wormlike micelles. Under various conditions, micelles can also form cubic and hexagonal phases, vesicles, lamellar sheets, disks, toroids, and networks. When sheared, wormlike micelles can stretch, break, entangle, and disentangle. Very long wormlike micelles, with contour lengths as large as several microns, can entangle with one another even at low volume fractions and form a gel-like phase.[12]

When a wormlike micelle solution is sheared in bulk, the micelles tend to align their long axes in the flow direction to reduce drag.[12] In 2005 Athanassios Panagiotopoulos of Princeton University and his then postdoctoral student, Gaurav Arya, now at the University of California, San Diego, found that wormlike micelles behave differently under narrow confinement.[13] Their simulations showed that when the distance between the shearing plates is comparable to the micelle diameter, the micelles, rather than align parallel to the shearing direction, align perpendicular to it and "logroll" about their long axes (see figure 4a). If the film thickness is increased to two or more micelle layers, the micelles sandwiched in the middle layer tend to align parallel to the shearing direction, while the micelles nearest the walls align either parallel or perpendicular to it.

Many bulk wormlike micelle solutions exhibit shear banding, a nonlinear rheological phenomenon that has important implications for drag reduction in pipe flows and oil recovery. Such solutions are described by three shear regimes: At small shear rates, the micelles arrange randomly and isotropically; at large shear rates they orient in the shear direction; and in between, at moderate shear rates, the two phases coexist, their interface forming a shear band (see figure 4b). That shifting morphology is reflected in the so-called flow curve, which shows shear stress as a function of regime, and then resumes increasing in the ordered regime. Such behavior is thought to be analogous to an instability found in polymer-melt extrusions at high temperature.

By contrast, the flow curve of a confined micelle solution suggests qualitatively different rheology, especially at high shear rates. Peter Olmsted of the University of Leeds, UK, along with Chloé Masselon and Annie Colin of CNRS in France, found that the flow curve for a confined system, rather than plateauing at moderate shear rates, grows continuously and exhibits larger fluctuations than a comparably sheared bulk system.[13]

Another recently observed phenomenon of wormlike micelles is irreversible gelation under confinement. When a wormlike micelle solution is sheared, it undergoes a liquid-to-gel phase transition, evidenced by a viscosity jump at a critical shear rate. That jump corresponds to the formation of flow-induced structures. But those structures are impermanent—the gel disintegrates within seconds after the cessation of flow.[14] By pumping the same wormlike micelle solution through a microchannel filled with randomly packed particles, our group, as part of a broad collaboration of research teams, produced shear and extensional flow rates high enough to form a permanent micellar gel.[15] The extreme and rapid straining of the wormlike micelles—extension rates were on the order of $10^6\ s^{-1}$, meaning that a stretching parcel of fluid doubles in length about once every microsecond—produced a gel that stayed stable for months (see figure 4c). The technique is a promising new approach for synthesizing biocompatible porous scaffolds and biomolecular encapsulations at ambient conditions.

With one polar head and two hydrophobic tails, phospholipids are another class of amphiphilic molecule. Self-assembly of phospholipids in an aqueous solution can generate lipid vesicles—spherical, bilayered lipid membranes that enclose an aqueous core.[16] By encapsulating functional molecules in the core and tailoring the properties of the membrane, one can make vesicles that act as biomimetic devices. Under certain conditions, lipid vesicles can further organize into structures such as tubular networks. Our group recently used a simple confinement-enhanced self-assembly method to form long, oriented lipid tubules in a thin film (see figshear rate. The flow curve for the bulk micelle solution increases in the unordered regime, plateaus in the two-phase

ure 5).[16] Lipid tubules with a variety of properties and functionalities can be constructed by combining appropriate vesicle building blocks. Most important, the method is inexpensive, is simple, and does not rely on external flow, temperature control, or catalyzing agents—highly desirable traits for a composite biomaterials fabrication technique.

Outlook

We have seen how even the simplest complex fluids can give rise to unexpected self-assembled morphologies that differ significantly from the morphologies of the bulk phase. The opportunities to synthesize more sophisticated materials with unique optical, rheological, and mechanical properties are truly exciting.

New technologies in small-angle scattering and microscopy will allow microstructural transitions in confined complex fluids to be probed with improved spatiotemporal resolution. Those insights will help shed light on the underlying mechanisms of self-assembly and lead to the design of new materials that take advantage of structural hierarchies. Computationally, new simulations are revealing unique morphologies in confined complex fluids. Some of them have been verified experimentally; others have yet to be observed. Experiments and simulations will continue to complement each other and serve to motivate and elucidate new structures.

One challenge going forward will be to integrate interfacial interactions, symmetry breaking, structural frustration, and confinement-induced entropy loss to manipulate and fine-tune supramolecular structure. For example, the assembly of asymmetric, chiral supramolecular structures has attracted attention due to its implications for the design of biomimetic materials such as DNA chains and enzymes. The combination of spatial confinement and manipulation of the intrinsic shape and associated curvature of self-assembling molecules has found some success, but more work is required. In addition, further research is needed to understand how confinement and external fields—flow fields, electric fields, and so on—can be coupled to tune the microstructures of complex fluids, both reversibly and irreversibly.

Another important yet unresolved question is how to make structures whose functional features span length scales from the molecular to the macroscopic—an essential step in the development of biomimetic materials and bio-inspired systems. The answer rests on the ability to combine multiple systems that, aided by confinement and other means, can act coherently over several length scales to provide integrated, multifunctional components. Many living systems, such as plants and nacre shells, do just that, controlling the composition, spatial position, and function of structures on more than one length scale (see, for example, the article by Eric Baer, Anne Hiltner, and Roger Morgan, PHYSICS TODAY, October 1992, page 60). So far, promising results using solution-to-gel techniques have incorporated top-to-bottom and bottom-to-top synthetic approaches. Researchers have coupled external fields with confinement to achieve controlled self-assembly of hybrid inorganic–organic structures.[2,17]

Finally, mass production of self-assembled materials will require a deep understanding of the interfacial behavior and forces needed to assemble, detach, and transfer nanocomponents. Though researchers have already made substantial progress in those areas, exciting work remains to successfully transfer knowledge from the lab into real technology. Perhaps then the ultimate freedom in confined complex fluids—the ability to use them to synthesize designer materials with exotic morphologies—will be in sight.

References

1. W. M. Gelbart, A. Ben-Shaul, *J. Phys. Chem.* **100**, 13169 (1996); O. E. Shklyaev, A. Q. Shen, *Mech. Res. Commun.* **36**, 121 (2009).
2. J. Fan et al., *Chem. Mater.* **20**, 909 (2008).
3. A. D. Rey, M. M. Denn, *Annu. Rev. Fluid Mech.* **34**, 233 (2002); M. C. Choi et al., *Proc. Natl. Acad. Sci. USA* **101**, 17340 (2004); T. Bellini et al., *Science* **294**, 1074 (2001).
4. M. Alcoutlabi, G. B. McKenna, *J. Phys. Condens. Matter* **17**, R461 (2005); M. D. Graham, *Annu. Rev. Fluid Mech.* (in press).
5. M. J. Fasolka, A. M. Mayes, *Annu. Rev. Mater. Res.* **31**, 323 (2001); J. Y. Cheng, A. M. Mayes, C. A. Ross, *Nat. Mater.* **3**, 823 (2004).
6. E. Kumacheva et al., *Phys. Rev. Lett.* **91**, 128301 (2003).
7. N. V. Dziomkina, G. J. Vancso, *Soft Matter* **1**, 265 (2005).
8. H. Löwen, *J. Phys. Condens. Matter* **21**, 474203 (2009); C. B. Hancock, G. Zografi, *J. Pharm. Sci.* **86**, 1 (1997).
9. A. S. Utada et al., *MRS Bull.* **32**, 702 (2007).
10. E. Lorenceau et al., *Langmuir* **21**, 9183 (2005).
11. E. Tumarkin, E. Kumacheva, *Chem. Soc. Rev.* **38**, 2161 (2009).
12. P. Boltenhagen et al., *Phys. Rev. Lett.* **79**, 2359 (1997); E. Cappelaere et al., *Phys. Rev. E* **56**, 1869 (1997); M. Vasudevan et al., *J. Rheol.* **52**, 527 (2008).
13. G. Arya, A. Z. Panagiotopoulos, *Phys. Rev. Lett.* **95**, 188301 (2005); C. Masselon, A. Colin, P. D. Olmsted, *Phys. Rev. E* **81**, 021502 (2010); J. F. Berret, in *Molecular Gels: Materials with Self-Assembled Fibrillar Networks*, R. Weiss, P. Terech, eds., Springer, Dordrecht, the Netherlands (2006), p. 667.
14. C. H. Liu, D. Pine, *Phys. Rev. Lett.* **77**, 2121 (1996).
15. M. Vasudevan et al., *Nat. Mater.* **9**, 436 (2010).
16. Y. C. Tan et al., *Lab Chip* **8**, 339 (2008); E. Elson et al., *Annu. Rev. Biophys.* **39**, 207 (2010). Movies showing tubule formation can be seen at http://microfluidics.me.washington.edu/video1 and http://microfluidics.me.washington.edu/video2.
17. I. Soten, G. A. Ozin, *Curr. Opin. Colloid Interface Sci.* **4**, 325 (1999); Y. Wu et al., *Nat. Mater.* **3**, 816 (2004); C. J. Brinker, D. R. Dunphy, *Curr. Opin. Colloid Interface Sci.* **11**, 126 (2006); S. Mann et al., *Chem. Mater.* **9**, 2300 (1997); A. Sellinger et al., *Nature* **394**, 256 (1998). ■

We thank Russell Todres of RWTH Aachen University, Germany, for his careful reading of the manuscript and valuable suggestions.