

Simple Ordering in Complex Fluids

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SIMPLE ORDERING IN COMPLEX FLUIDS

Colloidal particles suspended in solution provide intriguing models for studying phase transitions.

Alice P. Gast and William B. Russel

Ordering and the formation of crystals have long fascinated mankind. The reverence bestowed on gemstones and the fantastic properties attributed to crystalline matter arise from the unique optical, geometric and physical properties of the ordered state. Although scientific inquiry has focused mostly on molecular and atomic crystals, much also can be learned from the study of supermolecular and colloidal arrays.

Colloidal suspensions, commonly referred to simply as colloids, are composed of small particles that are 10–100 nm in diameter—too small to see with the unaided eye—and dispersed in a solvent. Everyday examples abound, from milk to inks and paints to fog and smoke. The best-known example of an ordered colloid—a colloidal crystal—is the opal, formed from a uniform array of silica spheres compressed and fused over geological timescales. In the laboratory, the achievable size and uniformity of colloidal particles make them useful as ceramic precursors, optical filters, porous sieves, encapsulants and carriers of active compounds, as well as in the liposome technology used by the cosmetics industry. In addition, colloids formed from polystyrene beads with specific functionalities attached, such as antigens or reagents, are finding use in biondiagnostics and combinatorial chemistry.

One important feature of colloids is that the submicrometer particles are subject to constant Brownian motion from the thermal fluctuations in the surrounding solvent. Thus, to some degree, the particles can be considered as effective molecules and treated according to the theories of statistical mechanics. Because the solvents often contain—in addition to the colloidal particles—dissolved ions, polymer molecules, surface-active molecules and other small solutes, colloids are referred to as a general class of complex fluids. Their complexity is ameliorated somewhat by treating all the colloidal particles or aggregates as an effective single-component system, with the interactions among particles being mediated by the small-molecule solutes and the solvent. In addition, since the volume of a suspension is typically 50% or more solvent, the interactions can be readily tuned through subtle changes in the solution chemistry rather than by difficult pressure and temperature excursions. Studies of colloids at high concentration have revealed a myriad of interesting phenomena, including crystallization into a variety of structures, crystal twinning, the glass transition,

binary alloy formation and dendritic growth instabilities (figure 1).

Hard spheres: Entropy creates order

The ability to tailor interactions between colloidal particles has provided fertile ground for scientists interested in the fundamental aspects of phase behavior.¹ Perhaps one of the most important answers to physicists' dreams has been the development of colloidal particles that interact by means of hard-sphere repulsions. Hard spheres interact with each other only when they touch, and then with a divergent repulsion representing their impenetrable physical volume. Thus, with hard particles, packing alone causes ordering and no heat or energy is liberated upon crystallization. This is a rather intuitive concept for anyone who has tried to pack a jar of marbles or rack a set of billiard balls; however, its thermodynamic consequences are more subtle.

Entropy is usually thought to bring about disorder. In a system of hard spheres, however, as in a set of schoolchildren spacing themselves apart before beginning their exercises, particles gain entropy by arranging themselves equidistantly from one another to maximize the space in their vicinity, and thus they are compelled to order. That entropy drives hard particles into crystalline arrays was first discovered through computer simulations over 40 years ago (see box 1 on page 26). This seemingly simple phase transition went without physical verification until the development of hard polymer and silica spheres. The key to full characterization of the transition was the use of a nonpolar suspending fluid that nearly matched the refractive index of the particles: Not only were the suspensions rendered optically transparent, but the ubiquitous van der Waals attraction between the spheres was suppressed sufficiently to be balanced by the particle-solvent interaction. These hard particles provided the opportunity to study crystallization, the glass transition, growth instabilities and nucleation in a system extensively investigated by means of computer simulation and statistical mechanics.

As noted in box 1, hard spheres first order when they occupy approximately 50% of the system volume. The onset of freezing immediately produces a solid at the melting volume fraction of $\phi = 0.545$, and the crystal can be further compressed up to the closest packing density of 0.74. Thus the phase diagram, while simple, has a remarkably large region of fluid–solid coexistence and a solid phase that persists over a fairly wide concentration range.

Hard spheres order into dense structures formed by stacking hexagonally ordered planes of spheres (figure 2). Until the past few years, computer simulations detected no energy difference between face-centered cubic (FCC)

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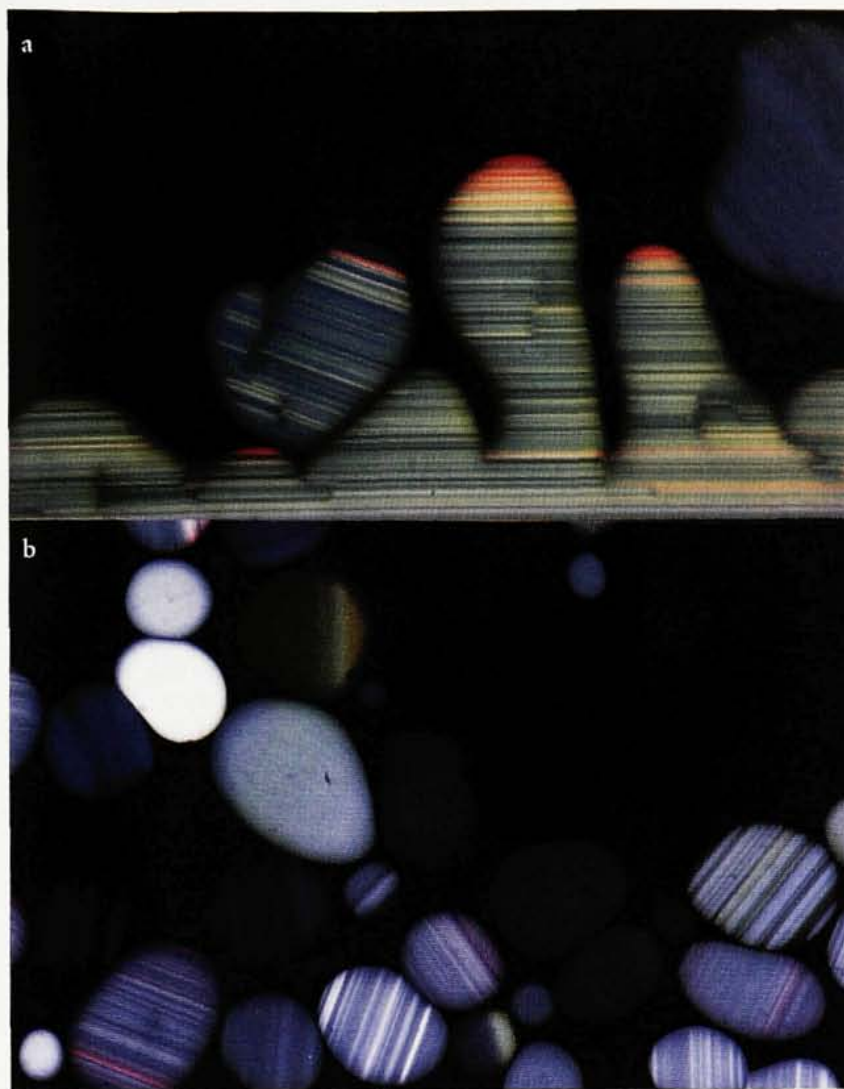


FIGURE 1. COLLOIDAL CRYSTALLITES of charged polystyrene spheres 67 nm in diameter at a volume fraction of $\phi = 0.017$ in a solution with a molar ionic strength of 10^{-6} .

a: Crystallites growing into disordered regions undergo an instability that produces these broad fingers, 100–200 μm across. **b:** Random switching between two FCC twin structures causes the striped appearance when viewed through crossed polarizers. (Photos by S. Nilsen and Y. Monovoukas.)

arrays, created by repeated stacking in the three available interstitial sites, and hexagonal close-packed (HCP) crystals, formed by repeated stacking in only two of the interstitial sites. The lowest-energy configuration has remained an open question in experiments on colloids, although the small energy differences between stacking arrangements detected in recent computer simulations and analysis indicate a preference for the FCC structure. Both ground-based experiments and those done under microgravity conditions in the space shuttle by Paul Chaikin and his coworkers at Princeton University and NASA indicate a prevalence of randomly stacked HCP structures, though an FCC component emerges if enough time is allowed.

Gravity clearly influences two features of the ordering transition. First, instabilities during crystal growth analogous to those observed in snowflakes produce millimeter-sized dendrites in microgravity (figure 3) and yet are suppressed by viscous stresses and sedimentation in normal gravity. Second, there is a glass transition for hard-sphere colloids in the vicinity of $\phi = 0.58$, identified by Peter Pusey and Bill van Meegen in 1986.² Often, a crystalline phase develops near the top of a colloidal glass over time, showing the glass to be a metastable phase caused by the arrested mobility of the particles that slight dilution due to sedimentation could relieve. Chaikin and his coworkers found that a sample at $\phi = 0.59$, which formed a persistent colloidal glass on the ground, crystallized in microgravity, albeit heterogeneously.³

The nucleation and growth of hard-sphere colloidal

crystals are readily studied by light scattering and microscopy. According to classic nucleation theory, the competition between the free energy driving the ordering transition and the energy required to create the new solid-liquid interface produces an energy barrier for growth and establishes a minimum size—the critical nucleus size—that crystallites must achieve before growing spontaneously.⁴ In 1995 Bruce Ackerson of Oklahoma State University and the late Klaus Schätzel detected the decrease in the critical nucleus size with supersaturation, observing a small value of around 10 particle radii in the middle of the coexistence region.⁵ Crystal growth is often limited by the diffusion of particles to the growing crystal front, resulting in the formation of dendrites mentioned above and shown in figure 3. Evidence for a region of lower concentration in the fluid around a growing crystallite, confirming the diffusion limitation, comes from the shape of the scattering structure factor at low angles, which exhibits a ring of high intensity. Low-angle and Bragg scattering studies are now assembling the experimental picture, supporting

aspects of the Ackerson-Schätzel model and detecting effects of interactions between crystals that are also seen in molecular systems.

Soft spheres: tunable repulsions

The addition of a “soft,” or long-range, repulsion to colloidal particles can keep them sufficiently separated that the van der Waals attraction is negligible, rendering the suspension stable against aggregation under a variety of conditions.^{4,6} Most commonly, aqueous suspensions are stabilized by the screened electrostatic repulsion between charges imparted to the particle surfaces; the range of the interaction is characterized by the Debye length κ^{-1} , which scales inversely with the square root of the ionic strength of the suspension.

Another way to prevent aggregation is to attach soluble polymer chains by one end to the particle surface, thus creating a dense “brush” with flexible bristles stretching toward the free solvent. An encounter between two particles compresses the brushes, generating a repulsion. In both charged and polymer brush suspensions, the soft repulsion extends over a range that can be comparable to or greater than the particle size.

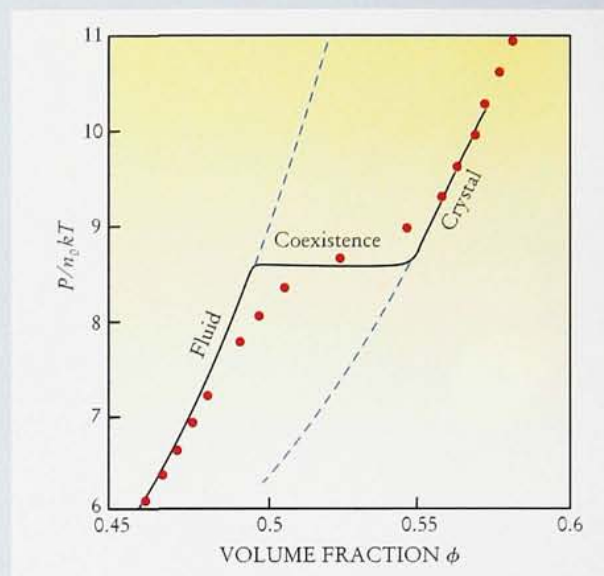
Particles interacting by means of such soft repulsion exhibit a Kirkwood-Alder transition but at quite low particle volume fractions. These tenuous “liquid crystals”—with particles spatially ordered but surrounded by fluid and separated in space by distances comparable to their size—are easily melted by flow. The soft-sphere disorder-order transition can be provoked by two means:

Box 1. Kirkwood–Alder Transition

In 1939, John G. Kirkwood speculated that repulsive particles would order at a density below the close-packed limit. Some years later, Kirkwood and his student Bernie J. Alder surmised that this transition should happen for hard spheres at a volume fraction of $\phi = 0.50$. The first-order solidification transition in hard spheres was first observed in 1957 through molecular dynamics calculations by Alder and Tom E. Wainwright at Lawrence Livermore National Laboratory in California, and in Monte Carlo simulations by William Wood and J. D. Jacobson at Los Alamos National Laboratory. In molecular dynamics, the equations of motion for all the particles in the simulation are solved for each time step. Performing the calculations was a major accomplishment in those days, given that computers were in their infancy (and required the laborious use of punched cards, paper tape and line printers): Hundreds of hours on an IBM-704 were needed to search for the transition at the highest densities in the molecular dynamics simulations (at the now paltry rate of 2000 collisions per hour for simulations with 108 particles). Therefore it is not surprising that 11 years passed before, in 1968, the efforts of William Hoover and Francis Ree and of Alder, Hoover, and William Young resulted in the accurate determination of the densities $\phi = 0.494$ and 0.545 for the fluid and solid when they coexist. Now referred to as the Kirkwood–Alder transition, this phase transition has become the cornerstone of our understanding of colloidal ordering.

The figure shows the equation of state that Alder, Hoover and Young found for hard spheres, presented as pressure (normalized by the thermal energy kT and the FCC close-pack-

ing density n_0) versus volume fraction ϕ (solid line). The first-order ordering transition begins at $\phi = 0.494$ and the solid first melts at $\phi = 0.545$, but both phases have metastable branches (dashed lines). The data (red dots) are from x-ray densitometry performed on an equilibrium sediment of polystyrene spheres 720 nm in diameter in a 3 millimolar salt solution by Maarten Rutgers and his colleagues at Princeton University and the Exxon Corporate Laboratory.



increasing the particle volume fraction or increasing the range of the repulsion. Increasing the range is easily accomplished in charged suspensions by removing screening ions from the fluid, thereby increasing the Debye length. As with hard spheres, the ordered soft particles assume cubic arrangements. The FCC phase prevails at higher concentrations or with shorter range repulsions. As the range of the repulsion is increased, a lower-density, body-centered cubic (BCC) phase forms, as shown in figure 4.

The scattering and microscopy techniques employed for studying hard spheres are also used to examine the

crystallization behavior of charged colloids and other soft spheres, often producing vivid colors (as seen on the cover and in figure 1) because of the strong diffraction.⁷ Again, the growth can be unstable,⁸ producing dendrites like the large fingers shown in figure 1a. The very slight energy difference between the two possibilities for stacking the hexagonally packed planes of FCC crystals produces stacking faults and twins, as evident in the striations shown on the cover and in figure 1b. These stacking faults have been directly visualized by Henk Lekkerkerker and his colleagues at Utrecht University through confocal scanning microscopy of fluorescently labeled silica particles. Diffusion is not always the limiting element in crystal growth: Thomas Palberg and his coworkers at the University of Mainz have detected BCC crystals that grow by reaction-limited kinetics.

The colloidal nature of soap molecules has been known to scientists for many years. In addition to their ability to support foam, clean surfaces and lower interfacial tension, soap molecules associate in water, with their oily tails aggregating into small structures known as micelles. The scattering of light from micelles is familiar to anyone who has noted the turbidity of leftover dish or bathwater.

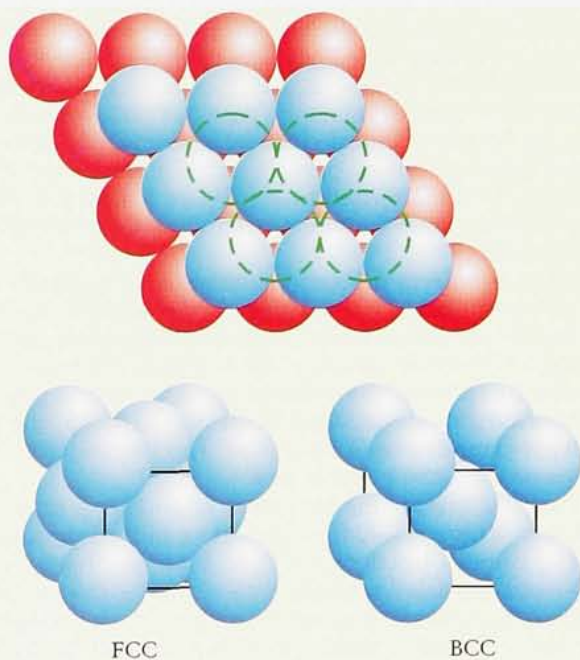


FIGURE 2. THE STRUCTURES formed in cubic packing of repulsive particles. Hard spheres order themselves in stacked hexagonal arrays (top). Orderings cycling through all three possible layer positions (red, blue, green, red and so on) form face-centered cubic (FCC) crystals; alternation between only two positions (for example, red, blue, red and so on) produces hexagonal close-packed (HCP) structures. The FCC and HCP structures are the most dense, both having a maximum packing fraction of $\phi = 0.74$. The body-centered cubic (BCC) structure has a maximum packing of $\phi = 0.68$ and is stabilized by repulsions having a longer range.



FIGURE 3. DENDRITIC GROWTH of crystallites of hard-sphere poly(methylmethacrylate) colloidal particles 508 nm in diameter at a volume fraction of $\phi = 0.504$ in a mixture of decalin and tetralin. Grown in microgravity on the space shuttle, the dendritic crystallites are 2–3 mm in diameter and persist for months. (Reprinted by permission from *Nature*, vol. 387, p. 883, copyright 1997, Macmillan Magazine Ltd.)

Such association colloids, as they are called, can also be formed on a larger scale by polymeric surfactants or by block copolymers consisting of two polymer chains covalently attached to one another. When mixed with a solvent that dissolves one of the chains but not the other, these copolymers produce spherical micelles with compact, insoluble cores surrounded by a polymer brush.

Polymeric micelles are critical to several applications, including separations, such as the scavenging of trace organics or metals for environmental processes; encapsulation, as in cosmetics and drug delivery; and use as rheological modifiers—for instance, as additives in lubricating oils to change the temperature behavior of the viscosity.

In addition, micelles provide a nice model system for studying the effect of curvature on polymer brushes. Polymers tethered to large particles or to the cores of large micelles have concentration profiles that are parabolic in form. The structure of chains attached to highly curved surfaces is better represented as a starlike configuration with a rapid power-law decay of the concentration profile. These two situations, illustrated in figure 5, produce subtly different interactions and qualitatively different phase behavior. The more brushlike systems with shorter-ranged and steeper repulsions order into FCC arrays observed for hard spheres, whereas the starlike micelles form BCC arrays.

At higher concentration, the polymeric nature of the interaction produces a curious melting of the micellar crystals; this is one example of a reentrant liquid-solid-liquid phase transition.⁹ The effect arises from increased screening in the semidilute polymer brushes, which causes them to relax from their highly stretched configuration at dilute concentrations and therefore interact less strongly with their neighbors.

BCC-FCC transition

The formation of BCC and FCC crystals in complex fluids is analogous to the ordering in metals, so the determination of the FCC-BCC phase boundary is of fundamental interest.¹⁰ Although many complex fluids exhibit a structural transition from the higher-density FCC phase to the lower-density BCC phase as the range of the repulsion increases, no general model for this crossover exists. Perhaps the earliest studies of this behavior were the simulations with inverse power-law potentials $U(r) \propto r^{-n}$ conducted by Jean-Pierre Hansen of the University of Paris and William Hoover and his coworkers at Lawrence Liver-

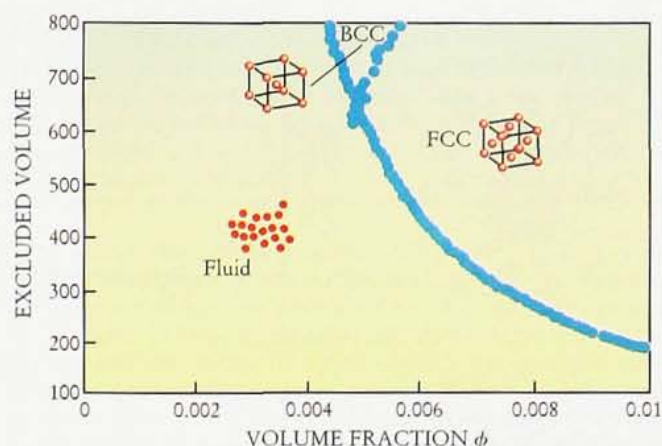


FIGURE 4. GENERALIZED PHASE DIAGRAM for soft spherical particles interacting through screened Coulomb repulsion (Yukawa potential). The vertical axis is the volume that is inaccessible to one particle due to the presence of another; it scales as the cube of the Debye screening length, which sets the characteristic range of the interaction. As the range or the volume fraction ϕ is increased, these particles order into either body-centered cubic (BCC) or face-centered cubic (FCC) arrays.

more National Laboratory in the early 1970s. They found that, for interaction potentials with $n < 7$, colloids froze into a stable BCC phase; subsequent concentration of this phase produced a BCC-FCC transition. More recent simulations and density functional calculations have found the triple point for BCC, FCC and liquid coexistence to be near $n = 6$. The basic principle is that, for moderately soft potentials, the FCC structure has the lower energy and the BCC has higher entropy. Thus, for a sufficiently high melting temperature, an FCC-BCC transition can precede the transition to the fluid. Indeed, in charged colloidal systems in the liquid phase, a transient BCC-like structure was observed in time-resolved scattering experiments by Ackerson and Noel Clark years ago at the University of Colorado.

BCC-FCC transitions are found experimentally in several complex fluids. In charged colloids, the BCC-FCC-liquid triple point occurs when the interparticle spacing is 4.9 times the Debye length. Polymeric micelles cross the polymorphic threshold when the hydrodynamic radius of the micelle is three times that of the core, and a similar transition is found in nanoparticles carrying fatty monolayers on their surfaces. The coexistence between BCC and FCC phases detected in charged colloids by Chaikin and his colleagues has verified the first-order nature of this phase transition.

Attractions: the “glue” that creates liquids

The disorder-order transition for particles having purely repulsive interactions persists when attractive interactions are added. In addition, attractions of sufficiently long range introduce a gas-liquid phase transition. There are several ways to control the attractive interactions. Sometimes the gas-liquid transition can be provoked by careful manipulation of hard-sphere systems, since the van der Waals attraction depends weakly on the temperature. In aqueous systems, adding electrolytes to screen the electrostatic repulsion between charged particles can induce aggregation by means of van der Waals attraction. The onset of aggregation, however, is generally abrupt, and produces persistent nonequilibrium aggregates that obscure the equilibrium gas-liquid phase transition.

A more popular approach is to add a nonadsorbing soluble polymer (or surfactant micelles or smaller colloidal

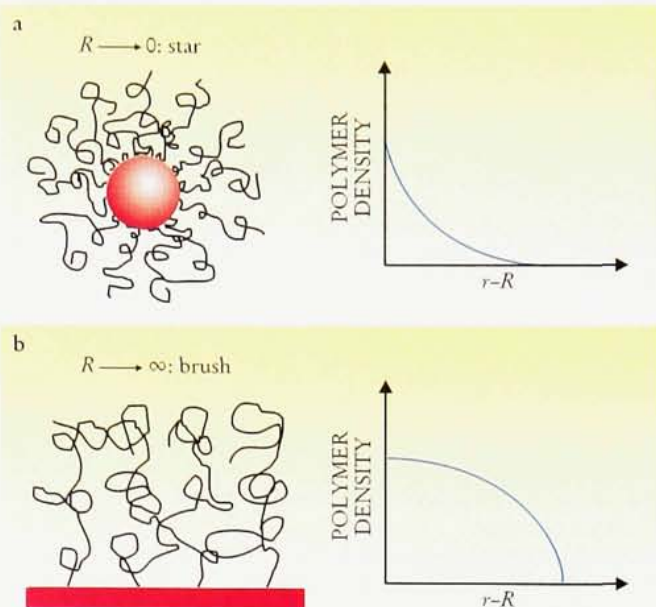


FIGURE 5. THE CONFIGURATION OF TETHERED POLYMERS, as well as their concentration profile as a function of distance r , depends on the radius R of the colloidal particles or micellar cores to which they are attached. **a:** On small particles or micelles, the polymers form a starlike configuration. **b:** Polymers form a planar brush on the surface of a large colloidal particle or micelle.

particles) to an otherwise stable suspension to produce a weak, long-range attraction between colloidal particles. The soluble additives are excluded from a region comparable to their size near the particle surface, producing what is called a depletion layer, as sketched in figure 6. When two particles approach closely enough for their depletion layers to overlap, the osmotic pressure exerted on each particle by the dissolved polymer outside the region of overlap causes a weak attraction. The magnitude is proportional to the polymer concentration, and the range scales with the depletion layer thickness (or polymer size), thereby allowing one to tune the interaction to produce the desired phase behavior. Aggregation caused by the depletion force was exploited in the 1930s to concentrate rubber latex particles, but scientific study began in earnest only 20 years ago in the groups of Agienus Vrij at Utrecht University and Brian Vincent at the University of Bristol.

Box 2. Colloidal Alloys in Binary Mixtures

Renewed interest in binary dispersions for depletion separation prompts a look back at the beautiful and complex structures created by Sei Hachisu (University of Tsukuba) and his coworkers in the 1980s.¹⁷ Motivated by the observation made by John Sanders (Commonwealth Scientific and Industrial Research Organisation) in the 1950s and Cherry Murray (Bell Laboratories) in 1978 that opals contain two narrow size ranges of silica spheres, Hachisu proceeded to create a myriad of unique structures from binary mixtures of uniformly sized colloidal particles. The structure and stability of the crystals that were formed depended critically on the particle sizes. Using a metallurgic microscope, Hachisu observed many lattices, including the simple NaCl, MgCu₂ (diamond lattice) and even a strange NaZn₁₃ array. These experiments further demonstrate that colloidal particles are useful model systems for the study of phase behavior.

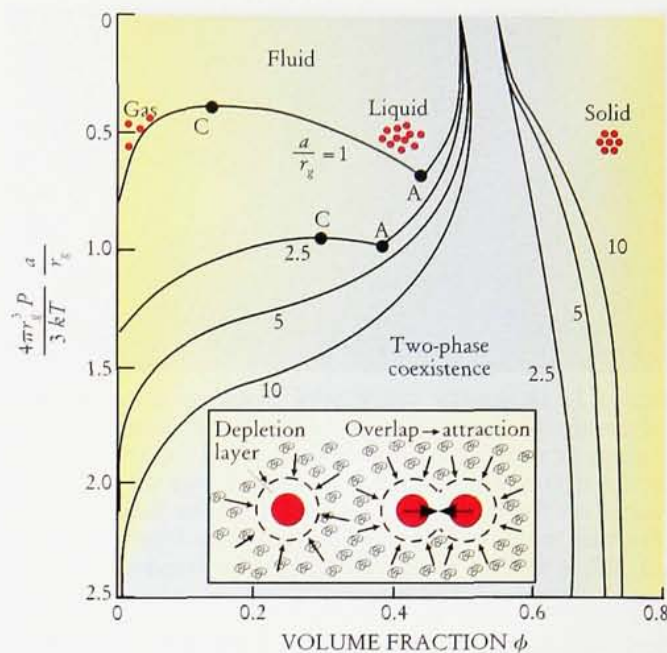


FIGURE 6. SCHEMATIC PHASE DIAGRAM for particles interacting by means of the attractive depletion force. This force arises from the osmotic pressure exerted on the particles from small nonadsorbing polymers that are excluded from a region called the depletion layer that surrounds each particle. The behavior of the colloid-polymer system depends on the ratio of the particle radius a to the polymer's radius of gyration r_g , as well as on the temperature T , the polymer osmotic pressure P , and the colloidal particle volume fraction ϕ . For small ratios a/r_g , the system has a stable liquid phase between the triple point (A) and the critical point (C). As the ratio increases, the critical point and triple point approach each other, until the liquid phase disappears for ratios greater than 3.

It was with the depletion interaction that Peter Sperry of the Rohm and Haas Co (experimentally) and we along with Carol Hall (theoretically) discovered 15 years ago that the presence of a gas-liquid transition depends keenly on the range of the attraction. As illustrated in figure 6, changing the particle-polymer size ratio produces a series of phase envelopes. The critical point disappears into an unstable regime when the polymer (and hence the attractive well) is about one-third the size of the particle. A similar absence of the gas-liquid transition is found for proteins and large molecules such as the fullerene C₆₀. Simple models by Marc Baus and his colleagues at the Free University of Brussels and George Benedek's group at MIT link the disappearance of the gas-liquid phase transition to the range of the attractive potential and the number of neighbors in the solid phase. Lekkerkerker and his coworkers have extended our earlier model to account for partitioning of the polymer between the two phases. Complementary experiments by Pusey and his colleagues have delineated the phase diagram of binary polymer-colloid systems, again noting the disappearance of the gas-liquid critical point.¹¹ The depletion mechanism has found important application in protein separations, as explored by Hall and her coworkers at North Carolina State University, and as a means to fractionate emulsion droplets with surfactant micelles, a technique pioneered by Jerome Bibette of the University of Bordeaux. Arjun Yodh and his colleagues at the University of Pennsylvania have exploited the depletion interaction to produce phase separation in binary dispersions (see box 2 on this page).

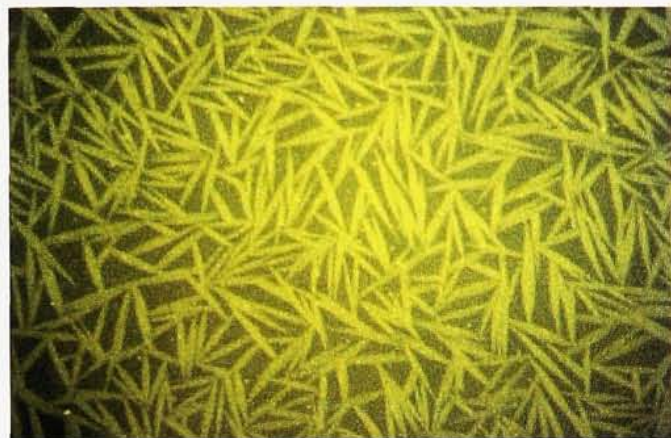
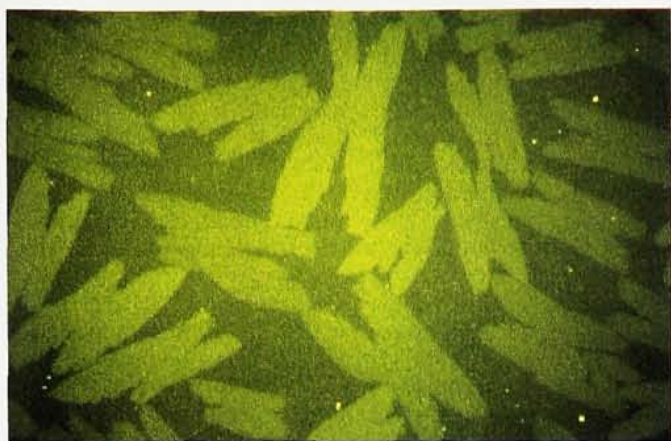


FIGURE 7. TWO-DIMENSIONAL CRYSTALS of the protein streptavidin bonded to a biotinylated lipid monolayer. The symmetry of the crystals (the individual light green objects) depends on the pH of the aqueous buffer solution on which they float: pH = 8, 4, 5.2 (from top to bottom). Each field of view is $350\ \mu\text{m} \times 550\ \mu\text{m}$.

tions using the adhesive-sphere potential. Then, by locating the systems on the adhesive-sphere phase diagram, they confirmed an idea advanced by Abraham George and W. William Wilson at Mississippi State University that only a narrow range of virial coefficients produce good protein crystals. Stronger attractions reduce mobility and increase the rate of crystallization, preventing the rearrangements necessary for defect-free crystals; weaker attractions require higher concentrations that promote the formation of glassy, rather than crystalline, phases.

Two-dimensional crystallization

The intriguing features of crystals and their beautiful symmetries persist when the system is confined to two dimensions. Many examples of two-dimensional ordered arrays are found throughout the world: rows of corn, the breeding grounds of the king penguin, the scales on a salmon and the paving stones on the rue Moufflard. On a slightly smaller yet not colloidal scale are the ingenious mesoscopic polymer objects created by George Whitesides and his coworkers at Harvard University.¹³ These shapes have both hydrophilic and hydrophobic edges and, when floated on a water surface, will assemble into ordered arrays in which the hydrophobic edges are connected. A myriad of structures can be envisioned and phase segregation can be realized by altering the object thickness.

When a system is strictly confined to two dimensions, the nature of the melting transition may change. This idea was first suggested over 25 years ago, and the transition from a two-dimensional solid to a two-dimensional liquid is termed the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) transition after its discoverers. The KTHNY theory predicts that two-dimensional solids melt by means of sequential and continuous phase transitions rather than a single, first-order, discontinuous transition. Two-dimensional crystals exhibit both quasi-long-range positional order and long-range bond orientation order. The proposed transition proceeds from this solid to a liquid through an intermediate phase, termed the hexatic, having quasi-long-range bond orientational order but short-range positional order. This theory has been much debated, with many computer simulations attempting to resolve the issue and, recently, colloids proving to be very useful models.

Confining charged colloidal particles between two flat plates, Cherry Murray and her coworkers at Bell Laboratories were able to observe the KTHNY transition through a hexatic phase with an optical microscope. Recently, Andy Marcus and Stuart Rice¹⁴ at the University of Chicago confined uncharged particles stabilized by short-range repulsions produced by bound polymers. Their experiments did identify an equilibrium hexatic phase, but unlike the predictions of KTHNY, this phase was separated from the solid and from the liquid by first-order phase transitions. As with the three-dimensional BCC-FCC and gas-liquid transitions, the range of the interparticle interactions may be a key to the phase behavior in two dimensions.

The complex structure of proteins can often be deciphered using the power of crystallography—but only if the proteins can be crystallized. Some proteins form two-dimensional arrays when attached to a lipid monolayer floating on top of an aqueous solution. The monolayer of

In the limit of very short range attractions between particles, the simplest model for the interparticle interaction is the adhesive hard-sphere potential of Rodney J. Baxter at the Australian National University. Extensive simulations and density functional calculations have identified the phase boundary (binodal) and limit of thermodynamic stability (spinodal) associated with the gas-liquid transition, a percolation transition and the liquid-solid transition. The general phase diagram resembles that of the depletion interaction shown in figure 6 for small depletion layer thickness, where the gas-liquid transition is unstable and subsumed into the gas-solid transition. Elegant experiments at Utrecht University by Kees de Kruif, Jan Dhont and their coworkers confirmed the spinodal and produced a poorly equilibrated fluid-solid transition.

The utility of the adhesive sphere model for complex fluids and protein solutions was illustrated by Chip Zukowski and his colleagues at the University of Illinois in 1996.¹² They measured the second virial coefficient to characterize protein-protein and other colloidal interac-

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proteins can then be transferred to an electron microscope grid for imaging and study by electron diffraction. This approach to protein crystallization was pioneered by Roger Kornberg and his colleagues at Stanford University in the early 1980s to characterize protein structure. The concentration and orientation of proteins into a monolayer reduces their degrees of freedom and can provoke ordering in systems eluding crystallization in solution. The groups of Kornberg and of Helmut Ringsdorf at the University of Mainz have used these techniques to characterize new structures and to assemble multilayers of two-dimensional arrays.¹⁵

These lipid-bound arrays provide another avenue toward a physical understanding of two-dimensional crystallization. For example, a two-dimensional growth instability analogous to that observed in colloidal suspensions occurs when impurities dilute the growing crystallites. Also, altering the acidity of the aqueous phase changes the protein-protein interactions and results in new crystalline lattice structures and morphologies for the dendrites produced by the instability. Figure 7 displays crystals of several shapes formed with the tetrameric protein streptavidin bound to a partially biotinylated lipid monolayer.¹⁶ Interestingly, binding streptavidin to biotin at two of four sites breaks the symmetry in the molecule and produces anisotropic and sometimes chiral morphologies. Thus the appearance of chiral structures—an area of fundamental interest—can be probed with these systems. Of greater importance is that with proteins comes the ability to perform point mutations—altering interactions in a specific way to study their impact on crystallization. Thus, although proteins remain complex in their detailed structure and interactions, they provide ample opportunity to study the general phenomenon of crystallization at both colloidal and molecular scales.

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