

Colloid Science



1.1 What is a colloid?

A colloid refers to a piece or chunk of matter dispersed in another phase. It is the size of the piece that matters.¹ A colloid is *big enough* to be much larger than the atoms or molecules around it (or inside it), but – as we will see shortly – *small enough* that it exhibits some properties of the molecular scale (namely, Brownian motion). Colloid is a term that has come to encompass solid particles suspended in a liquid (a colloidal dispersion), microscopic droplets in a liquid (an emulsion), or either solid or liquid phases suspended in a gas (an aerosol).

1.2 Gallery of colloids

Fig. 1.1 is a gallery of colloidal particles that have been used in our laboratory, including:

- polystyrene latex particles (obtained commercially and synthesized in-house)
- polystyrene dumbbells (or dicolloids)
- zeolite particles
- silica particles
- titania nanoparticles
- fluorinated ethylene propylene (FEP) particles

Many more materials consist of colloids than just these, including clays, milled organic crystals, carbon black, fumed silica, calcium carbonate fillers, ferrofluids, and others. Additional examples are shown in fig. 1.2 from my colleague Norman Wagner's lab.

1.3 Length scales

Because of its “macroscopic” dimensions, the electrostatic (and electrodynamic) or mechanical behavior of an individual colloidal particle can be modeled as a continuum – macroscopic theories such as continuum mechanics or electrodynamics with the use of constitutive relations (e.g. bulk moduli, dielectric constants, etc.) Of course, these boundaries are fuzzy. That's where some exciting science and interesting physics and chemistry often occur. All of the images, with the exception of figs.

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¹The IUPAC definition of a colloid is a “state of subdivision such that... particles dispersed in a medium have at least one dimension between approximately 1 nm and 1 μm ...”

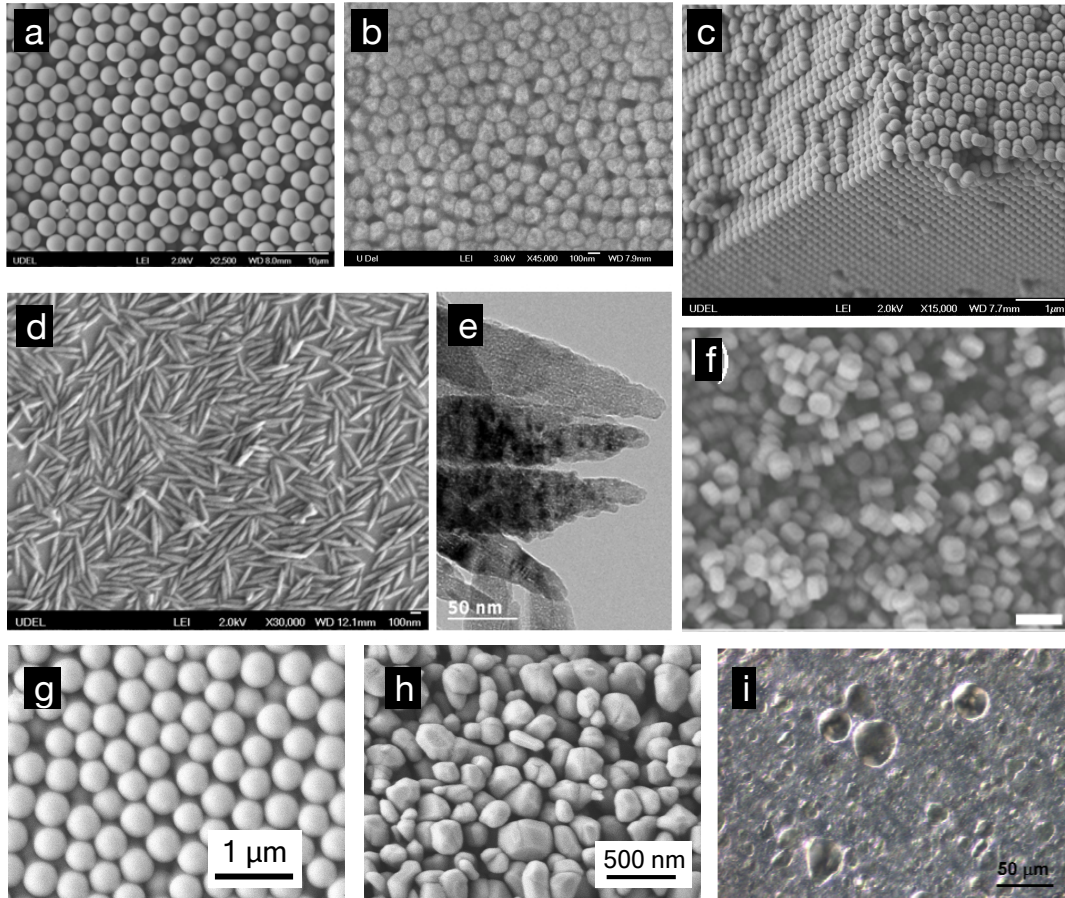


Fig. 1.1 A gallery of colloids and nanoparticles. (a) Monodisperse polystyrene latex; (b) fluorinated ethylene propylene (FEP); (c) polystyrene dumbbells in an ordered array; (d) titania nanospindles with (d) transmission electron microscopy; (f) ZSM-5 zeolite particles; (g) silica colloids; (h) commercial titania dispersion; (i) polydisperse colloids and particles of a wax-like particle.

1.1e and 1.1i, are taken with scanning electron microscopy. The polydisperse wax-like particles shown in fig. 1.1 were imaged using bright-field microscopy. Fig. 1.1e is a transmission electron micrograph that shows some of the detailed (heirarchical) structure of titania nanospindles grown from a sol-gel synthesis. (Sugimoto *et al.*, 2002; Sugimoto and Zhou, 2002; Sugimoto *et al.*, 2003a; Sugimoto *et al.*, 2003b) Sometimes we can think of macromolecules, proteins, or nanoparticles as on the smaller range of the colloidal scale, but in other instances its their molecular nature that seems to dominate their behavior.

Let's examine the relative sizes of a colloid and the molecules in the suspending phase. If we assume that a colloid is a hard sphere and think of its densest packing, a face-centered cubic crystal, then, at most, the centers of twelve identical colloidal neighbors can fit in a volume defined

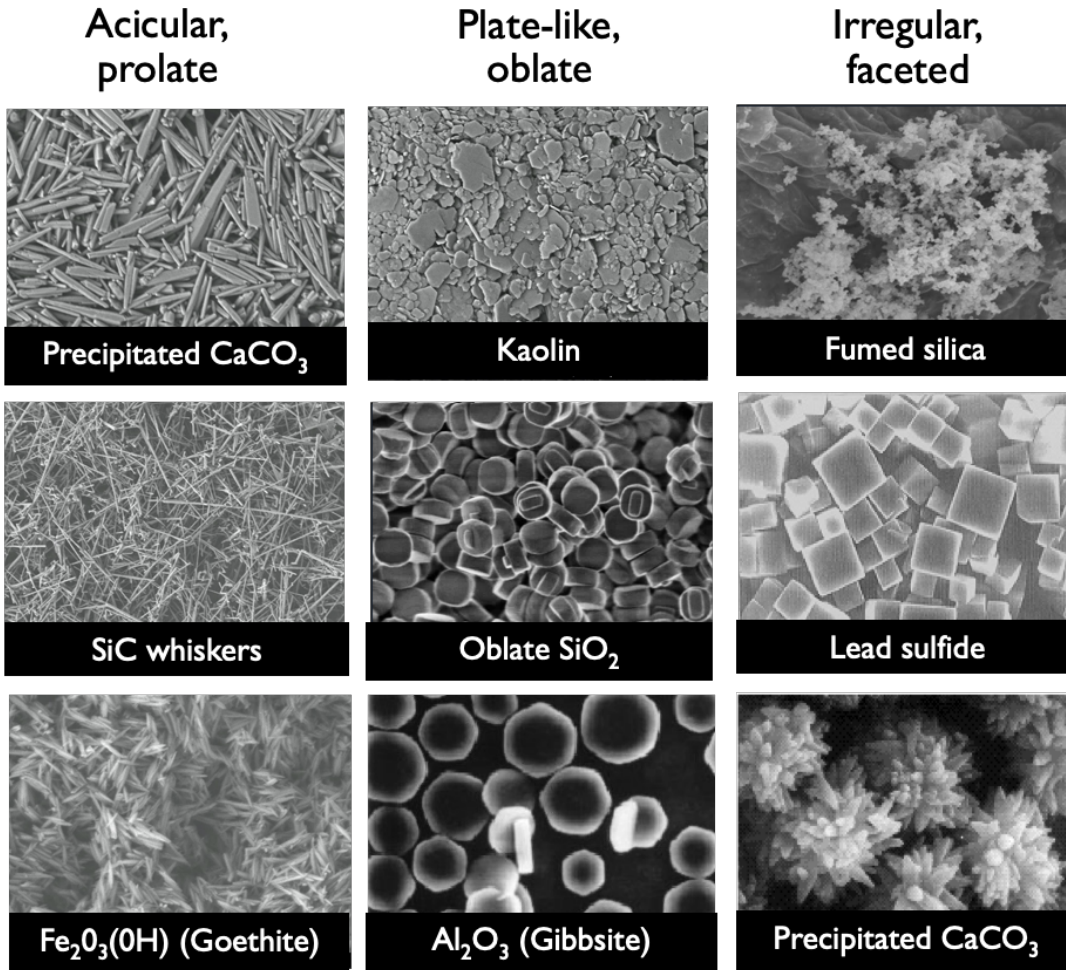


Fig. 1.2 More colloids. Images courtesy of Norman J. Wagner.

by

$$\frac{4}{3}\pi(2a)^3 - \frac{4}{3}\pi a^3 = \frac{28}{3}\pi a^3 \quad (1.1)$$

where a is the particle radius. How many water molecules would fit in that volume? The density of water at room temperature is 998 kg/m^3 and its molecular weight is 18.01528 g/mol (or 0.0180 kg/mol). Avagadro's constant is 6.0221409×10^{23} , giving us a volume of about $\bar{V} = 3 \times 10^{-29} \text{ m}^3$ per molecule.² So, whereas 12 colloids can fit around our central particle, the same volume would fit

$$\frac{28}{3} \frac{\pi a^3}{\bar{V}} = 1.2 \times 10^{11} \quad (1.2)$$

water molecules if the colloids are $1 \mu\text{m}$ in diameter.³

² $\bar{V}^{-1/3} \sim 3.1\text{\AA}$, so roughly 3 Ångstroms in diameter.

³*Something to consider:* How many polystyrene molecules (or styrene sub-units) make up a polystyrene latex particle? How many silicon and oxygen atoms are in a silica colloid?

The size difference with the molecular scale also means that there is a significant separation of timescales between molecules and colloids, too. A colloid is big, lumbering, and slow relative to the zipping molecules around it. This difference has interesting implications for the hydrodynamic and Brownian forces that we'll discuss a little later. The upper limit of the colloidal size comes with a decreasing thermal motion. Once particles are more than a few micrometers in all of their dimensions, they behave more like granular solids.

Colloids come in all shapes and sizes—spheres, rods, discs, cubes, even dumbbells and more. Somehow, the field tends to imagine colloids as spheres. It's more mathematically tractable in many cases to solve problems for spheres, such as their interactions or the drag force on them exerted by a fluid. But, we'll try to comment on the effects and influence of particle shape throughout this text.

By the way, why should we study colloid science? Well, many technologies and products rely on some form of a dispersion of colloids, whether they are active pharmaceutical ingredients (API's), foods, consumer products, or ceramics.⁴ It is also common to engineer materials on the colloidal scale to control their flow (rheology). We call this “building” or developing structure to engineer *complex fluids* and complex fluid rheology. One important and ubiquitous application is to design a *yield stress* in a fluid, such that it flows only when we want it to.⁵ (Nelson *et al.*, 2019) It's also an interesting and important length scale in physical biology, including the function and processes of cells and the organization and structure of biomaterials. And one final point: colloids are big, slow particles that can be seen under a microscope and yet can be modeled by the same statistical physics as molecules and atoms. They are wonderful experimental systems for studying fundamental physics and condensed matter.

⁴... flow batteries, polymer fillers, etc.

⁵It's the colloidal-scale *structure* that often differentiates complex fluids from simple fluids.

1.4 Historical notes

⁶*Soft matter* was a name coined by Pierre-Gilles de Gennes in his Nobel Prize talk. He didn't like the name “complex fluids” used at the time by many scientists and engineers to describe polymers, emulsions, and colloidal dispersions. (de Gennes, 1992)

⁷Κόλλα is the Greek word for glue.

As a subfield of soft matter science,⁶ colloid science is fairly old. It's not flashy and new, like polymers (mid-20th century) or *nanomaterials* (early 2000's). The foundations of colloid science date before even the emergence of our modern atomistic understanding of the natural world. The first use of the term *colloid* is attributed to Thomas Graham (1805–69), who found that certain putative solutes would not pass through a parchment membrane, but stayed on one side, as if held or “glued” together⁷ (Graham, 1861; Graham, 1864). Graham discovered that these “colloids” were actually small particles.

Around the same time as Graham's work, Robert Brown (1773–1858) was studying the animated motion of tiny particles (including organelles released from pollen grains) under a microscope (Brown, 1828). These tiny objects jiggled and jerked spontaneously, and appeared to change shape, presumably by rotating in his microscope's field of view. How fascinating this sight must have been! In the mind of an early 19th century

investigator, the distinctions between the animated matter of life and otherwise inanimate matter must have been somewhat blurry. Was this ubiquitous and unquenchable movement evidence of a “vital force” that powered life? There was no physical theory for such motion at the time – and there wouldn’t be until nearly a century later when Einstein, Sutherland, Langevin, Smoluchowski, Perrin, and others definitively proved the atomistic nature of matter⁸ and explained Brown’s movement as thermal motion through the kinetic theory of heat (we’ll get to that in a bit).

Brown was a meticulous experimentalist. Where others jumped to the conclusion that they had found evidence of a vital force, Brown carefully ground up all sorts of materials into well-characterized particle sizes – not just pollen grains. He tested inorganic and organic solids and substances that were once organic, but transformed (such as coal.) Brown observed that any of these particles, as long as they were about $1/30,000^{\text{th}}$ to $1/20,000^{\text{th}}$ of an inch in size ($0.85\text{--}1.3\ \mu\text{m}$), exhibited random motion when dispersed in water. He called them *molecules*.⁹

I’m fascinated by Brown’s experiments, but also by his dedication to sensible observation. One of his unique control samples was to grind up a piece of the Sphinx of Giza – you can never be too sure. Brown’s studies were performed just a decade after Mary Shelley’s *Frankenstein* in 1818, whose protagonist develops a technique to impart life into non-living matter. I’m sure that we don’t read *Frankenstein* today with the same sense of what might have been possible in the minds of those living in the early 19th century. Our thoughts, steered by deep-seated understanding of the physics and chemistry of biology, have to adopt a robust suspension of disbelief. In the minds of Shelley and Brown’s contemporaries, perhaps it was far more plausible that an unknown vital force could move into or out of the animate and inanimate.¹⁰

1.5 Time scales

We noted in section 1.1 that the size difference between colloids and molecules leads to the idea that characteristic *length scales* are at the very heart of the definition of a colloid. From these length scales, corresponding time scales emerge. Below we note a few of the important time and length scales in a colloidal suspension without concerning ourselves (yet) about the details of their origin or their derivation.

¹⁰In his recent book, England (2020) “explores the physics of what makes some configurations of matter lifelike and others inert” (Mukamel and Glaser, 2021). The ability to self-replicate, form ordered and functionally specialized structures, harness energy sources, and respond to environmental stimuli “can be understood through physical processes that occur in ordinary, lifeless materials when driven by an energy source.” His book reaches further back than Shelley, illustrating our human distinctions between living and non-living from the pentateuch’s Book of Exodus – Moses’ staff turning into a serpent, and the burning bush, which isn’t consumed by the fire (and also projects the voice of Moses’ God).

⁸Contemporary with the developing understanding of the electron and the nucleus and the Bohr model and the Schrödinger models of the atom.

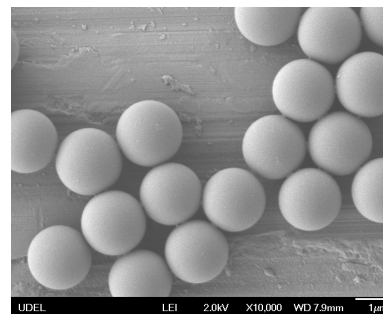


Fig. 1.3 Micrometer diameter polystyrene latex colloids.

⁹Brown’s “A brief account of microscopical observations made in the months of June, July and August, 1827, on the particles contained in the pollen of plants; and on the general existence of active molecules in organic and inorganic bodies” is dated July 30th, 1828.

Rotational diffusion? Timescale for molecular collisions in a fluid?

1.5.1 Vorticity timescale

A colloidal particle set in motion with radius a disturbs the surrounding fluid. The propagation of this disturbance is the *vorticity timescale*,

$$\tau_\eta = \frac{a^2}{\nu} = \frac{a^2 \eta_s}{\rho_s} \quad (1.3)$$

where ν is the kinematic viscosity (momentum diffusivity) of the fluid. For a 100 nm diameter particle suspended in water, which has $\nu \approx 10^6 \text{ m}^2/\text{s}$, $\tau_\eta \sim 2.5 \text{ ns}$. For a micrometer diameter particle, the time scale is 100 times larger, or about 250 ns. The vorticity time scale is one of the shortest that we will define. It has important implications for how we model the fluid mechanics (hydrodynamics) of colloidal suspensions.

1.5.2 Inertial timescale

Related to the vorticity timescale is the particle inertial timescale,

$$\tau_I = \frac{2\rho_p}{9\rho_s} \tau_\eta. \quad (1.4)$$

When a particle is pushed, by for instance, an external force or even the “impulse” of thermal motion, this is the time scale over which the particle moves “ballistically” – carried by its (and the surrounding fluid’s) inertia. When we model the dynamics of colloidal suspensions, the fast inertial timescale means that it can normally be neglected. The resulting equations of motion are overdamped, first-order equations. τ_I is of the same order of magnitude as τ_η .

1.5.3 Brownian timescale

Thermal fluctuations push our big colloidal particles around. The timescale over which the particles will move their own radius is the *Brownian timescale*,

$$\tau_B = \frac{\pi \eta a^3}{kT} \quad (1.5)$$

where kT has the usual meaning of thermal energy, the product of the Boltzmann coefficient k and absolute temperature T . This is the characteristic time scale on which particles tend to rearrange into new configurations – a fundamental *relaxation* time scale that governs not only a suspension’s dynamics, but also its mechanical properties (rheology), the kinetics of phase separation and flocculation (aggregation), and other phenomena and properties.

τ_B is typically much larger in magnitude than τ_I . For the same 100 nm diameter colloids, $\tau_B \approx 0.1 \text{ ms}$, which is $\mathcal{O}(10^4)$ longer than the inertial timescale. For a one-micrometer diameter colloid, $\tau_B \approx 100 \text{ ms}$ – still short enough that particles move sufficiently to rearrange and equilibrate. In fact, the particles move slowly enough and are large enough that they are easily tracked under a light microscope – enabling

colloids to be used as “model atoms” to test theories of condensed matter physics, as probes for microrheology experiments, or to test fundamental theories of the atomic nature of matter, as Jean Perrin and his students did in the early 20th century.

When a particle diameter reaches $10\ \mu\text{m}$ or so, the Brownian time is much longer – $\tau_B \sim 100\ \text{s}$ in water. The dynamics of the suspension slow and particles can no longer equilibrate on reasonable time scales. We’ve left the colloidal domain!

1.5.4 Separation of time and length scales

We remarked earlier about the separation of length and time scales earlier, but now it should be clearer. One of the important consequences of these is that the fluid phase of a colloidal dispersion will often be modeled as a *continuum*, much like the mechanical and electrodynamic properties of the colloids themselves. We can normally forget about its molecular nature and just use continuum mechanics models and their associated constitutive equations (e.g. viscosity) to account for their influence. Similarly, the Brownian forces are actually separated and modeled as random forces rather than collisions with the solvent molecules – the same collisions that also induce hydrodynamic drag forces.

Nevertheless, we should be mindful of the continuum approximation we are using. As particles become smaller – perhaps we can think of globular proteins or gold nanoparticles as colloids – the molecular nature of the surrounding material may become more important. The solvent may have a different structure in the vicinity of the particle. Ions in solution may bind to and crowd on the surface in ways that exert a more molecular nature, even for much larger colloids.

1.6 Energy scale

The fundamental unit of energy in the colloidal domain is *thermal energy*, kT . At room temperature, recall $kT = 4.11 \times 10^{-21}\ \text{J}$ – just 4 zeptojoules. From this, we can calculate characteristic Brownian forces and stresses. These characteristic forces and stresses

The characteristic Brownian forces for particles ranging in size (radius) between $1\ \text{nm}$ and $1\ \mu\text{m}$ are

$$F_B = \frac{kT}{a} \sim 10^{-12} \text{—} 10^{-15}\ \text{N} \quad (1.6)$$

which is on the order of femptonewtons to piconewtons at room temperature. Similarly, the characteristic Brownian stress, which can be thought of as the Brownian force per unit area or thermal energy per unit volume, is

$$\sigma_B = \frac{kT}{a^3} \sim 10^3 \text{—} 10^{-6}\ \text{Pa}. \quad (1.7)$$

The range of stress force and stress scales implies that the mechanical properties and rheology (flow) of colloidal dispersions can be designed over an extraordinarily wide range.

1.7 Surface chemistry

The study of colloids is intimately related to the fields of surface science and interfacial phenomena. After all, a colloidal dispersion, with its small particles, has an enormous surface area.¹¹ The chemistry and physical properties of the surface matter! The interface is also an important means to control the properties of dispersions – including their structure, flow, and stability.

¹¹*How much surface?*