From simple liquids to colloids and soft matter

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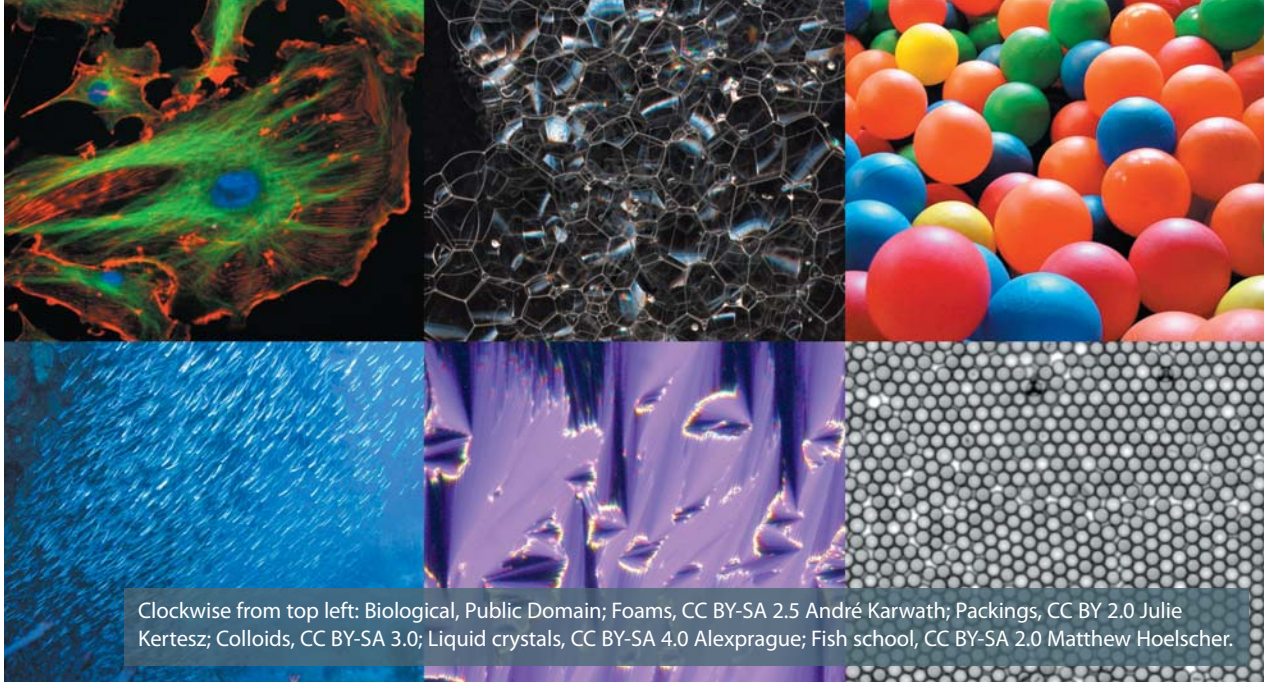

Clockwise from top left: Biological, Public Domain; Foams, CC BY-SA 2.5 André Karwath; Packings, CC BY 2.0 Julie Kertesz; Colloids, CC BY-SA 3.0; Liquid crystals, CC BY-SA 4.0 Alexprague; Fish school, CC BY-SA 2.0 Matthew Hoelscher.

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Soft matter, a diverse subject that crosses the boundaries of physics, chemistry, and materials science, continues to surprise with its rich phenomena.

In 1977 Victor Weisskopf published an essay entitled "About liquids," in which he argued that the existence of liquids is not at all self-evident: They belong to the "Who ordered that?" category.[1] "Assume that a group of intelligent theoretical physicists had lived in closed buildings from birth such that they never had occasion to see any natural structures," wrote Weisskopf. "They probably would predict the existence of atoms, of molecules, of solid crystals, both metals and insulators, of gases, but most likely not the existence of liquids."

It is not obvious that a separate state of matter should exist that is dense, disordered, strongly spatially correlated, and distinct from the gaseous and crystalline states. Weisskopf suggested in a throwaway sentence that the existence of liquids should necessarily follow from quantum mechanics. But is that true?

Until the 1950s, no theoretical framework existed to describe liquids. The great Lev Landau infamously argued that there is no theory of the dense liquid state. By the early 1970s, the field had changed significantly for two reasons. First, computer simulations made it possible to probe in unprecedented detail the microscopic behavior of simple, argon-like liquids by using first hard spheres and then the Lennard-Jones model. Second, a quantitative theory of the equilibrium structure and thermodynamic properties of liquids had emerged, accompanied by a growing understanding of the dynamics of simple liquids catalyzed by simulation studies.

An important assessment of the emerging theory appeared in 1976. As laid out in "What is 'liquid'? Understanding the states of matter,"[2] the structure of simple liquids is dominated by the harsh repulsions between the atomic cores, whereas thermodynamic properties depend on both the repulsive and attractive interactions, with the latter treated in a mean-field fashion. Remarkably, such ideas were present in the 1873 thesis of Johannes van der Waals.

Although the number of experimental and theoretical studies increased between 1976 and 1985, little about liquids appeared in *Reviews of Modern Physics*. That changed with the influential article of Pierre-Gilles de Gennes on

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the statics and dynamics of surface wetting.[3] The review, which admirably summarized the physics of the adsorption of fluids to substrates, interfacial tension, and surface phase transitions, focused primarily on simple liquids.

Of course, most molecules are not like argon: The Lennard-Jones model has its limitations. Nature provides polymers, surfactants, liquid crystals, and a whole zoo of colloidal particles that may or may not exhibit liquid phases. Those particles can combine to form an abundance of structures that are much richer than what's found in simple systems. Some of those diverse structures include membranes, gels and glasses, liquid-crystal phases, micellar solutions, and highly unusual crystalline phases.

Predicting the structure and dynamics of such complex phases of matter from the constituent building blocks and their interactions defines soft-matter science. Soft materials have properties that differ qualitatively from those of simple liquids; there is no corresponding states principle that enables one to map a polymer melt onto liquid argon. Although the behavior of soft materials often has no counterpart in other branches of physics, there can be profound links between different fields, such as the relationship between the director in smectic liquid crystals and the magnetic vector potential in superconductors,[4] or between the formation of disclination lines in nematic liquid crystals and the Kibble mechanism for the formation of topological defects (cosmic strings) as the early universe cooled.[5] De Gennes was renowned for making pertinent connections, as illustrated in his 1991 Nobel Prize in Physics lecture[6] and in the Nobel citation, which reads, "for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers."

Colloids provide a crucial link between simple liquids and complex fluids and soft matter. Suspensions of micron-sized polymethyl methacrylate particles immersed in a solvent mimic to an extraordinary degree the hard-sphere system. For example, colloidal particles undergo a fluid-crystal transition at the density predicted for hard spheres by computer simulations.[7] No liquid–gas transition occurs, either experimentally or theoretically, because there is no interparticle attraction.

When a nonadsorbing polymer, or more generally a depletant, is added, the effective interaction between two colloids acquires an attractive piece whose range is set by the size of the depletant and whose strength is set by its concentration. That entropic depletion mechanism[8] was first put forward by Sho Asakura and Fumio Oosawa in 1954. And when the depletant is similar in size to the colloid, the phase equilibria mimic that of a simple fluid, with the concentration of the depletant equivalent to inverse temperature. Reducing the size of the depletant reduces the range of the attractive interaction, and liquid–gas coexistence becomes metastable with respect to the fluid–crystal transition, so there is no stable liquid phase. Theoretical studies[9,10] of such colloidal phase behavior in the 1990s were confirmed soon thereafter by beautiful experiments.[11]

Advances in imaging and tracking nanometer- to micrometer-sized particles ensure that colloids will continue to serve as a model system to investigate basic physical phenomena, including the glass transition, jamming, random packings,[12–14] two-dimensional melting,[15] quasicrystals, and more. Many of those phenomena are observed in various soft-matter systems, such as foams, emulsions, micellar systems, and granular matter.

The diversity of topics is a defining feature of the soft-matter field. It now covers sand piles, patchy colloids, self-propelled colloidal particles, microswimmers, DNA origami, bubbles, droplets, and membranes. Soft-matter systems can be highly correlated due to high packing fractions and often exhibit a high surface-to-volume ratio, multiple components across different length scales, and a complex topology and geometry. Those features combine to generate dramatic new phenomena. Unsurprisingly, there is no single unifying theoretical framework.

An exciting new area of study is active matter, in which the constituent particles are maintained out of equilibrium through a constant input of energy. Systems being studied as part of that vibrant subfield include bacteria swarms, cytoskeletons of living cells, vibrated granular matter, and self-propelled colloidal particles. New theoretical approaches are required to describe the diverse, emergent dynamical phenomena encountered.[16,17] Soft-matter physics is sometimes viewed as the science of big atoms. That is misleading. Complex fluids give rise to exceptionally rich behavior that certainly does not exist in argon.

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