STRUCTURED FLUIDS

Fluids containing polyatomic structures manifest a wide variety of mechanical responses, and they can exhibit numerous forms of self-organization.

Thomas A. Witten

Water, gasoline, pancake syrup, mucus, salad oil, cornstarch-and-water paste, Silly Putty, liquid dishwashing soap, egg white, glycerin, Vaseline, ketchup, model airplane glue, paint, toothpaste—this motley list of substances seems to defy scientific classification. Water, gasoline, salad oil and glycerin are clearly liquids. The other substances, strictly speaking, are also liquids, since they all flow on the application of stress. But the name "liquid" hardly captures the variety of behavior in these substances. The substances differ from one another in their mechanical responses almost as much as they differ from solids. In the first place, they differ enormously from one another in viscosity, the quantitative measure of a liquid's flow response. Furthermore, many of them have striking properties whose description requires variables besides viscosity. Syrup becomes sticky as it dries. Liquid dishwashing soap has the same consistency as syrup, but it does not become sticky on drying. Mucus, egg white and model airplane glue are springy and rubbery. Silly Putty and cornstarch paste flow on a tilted surface but shatter like a brittle solid on sudden impact. Dishwashing soap in water easily forms masses of long-lived foam. Even the simplest flow properties of toothpaste are qualitatively unliquid-like: It comes out of its tube as a plug rather unlike an ordinary liquid, which flows fastest in the middle of the opening.

Many substances in the above list are nowadays called complex fluids or structured fluids. They owe their distinctive and unusual properties to large, polyatomic structures whose size is many times that of, for example, a water molecule. Fluids containing polyatomic structures manifest a wide variety of mechanical responses, and they can exhibit numerous forms of self-organization. By contrast, the main difference in mechanical response among small-molecule, simple liquids, such as water, gasoline, salad oil or glycerin, is the quantitative difference in their viscosities.

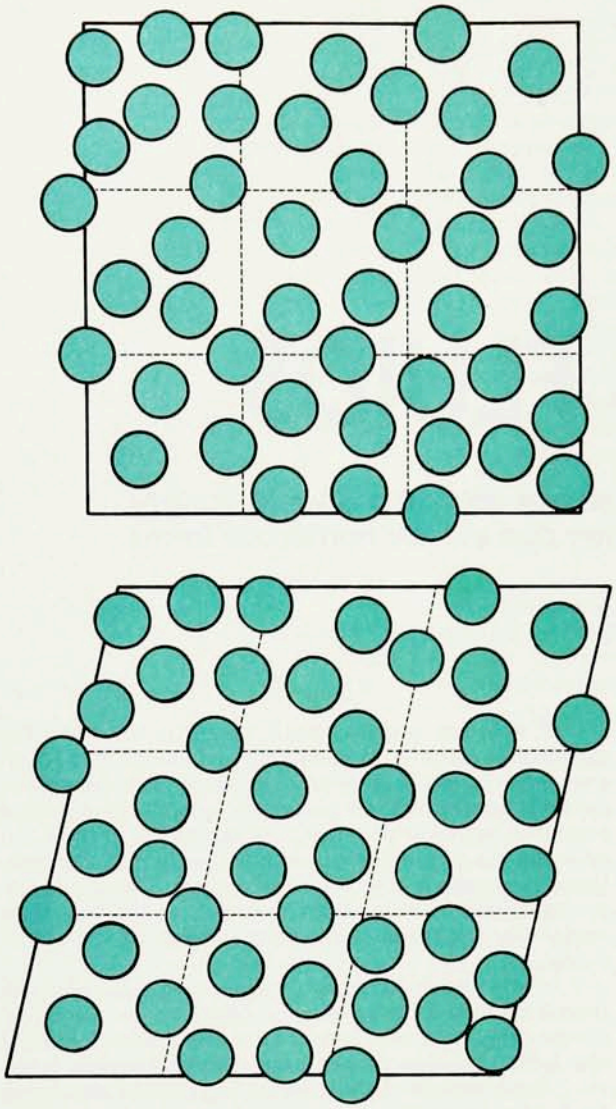
Thomas Witten is a professor in the James Franck Institute and the physics department of the University of Chicago.

It was not possible until recently to study the microscopic basis of complex-fluid behavior. Now, however, experimental probes such as electron microscopy and dynamic scattering allow us to study complex fluids with a resolution suited to the distinctive structures in them. In addition, the present-day sophistication in chemical synthesis has made it possible to make fluids whose polyatomic constituents are precisely known. Such fluids serve as models for the types of behavior possible in structured fluids.

In this article I discuss a variety of structured fluids from a microscopic point of view. I explore how the fluids' special properties arise from their molecular structures. I also highlight some properties of current scientific interest.[1] Some aspects of the complex behavior of structured fluids have been discussed in PHYSICS TODAY in the articles by Pierre-Gilles de Gennes, June 1983, page 33; by R. Byron Bird and Charles F. Curtiss, January 1984, page 36; and by Tom C. Lubensky and Philip A. Pincus, October 1984, page 44.

Simple versus structured

The fluids in the motley list above are very similar at the scale of individual atoms and bonds. Most consist of light atoms like carbon, hydrogen and oxygen held together by ordinary covalent bonds in permanent molecular arrangements. In *simple* fluids, these more or less compact molecules interact strongly with their immediate neighbors only. The length scales at which significant structure and dynamics occur are the size of a molecule—a few angstroms. The interaction energy of each molecule is on the order of the thermal energy kT, which at room temperature is on the order of 10^{-1} eV. The interaction energy cannot be much smaller, or the liquid would evaporate. It cannot be much bigger, or the liquid would solidify. The time scale τ of the molecular motion is comparable to the time interval between successive collisions of a molecule with its neighbors. For molecules of mass 20 amu having kinetic energy on the order of the thermal energy, this time is on the order of 10^{-12} sec at room temperature when the intermolecular separation in the fluid is 2 Å.



Molecules in an isotropic liquid (top) are pushed together along the diagonal from the upper left to the lower right corner of the volume when the liquid is suddenly subjected to a shear deformation (bottom). **Figure 1**

The characteristic time and energy scales discussed above are the features that give simple fluids their similar flow behavior. Deforming a fluid causes energy to be stored in it and subsequently dissipated. For example, figure 1 shows how a 20 % step strain disturbs the isotropic, equilibrium arrangement of atoms in a fluid. This disturbance costs free energy and requires work. For small strains the work per unit volume w is proportional to the square of the strain γ. The proportionality constant G_0—the short-time shear modulus—is roughly the free-energy density in the fluid. This free energy is in large part entropic (it would be entirely so in a hard-sphere fluid). Thus the modulus G_0 is of order kT per atom.

The fluid "forgets" the distortion imposed on it almost as soon as the distortion is applied. In a time on the order of the interval τ between successive molecular collisions, the initial anisotropy relaxes and the fluid regains its equilibrium state. At this point the work done on the fluid has been dissipated; the average dissipation rate $\dot{w}$ is roughly w/τ. The average strain rate $\dot{\gamma}$ producing this dissipation is of order γ/τ. Thus the dissipation rate may be written $\dot{w} \simeq G_0 \tau \dot{\gamma}^2$. This is just the dissipation law for a viscous liquid with viscosity $\eta \simeq G_0 \tau$. The above estimates for G_0 and τ give us reasonable values for the viscosity: A value on the order of $kT/(2\ \text{Å})^3$ for the modulus G_0 gives a value of roughly 10^{-2} for $G_0\tau$ in cgs units (poise). This is in the range of viscosity values observed for many light liquids, such as water.

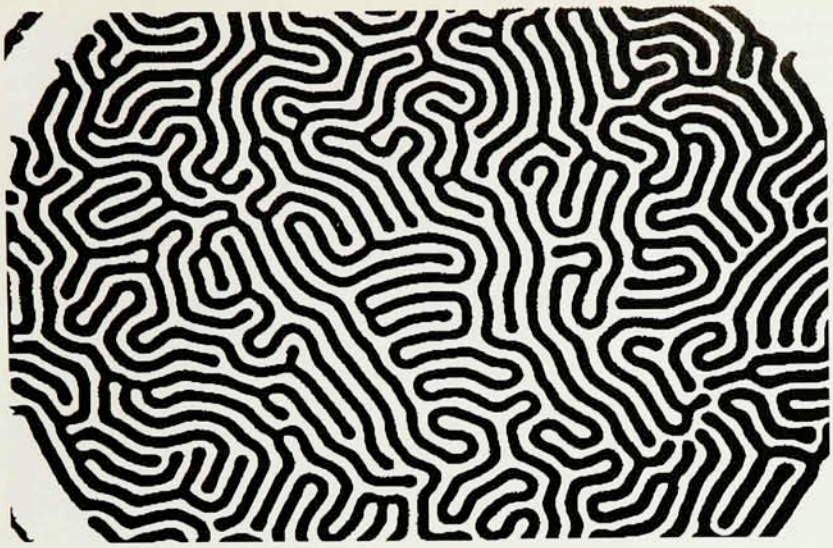
Let us contrast the behavior outlined above for simple liquids with that of a typical complex liquid. Consider, for example, polystyrene cement, a clear, viscous, springy liquid used to glue toy plastic models together. Polystyrene cement is usually a solution of long, flexible-chain molecules—polymers—in a small-molecule solvent, such as toluene. At length scales of a few angstroms, the resulting fluid resembles a simple liquid. The interaction energy and relaxation time of the solvent molecules and of the flexible units of the polymer are of the same order as in simple liquids. The distinctive features of the glue appear at larger length scales on the order of 100 Å, which is the average size of the polymer coil.

Bulk, tenuousness and flexibility

When discussing the properties of a complex fluid, it is useful to imagine that the large structures in the fluid are *indefinitely* large. Various aspects of the largeness of the structures lead to several types of scaling behavior in this limit. Thus in our polystyrene cement example, the viscosity should grow as a power of the polymer size. One obvious aspect of the largeness of these polymers that should produce scaling behavior is their sheer *bulk*, as measured, for example, by the mass of the polymer relative to that of a solvent molecule. A fluid containing bulky objects has relaxation processes whose characteristic time scales are much longer than the τ values discussed above for simple liquids. This has two effects. First, it tends to increase the viscosity, which grows with the relaxation time, as we have seen. But more importantly, it makes the fluid more sensitive to flow. Shear rates $\dot{\gamma}$ larger than the relaxation rate τ^{-1} cause substantial distortion to build up before the fluid can relax; accordingly, large perturbations occur. For example, the fluid viscosity may depend on the shear rate.

The molecular bulk also affects the interaction energy of a polymer. The interaction may be with the surrounding solvent or with external perturbations, such as the presence of a surface or an electric field. The molecular bulk magnifies the effect of these perturbations. Effects arising from this magnification occur very widely in structured fluids, as we shall see.

The molecular bulk alone cannot account for the high viscosity of polystyrene cement. Nor can it account for the



Labyrinthine pattern formed by a drop of ferrofluid between two horizontal glass plates about a millimeter apart, when the plates are inserted between the poles of a magnet, normal to the magnetic field. As the magnitude of the field increases from zero, the initially circular droplet breaks into spikes, which elongate and branch out to fill the area between the plates. The thickness of the ferrofluid channels (black) is comparable to the spacing between the plates.[3] (Courtesy of R. E. Rosensweig, Exxon Research and Engineering Company. **Figure 2**

cement's springiness. To understand these properties we have to invoke two further scaling properties of polymer chains. The first is that the polymers are *tenuous*. Each polymer chain, rather than collapsing upon itself, spreads out to pervade a volume much larger than the monomers themselves displace. Thus many chains share the same volume, and each chain can exert forces directly on indefinitely many others. The second scaling property is the *flexibility* of polymer chains: they are not quenched into some particular configuration but are free to explore an ensemble of configurations. The randomness in the configuration of each chain amounts to thermodynamic entropy, which may serve as a reservoir for heat and work.

Bulk, tenuousness and flexibility provide a way to account for the disparate properties seen in structured fluids. Many such fluids have only a subset of these three characteristics. Colloids, such as cornstarch-and-water paste, contain bulky particles that are neither tenuous nor flexible. Consequently, colloids lack the springiness of polymeric fluids, such as polystyrene cement, mucus or egg white. Colloidal aggregates, by contrast, consist of structures that are bulky and tenuous but not flexible. The rest of this article explores the consequences of bulk, tenuousness and flexibility in colloids, colloidal aggregates and two flexible structures, namely, polymers and surfactant assemblies. The article ends with a survey of a higher level of molecular organization, called association.

Colloids

Colloids are fluids containing compact, polyatomic particles suspended in a liquid. The particles are bulky, but they are neither tenuous nor flexible. A familiar example is black ink, which is made from colloidal carbon. Colloidal particles give distinctive physical properties to fluids. Thus the colloidal form of the carbon in black ink is what makes it absorb light so strongly. These distinctive physical properties are often incidental. Instead, the colloidal particles are often present to give the fluid some *chemical* property of interest. Examples are the cells in blood, manufactured particles that adsorb molecules on their surface, the light-sensitive grains in photographic film, and the pH-buffer particles in detergent motor oil. In other cases, such as paint and rubber cement, the colloidal particles produce the desired property not in the fluid but in the solid that forms when the solvent dries.[2]

But there are also colloids that are important for the *physical* properties they impart to fluids. One such colloid is xerographic toner. The 100-micron carbon-black-and-plastic particles in this black, flowing powder are large enough to respond strongly to gravity and to the electrostatic fields that define the xerographic image. They are also small enough to give a good image resolution. Another colloidal fluid of recent technological impact, called ferrofluid, is a suspension of 100-Å ferromagnetic particles. The size R of particles in a ferrofluid is chosen to be large enough that each particle has strong magnetic order but small enough that each particle has only a single magnetic domain. Application of a moderate magnetic field B to such a fluid can significantly alter the fluid's energy. The magnetic particles, each with a magnetic moment μ that varies as the particle volume R^3, begin to align when the field energy μB becomes comparable to the thermal energy kT. At room temperature, the alignment occurs at fields on the order of 10^3 gauss.

In practice, application of a magnetic field on the order of 100 gauss to a droplet of ferrofluid of radius 1 mm can cause the droplet's magnetic energy to be comparable to its surface energy. The magnetic energy therefore can have large, controllable effects on the flow and interfacial properties of the fluid.[3] (See figure 2.) These effects have been used in vacuum seals and bearings: A small amount of a ferrofluid suspended between magnetized bushings forms the contact between the moving and stationary parts.

Scientifically, colloids are useful as models of fluids and solids. This is because colloidal particles in colloids interact with one another in qualitatively the same way as small atoms and molecules do in normal fluids and solids. But the colloidal particles' larger size makes it more convenient to perturb and visualize their cooperative motions than those of small atoms or molecules. I noted above in discussing ferrofluids that the energy of a colloidal particle in an external field typically varies as the volume of the particle, and that at room temperature in moderate external fields this energy can be much greater than the thermal energy. The interaction energy can thus dominate the effects of translational entropy. As a further example of this effect, consider micron-size dielectric particles in a static electric field on the order of 100 V/cm. The interaction energy per particle is several times the particle's thermal energy at room temperature. Similarly, the interaction energy of colloidal particles with light can be on the order of the thermal energy when the light intensity is tens of watts per square centimeter.

Electron micrograph of an aggregate of 35-Å-radius particles of colloidal silica in water, formed under so-called diffusion-limited conditions. In diffusion-limited aggregation, small aggregates in Brownian motion stick together on collision to form larger aggregates. The hydrodynamic drag such an aggregate presents to the flow of the fluid in which it is immersed is comparable to that presented by a solid sphere of the size indicated by the circle. The average fraction of the sphere volume occupied by the aggregate particles is only a few percent, and it becomes progressively smaller with increasing aggregation. The fraction is expected to vary as the -1.3-rd power of the sphere radius. This "universal" scaling behavior, which is expected to hold for diffusion-limited aggregates, has been verified for a variety of materials. (From ref. 10.) **Figure 3**

Such intensities occur in an ordinary slide projector. Exploiting this effect, a recent experiment used standing light waves to induce crystalline order in a colloid.[4,5]

The magnified response of colloids to external fields shows up in a broader context. The effect of flow on a colloid also is enhanced relative to that on a small-molecule fluid. For example, the shear rates $\dot{\gamma}$ needed to significantly perturb a molecular fluid are of order τ^{-1}—that is, they may have to be as large as $10^{12}\,\mathrm{sec}^{-1}$. To obtain such shear rates in the laboratory requires heroic measures. A colloid, by contrast, can already be significantly perturbed at shear rates on the order of 10^2–$10^3\,\mathrm{sec}^{-1}$, which may readily be implemented in the lab. Taking advantage of this experimental convenience, physicists have recently observed the enhancement of diffusion on the application of shear. In shear flow they have discovered states of partial crystalline order, such as mutually uncorrelated strings of particles flowing along the streamlines.[6] Furthermore, the crystallization of colloidal fluids and the liquefaction of colloidal crystals have been observed under shear.

Colloidal aggregates

The interaction energy of two colloidal particles in a given solvent also is magnified because of their bulk. Consequently, small changes in the solvent can have a large effect on the interaction energy. This makes it possible to change the interaction between two colloidal particles abruptly from an effective hard-core repulsion to an attraction whose strength is many times kT. With such an attraction the particles must flocculate. This effect is exploited to sense small changes in a solution or to determine the presence or absence of a biological antigen—as in certain early pregnancy tests.

The enhancement of particle–particle interaction between colloids makes possible a form of self-organization not seen in simple molecular liquids, namely, the irreversible random aggregation of the particles. Aggregates such as the one shown in figure 3 form when the attraction between two particles in contact is so strong that they must stick together at the instant of their contact. An important consequence of the strong attraction is that colloidal particles cannot explore which of the possible contact configurations maximizes the amount of contact. Colloidal aggregates are therefore tenuous; they are unlike small-molecular precipitates, which form a dense particle phase. The average particle density within a radius r of a given particle decreases as r increases, as a negative power of r.[7] Thus the average density in an arbitrarily large aggregate becomes arbitrarily small. These aggregates are fractals.

Aggregated colloids show all the enhancement effects discussed above for dispersed colloids. In addition, they have properties arising from their tenuous structure. Even though a tenuous aggregate occupies an arbitrarily small fraction of the volume it pervades, it transmits forces efficiently thoughout that volume. An aggregate in a shear flow screens the surrounding solvent: The fluid is obliged to flow around rather than through the aggregate. The occluded volume is comparable to that pervaded by the aggregate, rather than to the much smaller volume actually occupied by it. This screening enhances viscosity: Since the flow is concentrated into a smaller volume, the viscous dissipation increases. With less than a percent of colloidal solid (by mass), one may readily reduce the unscreened volume to a small fraction of the total volume. The overall viscosity can easily be doubled; to achieve a comparable enhancement of the viscosity in a dispersed colloid requires a much larger fraction of colloidal solids. (The enhancement of the viscosity of colloidal aggregates can also be understood using the estimate $G_0\tau$ that we obtained above for the viscosity. In this case the appropriate value of the modulus G_0 is kT per aggregate, and the appropriate relaxation time τ is the time required for an aggregate to move by Brownian motion over distances comparable to its diameter. For an aggregate of radius R, the relaxation time is given by the Stokes diffusion law: $\tau \simeq \eta R^3/kT$, where η is the solvent viscosity.)

The enhancement of the viscosity of a fluid by colloidal aggregates makes certain aggregates valuable additives in food products such as ice cream. More generally, aggregates in a soft matrix like rubber make tough composite materials that can sustain large stresses. These composites are used in automobile tires and "superballs." How the composites attain their distinctive behavior is ill understood, however. The relationship between the fractal, tree-like structure of an aggregate and its detailed screening behavior and mechanical deformability is just beginning to be studied.

Polymers

Another way of producing a tenuous, polyatomic structure is to link small molecules together into a flexible chain to form a polymer. The successive bonds between the small molecules, or monomers, making up a flexible chain have

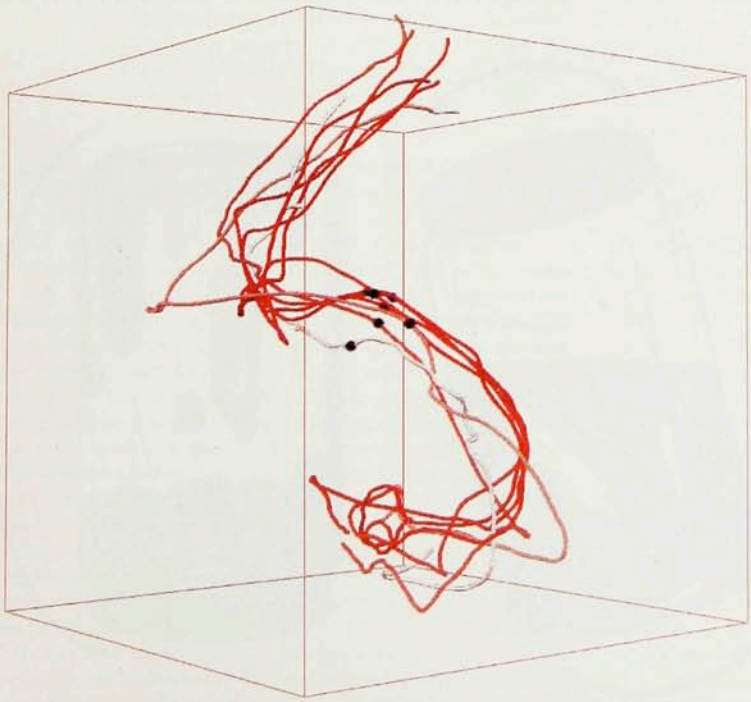
some randomness in their relative directions. Thus the directional correlation between bonds more than a few bond lengths apart becomes negligible; accordingly, a long polymer has the statistical properties of a random walk. In some situations the statistical properties of a long polymer are similar to those of a self-repelling random walk. Like colloidal aggregates, such polymers have spatial scaling properties of a fractal. The average monomer density in a polymer of size R scales as $R^{-4/3}$. (The power for a simple random walk is -1.) Chains whose pervaded-volume fraction is a tenth of a percent or less may be readily produced. In a solution of such polymers , there is room for a thousand chains in the volume pervaded by one chain.

Flexibility, the additional feature of a tenuous polymer chain, gives the chain properties that a tenuous aggregate does not have. The chain may be dramatically deformed by mild perturbations without permanent effects. Thus, the spontaneous thermal fluctuations in the end-to-end distance of a flexible polymer may be as large as the average end-to-end distance. Consequently, externally imposed energies as small as the thermal energy kT are sufficient to distort the shape of a polymer by factors of order unity.

Unlike rigid colloidal aggregates, polymers may be concentrated to volume fractions up to unity. In this solvent-free limit, called the melt state, chains interpenetrate and entangle strongly. Each chain interacts directly with hundreds of others, and the forces thus communicated can produce large, reversible deformation in each chain. Over short times this liquid reponds elastically to mechanical distortions, like a rubber band. Over longer times, the chains disentangle and forget their initial distortions. The relaxation times for disentanglement can easily be on the order of seconds. By mixing polymers of different lengths and architectures, one may produce liquids that behave like a tough rubber on short time scales, like a weak rubber on longer time scales and like a flowing latex at yet longer times.[8] This power to control the storage of energy over time allows one to adapt polymer solutions to the needs of a many-step manufacturing process, such as the assembly of a car tire. Similarly, many structured fluids used around the house, such as pancake syrup, shampoo and paint, are deliberately thickened to keep them from flowing too much during application. The polystyrene cement discussed above functions in the same way: Its viscosity is high enough that it holds its shape and does not flow away while it is being applied to the plastic pieces to be joined together. Once it has been applied, however, the solvent in the glue swells the plastic parts, which also consist of polymers. The chains in the two parts now become mobile and are free to entangle with one another. By the time the solvent evaporates, the chains have become fully entangled, welding the parts together.

The energy stored in a polymer when it is deformed has striking effects on a polymer fluid's flow properties. Elongating a chain produces spring tension along its length. This "normal stress" combines with other applied forces to accelerate each small volume of the fluid. The elastic energy stored in the polymer can easily exceed its kinetic energy, and this produces nonintuitive secondary flows and other hydrodynamic effects. One such effect of commercial importance is turbulent-drag reduction: Trace amounts of a polymer can substantially reduce the power required to push a turbulent fluid through a pipe, in spite of the small increase in viscosity due to the polymer.[9] Drag reducers are used in the Alaska oil pipeline. The polymers are thought to inhibit the nucleation of turbulent vortices in the fluid near the wall, but the detailed mechanism of drag reduction remains to be established.[10]

The deformability of a polymer has dramatic consequences when electrically charged species are attached along the polymer chain. Any nonzero linear density of the charge along a long enough chain is sufficient to stretch the chain from a random-walk configuration to that of a rigid rod, for which the end-to-end distance is proportional to the molecular weight. Polyelectrolytes, as such polymers are called, can be controlled in a fashion not possible for neutral polymers. When the electrostatic



Polymer in a melt in equilibrium is confined in its short-time dynamics to a contorted tube-like region because of the entanglements with other polymers in the melt (not shown). Configurations shown were obtained in a simulation at seven different times, at instants 1, 2, 4, 8, 16, 32 and 64 in arbitrary time units. Darker colors correspond to earlier times. The polymer was modeled as a chain of 400 slightly penetrable spheres connected by springs. The center of mass of the polymer does not move appreciably on the time scales shown, as indicated by the successive positions of the black dot, which stands for the chain's middle monomer. Each line represents the running average of the positions of 35 adjacent sphere centers along the chain.[20] (Courtesy of Gary Grest, Exxon Research and Engineering Company.) **Figure 4**

interaction along the chain is screened, by the addition of some salt or the presence of other chains, the polyelectrolyte chain shrinks in size. This alters fluid properties such as the viscosity and the modulus G_0. The decrease in size can lead to paradoxical effects, such as a decrease in the viscosity per chain with increasing concentration of chains.[11]. This effect has yet to be explained.

Another important consequence of the deformability of polymers is seen in their behavior near an interface. Even if the binding energy of a monomer to a surface or interface is much smaller than the thermal energy, the total binding energy of a polymer chain made up of such monomers may be several times the thermal energy. Then the polymer chain can increase its binding by flattening itself close to the surface with relatively little cost in deformation energy. This results in a zone of concentrated polymer loops that are much shorter than the chain as a whole. Being strongly bound, the chains in such a zone can be rinsed off the surface only with great difficulty, but they are easily displaced when incubated with a solution of similar polymers. A polymer's ability to interact arbitrarily strongly with an outside influence while retaining its mobility to explore configurations illustrates an important qualitative difference between structured fluids and conventional liquids and solids.

The deformability of polymers produces the unusual possibility of phase separation under flow. Phase separation in mixtures of simple liquids is diminished when the mixture flows. In certain polymer solutions, by contrast, application of shear seems to induce incipient phase separation in an otherwise miscible solution. The microscopic explanation for this seemingly contrary behavior is of great current interest.[12]

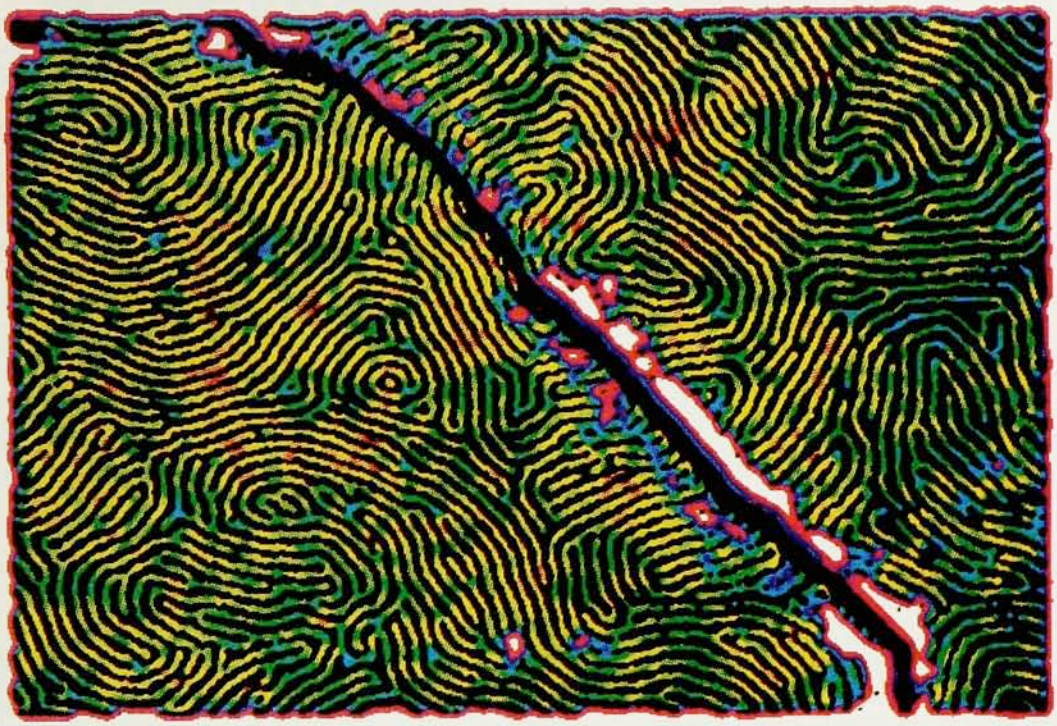
A polymer's ability to entangle and disentangle is a consequence of its tenuousness, it's flexibility and, in addition, its one-dimensional topology. (See figure 4.) Increasingly, chemical means of modifying this toplogy are being explored. One way to achieve such modification is cross-linking the chains. This is the process that turns a flowing latex into a solid piece of rubber, such as a rubber band. The crosslinks entrap most of the entanglements between the chains, so that the initial stress cannot relax or, put another way, so that the shear modulus G_0 cannot diminish. In addition to manipulating the topology by cross-linking, it is now possible to make large polymers in the form of stars, combs and loops. These changes in architecture strongly influence the processes by which an imposed stress is relaxed.[13] The entrapment of entanglements by cross-linking can be controlled by clever processing tricks. Polymer networks that have only a few trapped entanglements may be elongated a hundredfold without breaking; an ordinary rubber band, by contrast, can be elongated only about sixfold. These so-called unentangled networks provide a way to make polymer fibers whose strength approaches the limit set by their covalent bonds.[14]

Surfactant assemblies

Self-assembled surfactants are a further major category of structured fluid. A surfactant molecule is amphiphilic: It incorporates parts that if not connected would be strongly immiscible. A simple example is hexadecyl trimethylammonium bromide (CTAB)—an oily (that is, hydrophobic) 16-carbon chain with a bulky ammonium ion and a bromide counterion at one end. Isolated surfactant molecules cannot exist in either oil or water (except in extremely low concentrations). Instead, these molecules assemble themselves into micelles. A micelle is a configuration in which the molecules' immiscible parts clump together. In water, for example, the hydrophobic hydrocarbon tails will clump together, while the polar heads stay in contact with the water. In an oil the situation is inverted, so that the polar heads are all clumped together in the micelles.

Micelles typically have diameters on the order of tens of angstroms; they constitute a colloid-like polyatomic

Solutions of associating polymers have moderate viscosity values in a state of gentle flow (left). But such a solution gels under the application of shear, as when a jar containing it is rapidly inverted (right). **Figure 5**



Block copolymers made up of two immiscible polymer species joined end to end form an intricate pattern of domains when precipitated from a "good" solvent—one in which monomers of each species repel each other as well as monomers of the other species. This image was obtained from an electron micrograph of a drop of the copolymer solution after the solvent had evaporated. The polymer species show up as dark and light stripes in the electron micrograph. The stripes are about 400 Å wide. The micrograph was analysed to obtain the length of the interface per unit area between the two polymer species. This interface density is a measure of the interfacial energy driving the observed microphase separation. Red color indicates a greater-than-average interface density; blue and violet colors indicate smaller-than-average interface density. The color pattern shows that the variation in interfacial energy density are correlated over distances much larger than the stripe widths. The black diagonal stripe in the middle resulted from a fracture that was deliberately introduced in the copolymer droplet by shearing the microscope slides. Clearly, the copolymer assembly fractures preferentially normal to the cylindrical regions. The copolymer weighed 47 000 amu. (Micrograph courtesy of C. Henkee and E. N. Thomas, Univ. of Mass., Amherst.[21] The color image processing was done by Mark Gannon, University of Chicago.) **Figure 6**

species in their own right. Furthermore, a micelle-containing fluid shows interfacial properties unlike anything discussed above. Any water–oil interface clearly forms a very favorable environment for a surfactant; at the interface the molecule's polar head can be in water and the hydrophobic tail can be in oil. Accordingly, surfactants assemble readily at these interfaces. The assembly's energy is lower than that of a random dispersion of surfactants in either oil or water. The lowering of the energy amounts to a lowering of the interfacial free energy, or the interfacial tension. Surfactants thus make water and oil more nearly miscible, promoting emulsification. In a similar fashion, they make water and air more nearly miscible, stabilizing foam. Surfactants may also adsorb strongly to solid surfaces and thereby affect their wetting properties. The action of detergents, which among other things reduce the adhesion of oily molecules to glass-like surfaces, is an example of these effects.

In certain conditions a surfactant can reduce the interfacial tension nearly to zero, allowing the interfacial area to grow spontaneously. The result is a microemulsion—a thermodynamically stable mixture of oil, water and surfactant that is full of fluctuating oil–water interfaces. The entropy of the fluctuating interfaces may be regarded as the force that drives this mixing.[15] To gain the entropy, the interfaces must be flexible. The flexibility of any surface is characterized by its bending modulus, which has the dimensions of energy. Good microemulsions should have bending moduli of order kT, so that their interfaces fluctuate readily. The interfaces in both micelles and microemulsions may be spherical, or they may have the topology of a line or plane. These surfactant-coated interfaces are polyatomic structures that bear many resemblances to the structures discussed above. For example, CTAB forms flexible, wormlike linear micelles in water doped with certain cosolvents.[16] These micelles become entangled and raise the viscosity of water in much the same way polymers do. But unlike polymers, the micelles can break and re-form themselves.[17] Wormlike micelles are used to thicken some shampoos.

Surfactants may also assemble in a planar topology. These fluctuating sheets may form ordered lamellar

structures, even at very low concentrations (volume fractions on the order of or less than 1%). (See PHYSICS TODAY, August 1989, page 17.) The appearance of long-range order in such a dilute system is a striking property of fluctuating surfactant layers.

Association

The broad range of behavior discussed above is augumented even further when the extended structures responsible for it are made to associate. The cooperative, long-lived adsorption of a polymer to a surface discussed above is an example of association of structures. Many varieties of association occur in structured fluids. For example, silica colloidal aggregates in water may be made to associate with one another via hydrogen bonds. The result is a type of gel network whose links may be broken and readily reformed. Such a "network fluid" holds its shape in quiescent conditions but flows under sufficiently strong shear. Furthermore, on removal of the strong shear, the network maintains the shape it had at the instant the shear was removed. These associating aggregates are used to keep paint from running before it dries.

One can make polymers associate by attaching immiscible chemical groups sparsely along the chains. Like surfactants, these groups assemble themselves into micelles and effectively provide cross-links between the polymers. The cross-links are not permanent; they have a finite lifetime on the order of seconds. Such a polymer solution shows a new form of response to shear, namely, shear-induced reversible gelation. Reversible gelation, of which figure 5 shows an example, becomes possible because the network topology, being labile, is free to respond to the state of flow. The microscopic mechanism responsible for shear-induced gelation remains an unsolved puzzle.[18]

Another form of polymer association occurs in block copolymers, which consist of two or more mutually immiscible polymers joined together in a linear chain. Block copolymers, being amphiphilic, have properties similar to those of surfactants. But the polymers' entanglement and deformability cause their resulting micellar microdomains to have some distinctive properties. An example of commercial importance is Kraton, a rubbery polymer tipped at each end with a small section of an immiscible, glass-forming polymer. The ends of the Kraton polymer congregate into spherical micelles, each micelle containing many chain ends. The midsections of such a copolymer cannot disentangle themselves, and a strong rubbery material results. But when the material is heated above about 100 °C, the spherical micelles at the ends melt and become more miscible, so that the material flows. It can then be molded and processed. Such polymers, called thermoplastic elastomers, are used, for example, in adhesive coatings and for the elastic stripes painted on disposable diapers.

Block copolymers can form a rich variety of extended structures. Figure 6 shows an example. The microdomain liquid shown in the figure is very different from a simple polymer melt. Here the polymers minimize the interfacial area by stretching out to allow thicker domains. Thus they store considerable elastic energy. This stored energy produces the striped morphology seen in the figure. It also is expected to affect the elastic and flow responses of the material drastically. The competition between the polymer's elasticity and immiscibility has been shown to lead to a wealth of distinctive domain structures.[19]

Solids or liquids?

Traditionally, condensed matter science has focussed on small-molecule solids and liquids. Fundamental similarities between small-molecule liquids limit the range of macroscopic behavior those liquids can show. Structured fluids provide us with a means to escape from some of those limitations and produce materials that act ambivalently. They may act like solids or liquids depending on the time scale or on how strongly they are perturbed. They have other properties that defy conventional notions of solidity and liquidity. Many of these properties arise from large-scale statistical features of the constituent polyatomic structures; such properties can often be understood in a simple and general way.

In this article I have discussed only a fraction of these properties, emphasizing structured fluids encountered in everyday life. I have omitted altogether exciting areas like liquid crystals and interfacial flows. The recent progress in understanding structured fluids surveyed in the article gives a tantalizing glimpse of new types of cooperative phenomena. Further exploration of these phenomena promises to expand our notions of how condensed matter can behave.

• • •

I am grateful to Sam Safran, Phil Pincus, Bruno Zimm, Dale Pearson, John Marko, Henry Princen and Frank Malihi for helpful advice and information.

References

1. Many of the phenomena discussed in this article are reviewed in more detail in S. A. Safran, N. Clark, eds., *Physics of Complex and Supermolecular Fluids*, Wiley, New York (1987).
2. See, for example, K. Kendall, Contemp. Phys. **21**, 277 (1980).
3. See, for example, R. E. Rosensweig, in *Physics of Complex and Supermolecular Fluids*, S. A. Safran, N. A. Clark, Wiley, New York (1987), p. 699.
4. A. Chowdhury, B. J. Ackerson, N. A. Clark, Phys. Rev. Lett. **55**, 833 (1985).
5. M. M. Burns, J. M. Fournier, J. A. Golovchenko, Phys. Rev. Letts. **63**, 1233 (1989).
6. B. Ackerson, in *Physics of Complex and Supermolecular Fluids*, S. A. Safran, N. Clark, eds., Wiley, New York (1987), p. 553.
7. See, for example, M. Y. Lin, H. N. Lindsay, D. A. Weitz, R. C. Ball, R. Klein, Nature **339**, 360 (1989). R. Jullien, R. Botet, *Aggregation and Fractal Aggregates*, World Scientific, Singapore (1987).
8. For a recent review, see D. S. Pearson, Rubber Chem Technol. **60**, 439 (1987).
9. J. Lumley, Annu. Rev. Fluid Mech. 367 (1969). **[vol??]**
10. For a discussion of possible mechanisms, see P. G. de Gennes, Physica (Utrecht) **140A**, 9 (1986); G. Ryskin, Phys. Rev. Lett. **59**, 2059 (1987); W. M. Kulicke, M. Kotter, H. Grager, Adv. Polymer Sci. **89**, 1 (1989).
11. R. M. Davis, W. B. Russel, Macromolecules **20**, 518 (1987).
12. E. Helfand, G. H. Fredrickson, Phys. Rev. Lett. **62**, 2468 (1989); A. Onuki, Phys Rev. Lett. **62** 2472 (1989).
13. M. Doi, S. F. Edwards, *The Theory of Polymer Dynamics*, Oxford U. P., Oxford (1986).
14. P. A. Irvine, P. Smith, Macromolecules **19**, 240 (1986).
15. See, for example, M. E. Cates, D. Andelman, S. A. Safran, D. Roux, Langmuir **4**, 802 (1988).
16. J. Candau, in *Physics of Complex and Supermolecular Fluids*, S. A. Safran, N. A. Clark, eds., Wiley, New York (1987), p. 569.
17. See, for example, M. E. Cates, J. Phys. (Paris) **49**, 1593 (1988).
18. T. A. Witten, J. Phys. (Paris) **49**, 1055 (1988).
19. E. L. Thomas, D. J. Kinning, D. B. Alward, C. S. Henkee, Macromolecules **20**, 2934 (1987).
20. K. Kremer, G. S. Grest, J. Chem. Phys. **92**, 5057 (1990).
21. Chris S. Henkee, unpublished. See also C. S. Henkee, E. L. Thomas, L. J. Fetters, J. Mater. Sci. **23**, 1685 (1988); C. S. Henkee, E. L. Thomas, D. C. Martin, L. J. Fetters, Polym. Prepr., **29**, 462 (1988). ■