Ultradivided matter

Colloids

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Pierre-Gilles de Gennes

Chemists in the nineteenth century recognized the existence of 'misbehaving' systems: hydrated alumina, starch, dextrin and gelatin, for example. Wolfgang Ostwald grouped them into a separate category, and coined the name 'colloids' (meaning 'glue-like'). Thomas Graham showed that the constituent objects had low mobility, and became convinced that they were aggregates of smaller molecules. They could be metal particles (such as in the gold colloids made by Faraday), oxides or organic systems.

This colloid concept was vague, at first even counterproductive, and delayed the birth of polymer science — for instance, rubber vulcanization was claimed not to be a chemical reaction (what we now call crosslinking) but rather a modification of an aggregated state. Ultimately, thanks to Hermann Staudinger, polymers were clearly identified and taken out of the colloid group. But colloids are clearly important: white paint, for instance, is a colloid based on titanium oxide and water. Most foods, cosmetics and inks are made up of colloidal structures.

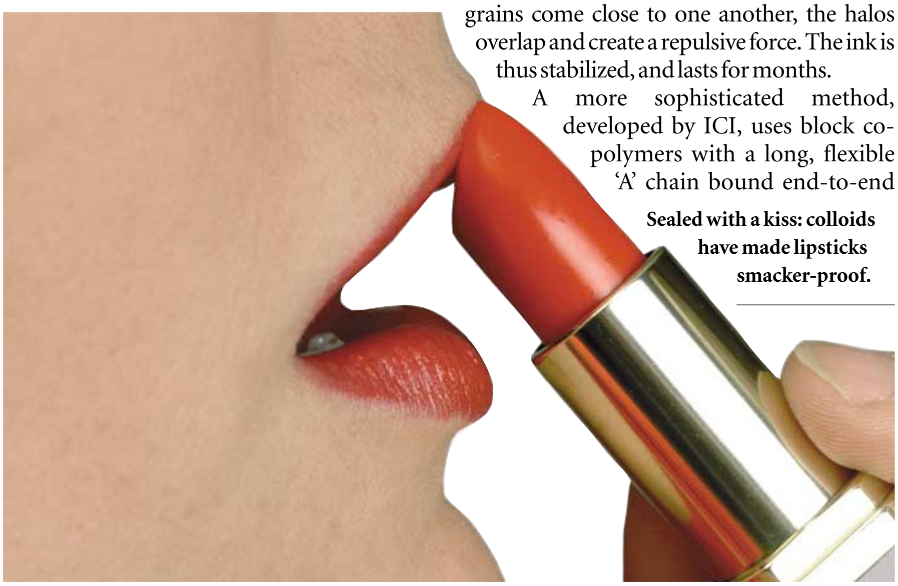
As time went on, colloids became a well-defined family of objects — more properly defined as ultradivided matter. The family has many members: soap micelles, emulsions, suspensions of solids (with sizes from micrometres to nanometres), and newborn objects such as latex particles (which can be admirably tuned in composition and calibrated in size). A common feature is that the particles are floating in a solvent; if it is not too concentrated, a colloid can flow freely, which is convenient for industry.

Colloids differ fundamentally from solutions. In a solution, say of water and alcohol, all the relevant interactions (water–water, water–alcohol and alcohol–alcohol) are comparable to the thermal energy, kT. Thus, even if water 'prefers' water and so on, the tendency towards disorder — entropy — is dominant: the water–alcohol system does not segregate and, fortunately, remains a good solution. In contrast, ultradivided matter is unstable because of large interfacial energies, and the particle–particle interactions are stronger than kT. If the system is to remain fluid, the particles must not clump; the interactions have to be repulsive.

Neutral particles in a common solvent attract each other by Van der Waals forces, thus clumping together. How can this be avoided? Grains in water often carry an electric charge and repel each other by Coulomb forces. This is the stabilization process found by Faraday for gold colloids in pure water. The Dutch school of Verwey, Overbeck, Vrij and colleagues clarified this long ago. If salt is added, the Coulomb repulsions are screened out and the system clumps. Faraday detected this by a change of colour (from red to blue). Red corresponds to absorption of light by individual grains, blue to clumped systems.

It is often difficult to keep water salt-free on an industrial scale, so colloids must be protected by other means. The scribes of ancient Egypt needed ink, which was based on carbon black mixed with water. But this two-component mixture is unstable: the carbon grains attract each other by Van der Waals forces, clumping together and forming sediment within a few minutes. So the wise Egyptians added arabic gum (a polysaccharide obtained from the acacia tree). This is a long-chain polymer, which adsorbs onto the carbon grains, forming a 'halo' around each one. When two grains come close to one another, the halos overlap and create a repulsive force. The ink is thus stabilized, and lasts for months.

A more sophisticated method, developed by ICI, uses block co-polymers with a long, flexible 'A' chain bound end-to-end to another chain, 'B'. If the system is arranged so that A sticks to the grains, whereas B prefers the solvent, then a protecting halo of B is formed around each grain. This has been used in paints and is more efficient (but more expensive) than simple adsorption.



Sealed with a kiss: colloids have made lipsticks smacker-proof.

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Two important industrial challenges have recently been solved by using suitable colloid systems. The first is to make water-based paints, thus avoiding toxic solvents, that give a painted water-resistant surface. One trick is to start from a standard suspension of negatively charged pigment (plus Na^+ ions to balance the charge) in which the grains are electrostatically stable. This is then deposited in conjunction with a solution of Ba^{2+}. The Ba^{2+} forms permanent bonds between two grains, and the deposited paint is thus water-stable. This role of multivalent ions is currently the subject of Byzantine discussions between theorists—but the technique works!

The second challenge is that lipsticks, which are based on pigments and waxes, must be soft when deposited but should not be transferable during a kiss. An efficient, non-transferring lipstick has recently been invented, incorporating a block co-polymer that is transformed by saliva into a robust gel.

There are many unanswered questions in the theory of colloids: for instance, some charged grains do not repel each other properly. This can be due to the presence of multivalent ions (as mentioned above), or to some local arrangement of the ions (at small intergrain distances). This is important for biological molecules such as DNA and proteins. But colloid science is thriving, from cheap clays to sophisticated pharmaceutical systems, mainly because of the inventive minds of engineers, with the help of many available techniques (from expensive neutrons to cheap atomic force microscopes), and also with the modest assistance of theorists. ■

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FURTHER READING

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