

Monodisperse Colloidal Systems — Fascinating and Useful*

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Abstract

Monodisperse colloidal systems may form spontaneously (protein solutions, micellar solutions, micro-emulsions) or be obtained by fractionation (Perrin's suspensions of gamboge) or by cleverly controlled particle growth (Au, S, latex). The controlled particle growth consists of a nucleation or seeding phase and a growth phase in which the size distribution is narrowed. The size and size distribution can be checked by a variety of techniques, such as centrifugation, light scattering and electronmicroscopy.

Monodisperse systems have many applications, most of them in checking theories of fundamental aspects of colloid science, but also several in industry.

Introduction

For my subject I have chosen monodisperse colloids, i.e. dispersed systems in which all particles have the same or nearly the same size. It is a curious fact that colloid scientists have been interested in monodisperse (or isodisperse or homodisperse) sols from the early days of this science. Zsigmondy's gold sols¹, La Mer's sulfur sols² and the Dow Chemical Company latices³ immediately come to the mind as examples of monodisperse systems.

From where this interest in what appears to be a highly specialized and rare type of system? In the first place colloid scientists can often explain the properties of suspensions as due to the sum of contributions of individual particles or pairs of particles. Then, obviously explanations are more satisfactory and can be tested more critically if all particles have the same size.

A second, more emotional, aspect may help to explain this preference for monodispersity. We are chemists, trained to thinking in molecules, and the particles in suspensions and emulsions are the colloid chemist's 'molecules'. To a chemist all molecules of the same substance should have rigorously the same size (this with apologies to the polymer chemists).

The idea that colloid particles are molecules brings me to the early and very fundamental application

was to establish the reality of molecules by showing that colloidal particles, which are individually visible, behave quantitatively just as the elusive and invisible molecules. Around that time Einstein⁵ and Von Smoluchowski⁶ had given a theoretical treatment of this irregular thermal motion of particles and molecules, and in particular they had derived equations, in which Avogadro's constant, N_{Av} , is brought in relation to the r.m.s. displacement of particles in Brownian motion. These equations are

$$\langle x^2 \rangle = 2Dt \quad (1)$$

and

$$D = \frac{RT}{N_{Av}} \frac{1}{6\pi a} \quad (2)$$

where $\langle x^2 \rangle$ is the average square of the displacement in the x -direction

of monodisperse systems by Jean Perrin⁴. In the early years of this century Perrin was studying Brownian motion. One of his aims

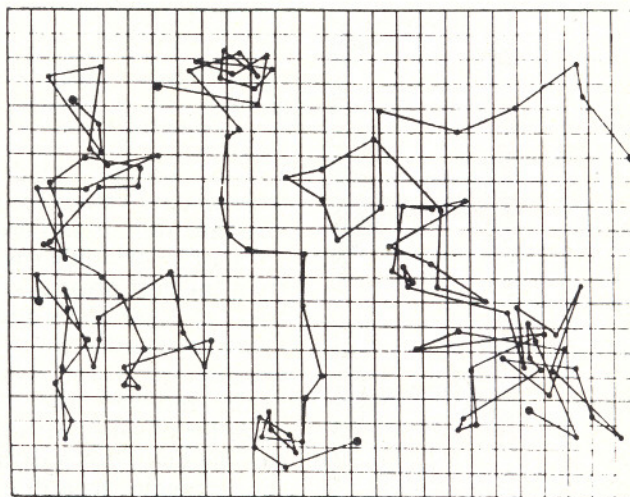


Figure 1. Brownian displacement of spherical particles (radius $a = 0.52 \mu\text{m}$) at 30 second intervals. The particles are suspended in water at 20°C . The squares of the lattice have a side of $3.125 \mu\text{m}$. From Perrin, *Les Atomes* 4.

* A. E. Alexander Memorial Lecture. (Abridged version).

Professor J Th. G Overbeek was Professor of Physical Chemistry in the van't Hoff Laboratory of the University of Utrecht for over 30 years until his recent retirement. He is one of the world's leading colloid scientists and was the Inaugural A. E. Alexander Memorial Lecturer. Professor Overbeek's visit was underwritten by a substantial donation to the A. E. Alexander Memorial fund by the Potter Foundation. This paper is an abridged version of the lecture presented at the Conference of the RACI Division of Colloid and Surface Chemistry, in Terrigal in February 1981.



in time t . D is the diffusion coefficient of the particles, R the gas constant, T the temperature, η viscosity of the medium and a the radius of the spherical particle.

Figure 1 gives an example of three series of measurements of the displacement of spherical particles ($a = 0.52 \mu\text{m}$) in consecutive intervals of 30 seconds. The particles are suspended in water at 20°C .

Since the vertical component of Brownian motion can overcome the force of gravity to a certain degree, a suspension of small particles does not settle to a dense layer at the bottom of the container, but shows a concentration that decreases exponentially with the height above the bottom, very similar, but on a vastly smaller scale, to the distribution in density in the atmosphere. Figure 2 shows the effect for two suspensions in water at level intervals of $10 \mu\text{m}$ and $12 \mu\text{m}$ resp.

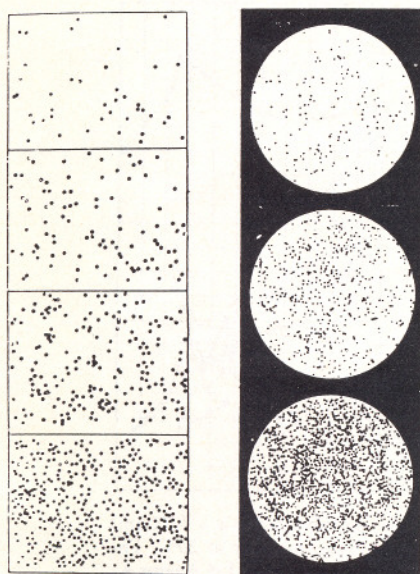


Figure 2. Two examples of the sedimentation equilibrium of suspensions. Fig. 2a for spheres of gamboge ($a = 0.29 \mu\text{m}$) at levels, $10 \mu\text{m}$ apart. Fig. 2b for spheres of mastic ($a = 0.52 \mu\text{m}$) at levels $12 \mu\text{m}$ apart. From Perrin, *Ann Chim. Phys.* 4.

For a valid determination of Avogadro's constant from such measurements the suspensions should be monodisperse and the size (and density) of the particles accurately known. Perrin describes how he and his students prepared these suspensions by dissolving gamboge or mastic in methanol and then precipitating the resin again by dilution with large volumes of water, leading to

emulsions of spherical particles, widely varying in size. He then subjected these emulsions to fractional centrifugation, finally obtaining small quantities of monodispersed particles. He states that in one case, starting with a kg of gamboge he obtained a few hundred milligram of uniform particles after several months of centrifugations. Figure 3 shows how a small amount of such a suspension, dried on a microscope slide, contains long rows of uniform particles from which the particle diameter may be derived.

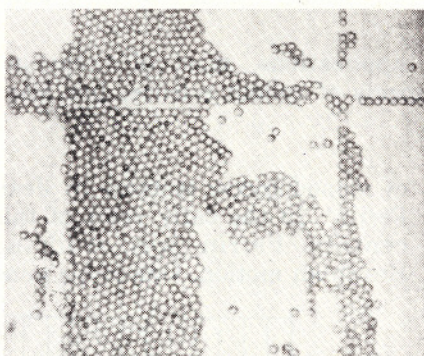


Figure 3. Microscope image of one of Perrin's suspensions dried on a microscope slide. From Perrin, *Les Atomes* 4.

From these and similar experiments values for Avogadro's constant were found around 6.0 to $7.0 \times 10^{23} \text{ mol}^{-1}$, only slightly higher than the best present value. At the time of their determination this constituted a veritable breakthrough for which Perrin justly received the 1926 Nobel prize for physics, with the citation that he had "put a definite end to the struggle regarding the real existence of molecules". In the same year two more colloid scientists received the Nobel prize, Zsigmondy, the postponed 1925 prize for chemistry and Svedberg, the 1926 prize for chemistry. Both play a role in my story about monodisperse systems. Zsigmondy's Nobel citation contained the words: "for proving the heterogeneous nature of colloidal solutions" (referring to his invention of the ultramicroscope) and "for the methods used which have laid the foundation of modern colloid chemistry". Among these methods the preparation and study of gold sols stands out. He used, with preference, the reduction of gold chloride solutions with formaldehyde and stressed

the need for extreme cleanliness. In his book he mentions that all his students had to master the preparation of the formaldehyde gold sol, in order to become aware of the need for precise and clean work in colloid chemistry. His big contribution to the knowledge of monodisperse systems is the working out of the seed method ("Keimverfahren")⁷ in which all the gold formed in the reduction process precipitates on nuclei added at the start of the process (the extremely fine Faraday gold sol⁸ with a particle diameter of about 3 nm , obtained by reduction with phosphorus dissolved in ether, often serves as the seed solution). Figure 4 shows that the number of gold particles that is observed at the end of the reduction is strictly proportional to the amount of seed solution, which proves that no new nuclei have been formed.

Zsigmondy mentions repeatedly that his gold sols (also the formaldehyde gold sols prepared without seed solution) are rather monodisperse. He concludes from the rate of reduction⁹ that the diameter of the particles grows at a constant rate until close to the end of the process, but he does not give a very stringent proof of the monodispersity.

Later experiments by Westgren¹⁰, however showed that Zsigmondy-type gold sols can be nearly ideally monodisperse. Westgren repeated Perrin's sedimentation experiments with Se sols and Au sols. With two sets of gold particles (radii 21 nm and 26 nm) he found not only a perfectly exponential decay of the concentration with height, but he found also a value of $6.05 \times 10^{23} \text{ mol}^{-1}$ for Avogadro's constant, very close to the present-day best value. These results prove that the particles must have been monodisperse.

And here we find a link with Svedberg. He was awarded the Nobel prize for his work on disperse systems, especially on their Brownian motion, but at the time of the Nobel prize ceremony he was concentrating his attention on his newly developed ultracentrifuge¹¹. One of the earliest experiments with a still rather primitive, mechanically-driven

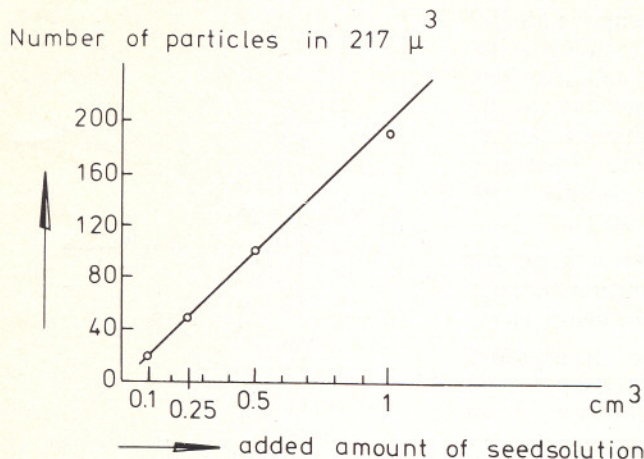


Figure 4. Showing that in the reduction of a constant amount of gold chloride by formaldehyde the number of particles observed is strictly proportional to the volume of seed solution (Faraday gold sol obtained by reduction with phosphorus). From Zsigmondy⁷.

ultracentrifuge was the centrifugation of gold sols. He investigated not only the sedimentation of gold sols and the like, but also that of protein solutions. He showed convincingly both in sedimentation velocity and in sedimentation equilibrium experiments, that proteins are truly monodisperse. His preparations might contain some impurities or a small fraction of aggregates but the bulk of the material behaved as true molecules, all of the same size. Figure 5 shows the difference in sedimentation rate between a monodisperse protein sedimenting with a sharp boundary and a polydisperse gold sol, where the sedimenting boundary becomes increasingly vague with time.

Svedberg's early values for the molecular weight of hemoglobin ($M = 68\ 000$), phycoerythrin ($M = 208\ 000$), phycocyanine ($M = 106\ 000$) and egg albumin ($M = 34\ 500$) may not be the best available now, but they are still close to the mark and at that time the monodispersity was the main point, proving that proteins were well defined molecules, rather than aggregates of smaller polypeptides.

What a difference between the work of these three great men! Perrin painstakingly, practically handpicking his resin particles, Zsigmondy introducing a chemical method still much in use today for preparing monodisperse systems and Svedberg, turning to nature and finding his monodisperse solutions nearly ready-made.

Preparation of Monodisperse Systems

If we discard fractional centrifugation as not very practical and realize that finding monodisperse suspensions ready-made in nature is of very limited applicability, we want to know the essential requirements for preparing monodisperse systems.

Remarkably enough, all methods used so far can be derived from Zsigmondy's seed method. The method has been refined and diversified, but the principle is always the same:

Arrange the formation of the dispersed material in such a way that all nucleation takes place in a very short period and supply additional material so slowly that it can find its way to the nuclei without the supersaturation reaching a level at which further nucleation could occur.

La Mer¹² expressed this in a simple diagram relating to his preparation of sulfur sols from acidified thiosulfate (figure 6). Sulfur is formed by a chemical reaction, its concentration increases, and ultimately rises so far above the

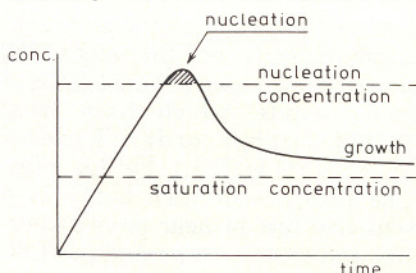


Figure 6. Illustrating the formation of a monodisperse system by controlled nucleation and growth.

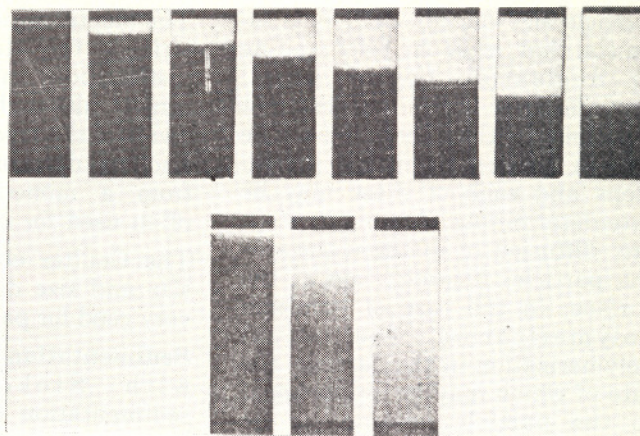


Figure 5. Progress in time of sedimentation of hemocyanine (from snails' blood), sedimenting with a sharp boundary and of a polydisperse gold sol, sedimenting with an increasingly broadening boundary. From Svedberg¹⁰.

saturation concentration that nucleation occurs. This results in the formation of many nuclei in a short burst. They grow rapidly, which lowers the concentration to a value below the nucleation concentration, but high enough to allow particle growth to occur at a rate that just consumes all further sulfur that is generated.

The nucleation burst may be replaced by the addition of seed particles.

It is through the work of La Mer and his associates that colloid scientists became aware of the wide potential of the controlled nucleation and growth method for preparing monodisperse systems, not only in water but also in gases as **aerosols**.

The method has been applied to a great variety of systems, such as aerosols of dioctylphthalate, oleic acid and other oils¹³ (often using NaCl seed particles), and hydrosols of gold¹, sulfur¹⁴, silver halides^{15,16}, chromium hydroxide¹⁷, aluminium hydroxide¹⁸, and silica¹⁹. A very well known application is the formation of monodisperse latex in emulsion polymerization²⁰.

These systems and several others have found a variety of applications in the study of light scattering, coagulation, rheology, etc. We will come back to these applications later.

Why Seeding or Early Nucleation nearly always leads to Monodispersity

To obtain monodispersity (or to put it more accurately: a narrow

particle size distribution) it is essential that, after the brief seeding or nucleation period, small particles grow faster or at least not more slowly than large ones. The growth process contains several steps and each of these may be rate-determining. The main steps are: diffusion of material towards the particle; incorporation at the surface; in the case of emulsion polymerization, the actual polymerization in the particle, the rate of which may be proportional to the particle volume, or be independent of particle size (Smith and Ewart²¹) or in between these extremes. Each of these steps leads to a growth law of the form

$$\frac{da}{dt} = ka^n \quad (3)$$

where n varies from -2 to $+1$. For all $n \neq 1$ the relative particle size distribution ($\Delta a/a$) sharpens with growth (small particles grow relatively faster) and even for $n = 1$ (bulk reaction proportional to volume) the relative distribution does not widen. So, whatever the details of the growth process (aggregation excluded) the distribution improves with growth or at worst remains constant (Bradford, Vanderhoff and Alfrey²², Overbeek²³).

Methods for the Determination of Particle Sizes and Particle Size Distributions

For the determination of particle sizes, direct observation in the **microscope**, although obvious, is only feasible in the rare cases where large particles ($>1 \mu\text{m}$) are involved. When the particles are in contact and form a regular pattern as shown in figure 3 even somewhat smaller sizes may do.

By introducing dark field illumination and so converting the microscope to an **ultramicroscope** Zsigmondy extended the range of observation down to particles of about 10 nm, and by counting the particles in a known volume of the dispersion could obtain their average size. The ultramicroscope gives only rather qualitative information on the size distribution from an estimate of the intensity of the light scattered per particle.

The **electronmicroscope** is ideally suited for determining size distributions in the colloidal size range, although one has to be aware of the possibility of artefacts and of deformations. Particles from a monodisperse latex are often used for calibration.

The Coulter **counter** is good for size and size distribution but not very good for particles below $1 \mu\text{m}$.

Sedimentation rate, interpreted with Stokes' law, and sedimentation equilibrium have been used with normal gravity and with the ultracentrifuge¹¹. They are suitable for average size and size distribution, especially if the size distribution is wide.

Although **light scattering** by colloids has been known since Tyndall²⁴, the use of light scattering for the determination of particle sizes and size distribution dates really from 1944 when Debye²⁵ applied the method to solutions of micelles and polymers.

For small particles that do not absorb the light, light scattering leads only to an average particle size (molecular weight), but when the particle radius is more than about one-third of the wavelength (λ) of light, interference due to length differences between different pathways of light starts to become important, the scattering develops maxima and minima as a function of the scattering angle and these allow an estimate of the size distribution. Figure 7 shows such a pronounced profile for sulfur particles in water scattering red light.

This feature can be used in at least two different ways. Since the angular position of maxima and minima depends on a/λ , rather than on a or λ separately, they shift when the wavelength is changed. Thus, if white light is scattered, not only the intensity but also the color of the scattered light depends on the angle. In practice one sees a series of red and green bands, which have been called Higher order Tyndall Spectra (H.O.T.S.) by La Mer. The presence of such bands is a sensitive test of near monodispersity and their number and position allow the particle size to be estimated. It is also possible to measure the intensity and

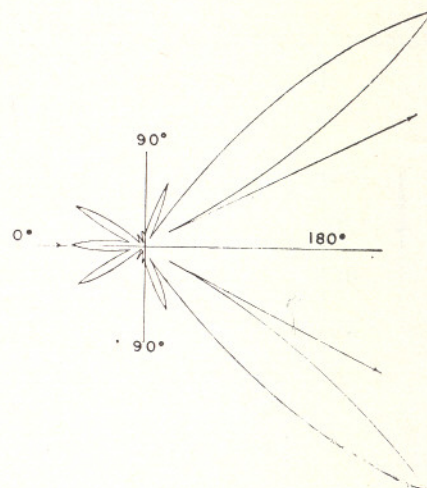


Figure 7. Intensity of the vertically polarized component of the light scattered by a spherical sulfur particle in water according to the Mie theory, $a = 3\lambda/\pi$. Incident light and direction of observation are horizontal. The distance of the centre of the figure to the contour is proportional to the scattered intensity. For a small particle ($(a/\lambda) \rightarrow 0$) the contour is a circle. Reprinted with permission from I. Johnson and V. K. La Mer, *J. Amer. Chem. Soc.* 69, 1947 1186. Copyright 1947, American Chemical Society.

polarization of the scattered light at a number of angles, compute these values from the Mie theory²⁶ for chosen sizes and distribution widths and see which combination of values fits the data best. This approach has been used by Kerker and associates²⁷.

With the availability of lasers as light sources it has become possible to study the change in wavelength of the scattered light, as compared to the incoming beam. The Brownian motion of the particles in a suspension causes such a shift in wavelength and by analysing this shift by photon correlation spectroscopy²⁸ the diffusion coefficients, the radius of the particles (see eqns. (1) and (2)), and in principle also their size distribution can be determined.

The Experimental Situation

Let us now turn to experiments on monodisperse systems and see how well the theories explain them.

Zsigmondy¹ mentions repeatedly that good formaldehyde **gold sols** have rather uniform particles, and that the seed method allows one to prepare sols with uniform particles of a predetermined size.

Many years later Turkevich and coworkers²⁹ studied gold sols prepared in many different ways,

measured their size distribution by electron microscopy and found an "exponential law of growth" using light absorption. They found that reduction (without seeding) by sodium citrate led to rather monodisperse sols ($a = 9 - 10$ nm, spread about 10%) which could be grown by further reduction by hydroxylamine to $a \approx 50$ nm with the relative width of the distribution remaining unchanged.

Aerosols generated by condensation of vapors on nuclei of NaCl, AgCl and the like, prepared by the method of Sinclair and La Mer¹³ and refinements of it³⁰, vary in radius from about 10 nm to about $1 \mu\text{m}$ with geometric mean standard deviations of the order of 10-20%, in favorable cases even as low as 3%.

La Mer's sulfur sols can have a very narrow size distribution as shown by their light scattering³¹ and as expected from diffusion controlled growth ($d(\bar{a})^2/dt = \text{const.}$).

Kerker et al.²⁷ in very careful experiments with sulfur sols showed that the relative size distribution (found from an analysis of the Mie light scattering) narrows during the first hours of the preparation, broadens rapidly between 3 and 3.5 hours (some coagulation?) and then stays about constant (Fig. 8). In contrast with La Mer's data they conclude that the volume growth is constant in time ($d(\bar{a})^3/dt = \text{const.}$). The difference may be due to slightly different experimental conditions. Figure 8 shows how the size distribution changes with time.

By studying the competitive growth in an **emulsion polymerization** seeded with a mixture of two monodisperse polystyrene latices of different sizes, Bradford, Vanderhoff and Alfrey²² concluded that n in our eq. (3) has values between 0 and 0.5, and certainly not $n = -2$ as required in Smith and Ewart's theory²¹. Bradford et al.'s n value points to a mixture of surface reaction ($n = 0$) and reaction in the bulk of the particles ($n = 1$) and is just good enough for some sharpening of the distribution with progress of the reaction. This technique of competitive growth

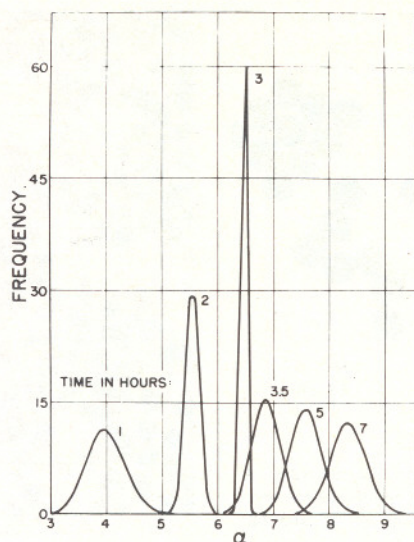


Figure 8. Size distribution in La Mer type sulfur sols at different times after mixing of the ingredients ($\text{Na}_2\text{S}_2\text{O}_3$ and HCl). $a = 2 a/\lambda$, where λ is the wavelength of light (436 nm) is plotted on the abscissa. Each unit corresponds to 69.4 nm in the radius. From ref. 27. Reprinted with permission from *J. Phys. Chem.* 67, 1963, 2111. Copyright 1963, American Chemical Society.

(also used by Turkevich²⁹ in his work on gold sols) appears to be a powerful technique for studying reaction mechanisms since it is enough to measure the shift of the two peaks in a bimodal distribution, easily done by electron microscopy, rather than having to determine a size distribution in detail.

Monodisperse sols of **silver halides** have been prepared in various ways. All methods have in common that the nucleation or seeding stage is separated in time from the growth phase. The particles formed are rounded cubes, octahedra or other crystal shapes, **rarely spheres**. Ottewill and Woodbridge¹⁵ prepared silver halides by careful dilution of complex solutions or in the case of AgBr, which is 40 times more soluble at 100 °C than at 20 °C by cooling of a hot solution (Fig. 9). Klein and Moisar¹⁶ obtained monodisperse crystals by preparing nuclei of silver halide in gelatin solution and allowing these nuclei to grow by careful addition of further halide and silver nitrate.

Fairly recently Matijevic and coworkers have added a group of metal oxides and hydrous oxides to the systems that can be prepared in relatively monodisperse form.

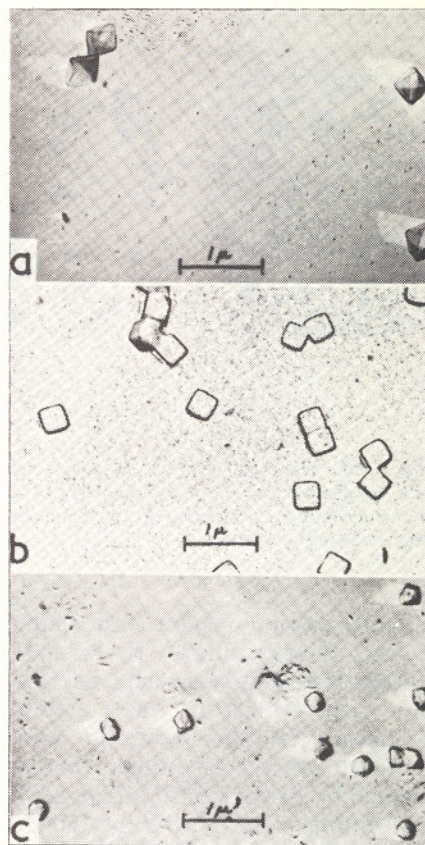


Figure 9. Electron micrographs of carbon replicas shadowed with Cr at a 60° angle. a AgBr prepared from excess NH_4Br . b AgBr prepared by cooling a 2×10^{-5} M solution from 100°C to room temperature. c AgBr prepared from excess AgNO_3 . Reprinted with permission from R. H. Ottewill and R. F. Woodbridge, *J. Colloid Sci.* 16, 1961, 588.

The first of the group was chromium hydroxide¹⁷, followed by various others and including now at least the hydrous oxides of Cu, Fe and Al, TiO_2 and basic ferric sulfates^{18, 32}. The technique used consists in allowing solutions of the metal sols, usually in the presence of complex forming sulfate or phosphate ions, to hydrolyse slowly at elevated temperatures. It seems that the slow hydrolysis provides the material of the particles which reaches a concentration at which a burst of nucleation occurs, after which the growth with narrow size distribution continues. The conditions of hydrolysis vary between the different metals. The particles are sometimes spherical, but many deviating forms have been found. Figure 10 gives a few examples. Particles may be clearly crystalline or amorphous.

As a last example we mention silica particles. In view of the many applications of colloidal

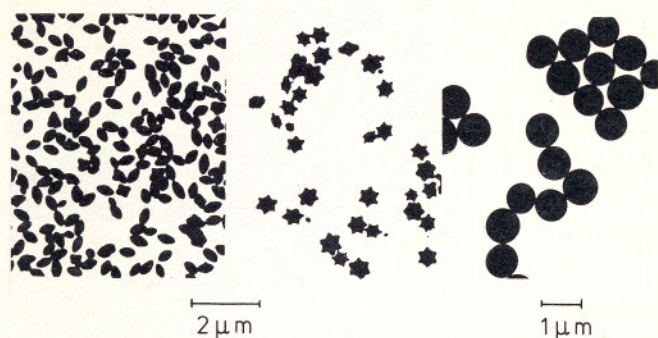


Figure 10. From left to right: electron micrographs of particles of α - Fe_2O_3 obtained from nitrate solution; α - Fe_2O_3 from perchlorate solution; aluminium hydroxide from $\text{Al}_2(\text{SO}_4)_3$ solution. From refs 17 and 18. Reprinted with permission.

silica (known as Ludox and under other tradenames) it is not unexpected that sols with a narrow size distribution have been prepared. In the Bechtold and Snyder¹⁹ process a seed solution is formed by heating 3.5% silicic acid containing some NaOH to 100°C. The seed particles are 2-3 nm in radius. These particles are allowed to grow by addition of a similar solution containing smaller particles. The added silica passes from the small particles to the large ones leading to final radii of 5-65 nm. More porous particles, but having quite a narrow size distribution are prepared according to Stober, Fink and Bohn³³ by hydrolysis of ethylorthosilicate in alcoholic solution in the presence of ammonia. The slow reaction in which particles of up to 1 μm diameter may be formed, presumably passes a state of nucleation followed by growth. Figure 11 gives three examples of such particles with surfaces afterwards esterified with stearyl alcohol, prepared by Van Helden and Vrij³⁴.

An interesting question presents itself now. Would it be possible to prepare monodisperse systems from any desired substance? A definitive answer cannot yet be given, but for substances of sufficiently low solubility the chances seem to be good. Providing the burst of nuclei or using a seed solution, possibly heterogeneous (e.g., gold nuclei for silver particles) should be feasible. The essential difficulty may then be to

provide further material slowly by chemical reaction, change of temperature, even slow addition, especially if nuclei are already formed at small supersaturation.

Applications

In the applications of monodisperse systems two aspects can be distinguished. In the first group of applications monodispersity is essential for testing theories or for using these systems as models. In the second group monodisperse systems are used in production processes.

Testing theories; use as models

- The very important aspects of investigating Brownian motion and determining Avogadro's constant have been discussed already.
- At least two aspects of colloid stability have been approached with monodisperse latices. An experimental proof of a refinement of Smoluchowski's³⁵ theory of rapid coagulation has been given by Lichtenbelt *et al.*³⁶. The influence of particle size on the rate of slow coagulation was investigated by Ottewill and Shaw³⁷ and found not to agree with the theoretical expectations. Wiese and Healy³⁸ have made an interesting, but not completely convincing, attempt to reconcile theory and experiment. Further work with

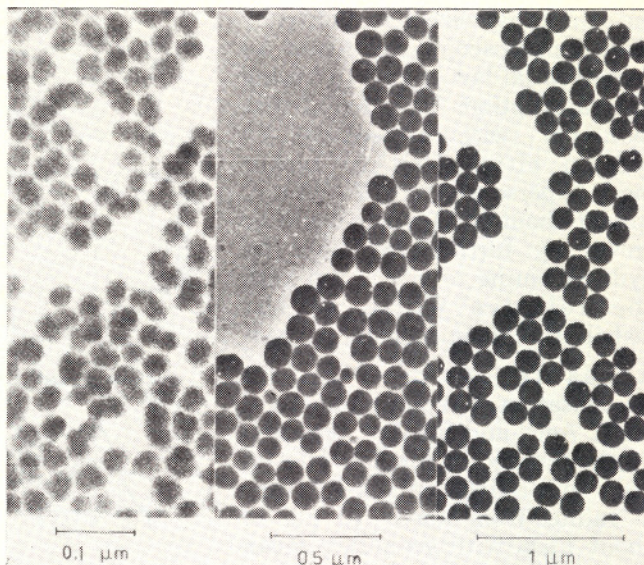


Figure 11. Electron micrographs of three different silica samples prepared by hydrolysis of ethyl silicate and coated with stearyl groups. Reprinted from ref. 34 with the author's permission.

other monodisperse systems might shed more light on this problem.

- Reaction mechanisms of the emulsion polymerization^{3,22} and of the formation of sulfur from $\text{S}_2\text{O}_3^{2-} + \text{H}^+$ ³¹ have been tackled with monodisperse latices or sulfur sols respectively.
- Monodisperse dispersions have been used to check the theory of light scattering. Later, the confidence in the theory became so strong that light scattering was used to obtain information on dispersions^{27,39}.
- Diffusion coefficients in supersaturated (but very dilute) solutions have been determined by La Mer and coworkers^{12,31}.
- La Mer and Gruen¹³ could confirm the Kelvin equation from the swelling of aerosol particles with toluene or chloroform. Ugelstad⁴⁰ prevented the degradation of emulsions by diffusion driven by the Kelvin effect by adding oil soluble solutes of low water solubility to the emulsified oil, and on the same basis could prepare monodisperse latices of very large (10-15 μm) droplet size.
- Concentrated monodisperse latices, silica sols and microemulsions have been used as models for hard sphere (and soft sphere) liquids⁴¹ and phase transitions of these liquids to crystalline 'solids' have been observed^{42,43}.

- h. Dilute and concentrated monodisperse suspensions (and emulsions) are good for rheological studies.
- i. The influence of particle size on the retention of aerosols in filters and in the lung⁴⁴ and on the deposition on leaves has been measured.

Technical Applications

- a. Polystyrene and other hard latices serve as calibration standards for electronmicroscopy^{3, 20}
- b. The iridescent colors of precious opals appear to be caused by a regular packing of silica spheres about 100-300 nm in diameter⁴⁵. Gaskin and Darragh⁴⁶ patented a process for making synthetic opal-like material based on such a silica 'lattice' in which the space between the spheres was filled with a material having about the same refractive index as the silica particles. Similar optical effects are given by latex 'crystals'.
- c. It has been suggested⁴⁷ to use the surface structure of dried and partly coalesced layers of latex particles as diffraction gratings (figure 12).
- d. Packed monodisperse spheres e.g. of SiO₂ can form a base for catalysts with a well defined, rather open, pore structure. The same structure is useful in chromatographic columns.
- e. Optical effects of thin layers of deposited silica and other particles are used in antireflection coatings.
- f. Composite materials e.g. silica in rubber can be based on monodisperse particles.
- g. In photography monodisperse AgBr may have an advantage. Colloidal silica plays an essential role in Polaroid photographic material⁴⁸, in the layer in which the silver image is developed.
- h. Colloidal silica has many other applications, such as forming thin insulating layers, hydrophilizing surfaces, changing viscosity, friction and adhesion. For more details we refer to Iler's book¹⁹.
- i. Monodisperse dispersed dyestuffs would have optical

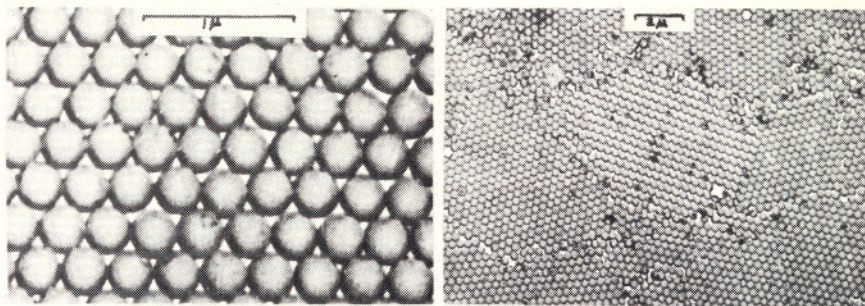


Figure 12. Crystalline latex formed by allowing latex to dry out to a film of about 2 mm thick. The electron micrographs are made from silicon oxide replicas of the surfaces of these films. From: E. B. Bradford, *J. Appl. Phys.* 23, 1952, 609.

advantages if the size of the particles is matched to the optical absorption coefficient.

- j. Pharmaceutical and agricultural preparations will probably act more reproducibly if they are monodisperse.

In many of these practical applications strict monodispersity is not so important as the fact that particles are in a suitable size range and that both extremely small and very large particles are avoided.

Conclusion

Monodisperse systems are pretty to look at, it is fascinating how they are made, by nature or by man. They have found and still find numerous applications in fundamental science. There are interesting although — as yet — relatively few technical applications. It seems that apart from the cases of silica and latex, there may well be still undiscovered (or undisclosed) fields of application such as exploiting the optical effects but also in magnetic tapes or fluorescent screens. This may be an area of 'solutions in search of problems to be solved'.

Acknowledgement

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