

A life in suspense

Tipsy, clinging, and very superficial: the colloids – Strolling through restless molecules: Brownian motion – Osmosis, the breath of a scattered world – Molding a microworld: how to keep colloids under control – Softness without limits: colloidal aggregates and fractal geometry (with a yoghurt for dessert) – A love/hate relationship: electric ambivalence, volcanic landscapes, and concrete – From lowlands fog to Titian's palette: scattering light and colours – E-paper: when colloids become writers – Gorgeous sunsets and blue moons: the aerosols' deceptive beauty.

The time has come, my lady reader, to leave our *tête-a-tête* temporarily and address a wider audience, hoping there is one. So, what would I like to tell you about? Many, many things. Starting with the most palatable stuff, my tentative wishlist would include:

tea and coffee, ricotta and whipped cream, mayonnaise and yoghurt, rice and sand, soap and toothpaste, inks and paints, milk and airborne particles, contact lenses and jelly, ice and shaving creams, tyres and proteins, spiders and artificial fabrics, polystyrene and bath foams, concrete and chocolate, glass and opals, crude oil and thermal waters, camera films and clays, drugs and bacteria, cells and soap bubbles. . .

. . . and continue for quite a while. To avoid making my editor nervous, I shall only let myself hop here and there among these and other topics, trying at least to make you scent their fragrance. But what does all this stuff have in common? To be honest, it looks like a hodgepodge of things, some obviously related, others less so. No problem for tea and coffee, soap and toothpaste, drugs and bacteria, you may say, but milk and dust particles, tyres and proteins, cells and soap bubbles seem to be totally unrelated to each other.

No impression could be more wrong. The main aim of this book, perhaps the only message I wish to deliver, is that *all* these materials share a common

basic feature. I hope this will be much clearer by the end, but I will just touch on this point with a simple comparison. Consider a beautiful mountain forest. To the forest ranger, the woodland is basically made up of pines, firs, spruces, larches, and brushwood. As a first step, he does not need to know much more to judge whether a tree is diseased, plan where to plant new trees, sketch new trails, or guard the wood from pyromaniacs. However, understanding *why* some plants are diseased and deciding whether they can be healed or must sadly be cut down, is another story. There, the ranger must resort to the botanist's help.

For a botanist, a wood is a quite different thing, for each pine, spruce, or larch is made of roots, trunk, branches, and seed-bearing cones. To get to the bottom of the matter, the botanist has in a sense to descend several floors and, instead of considering structures with a scale of tens of meters, look carefully at much smaller objects. But certainly not the smallest. For a biologist any tree, and in the end the forest itself, is an ensemble of cells and stuff – like wood – that these cells produce. And within each cell there are smaller organelles that we must peer at, if we really want to understand why a plant becomes diseased or how it reproduces. We have gone many steps further down, and now the wood is made of little building blocks the size of a thousandth of a millimeter or less.

However, they taught us at school (or they should have) that everything, including a cell, is made of molecules, which are in turn little families of atoms. For an atomic physicist, therefore, a wood is basically made of atoms. You might now think we have reached the ground floor, since these little building blocks are ten or a hundred thousand times smaller than a cell. But in fact there is a basement too, and a very deep one. A nuclear physicist is interested in what we can find *inside* the atom, things such as the nucleus that, although the largest object inside, is 100,000 times smaller than an atom. Our descent to the underworld seems to have no end. To tell the whole truth, physicists believe today that, to grasp what the world is really made of, we have to look at things and distances that are dwarfed by the atomic nucleus as much as the latter is dwarfed by a fir tree.

A wood may therefore have many increasingly refined *description levels*, each of them perfectly legitimate and self-contained, although related to the others. For instance, the forest ranger does not need to know that the forest is made of atoms, and he could not care less about electrons, protons, or quarks. If we look carefully at our descent to the underworld, however, we may notice that at one point we suddenly made a big jump, for two of these levels are much farther apart than the others. And the level that we missed, the one in between, is the richest one of all. Let me explain. To describe the basic structures of a conifer and their functions, a botanist does not need too many concepts. The biologist's task is a bit more challenging, since the different kinds of cells and biological materials that make up these structures are quite numerous, but that is enough for her (or at least it was until a few decades ago). At the other end of the scale the list is not too long either, for there

are only about a hundred different types of atom, and only a few of them are plentiful in living beings. For the particle physicist, finally, the task is even easier, because the basic constituents of nature are really very few, far fewer than we believed some decades ago. The missing link between cells and atoms, however, is radically different, since the different kinds of molecules that make up a cell are numbered in *billions*.

Sure, you may say that we cheated by overlooking the *chemists*, who are able to find, study, modify, or even design from scratch an endless number of molecules. Absolutely true. Chemistry is wonderful, and I am deeply respectful of chemists and of their terrific ability. But *this is not enough*. Agreed, molecules are the real building blocks of the whole Universe, or at least of that part of the Universe we usually care about (atoms and the particles they are made of are only useful for understanding how molecules are made or react, but then we can almost forget about them). But if you were shown a heap of bricks, tubes, and cables you would probably find it hard to picture the house that could be made out of them. It is far easier if you are shown a roof, bearing and partition walls, pre-assembled plumbing and electric lines. It is not just the endless number of different molecules which makes biological materials so complicated, but rather that they, in turn, join into larger structures, each of them with a precise identity and function.

Simple stuff does not usually share this property. In a glass of water, in a pencil lead, even in the chips of your mobile phone, there is little that lies in between atoms or molecules and the object you see in front of you. In contrast, for the materials we shall talk about these intermediate blocks do exist, even if (despite being much larger than molecules) they are usually too small to be seen. Sometimes they exist only *within* the material, and disintegrate into simple molecules if we try to take them out. These materials differ from simple stuff in rather the way that a prefab, where prepackaged elements are simply assembled, differs from a traditional house built brick by brick. Compared with this simple example, however, building new materials starting from these blocks, rather than from simple atoms and molecules, opens up many possibilities still not fully explored. We shall gradually meet these little blocks, and learn to tell one kind from another. All of them belong to a kind of “Middle-earth” between the tiny, *micro*-scopic world of molecules and the large-scale, *macro*-scopic stuff we meet in our everyday life, and we shall therefore call them *meso*-scopic objects. My purpose is to suggest that you embark upon a journey through this Middle Earth.

Before starting, let us give a name to these peculiar “pre-assembled” materials. To tell the truth, there isn’t a single name to label them, though in most cases, for reasons we shall see, they are dubbed *soft matter*. Now, this term is surely suitable for ricotta, whipped cream, toothpaste, and to a lesser extent for tires, or even spiders. Yet coffee, milk, or crude oil are really *too* soft, to the point that they are not even solids, but liquids. Fog is not even strictly a liquid (though we get damp enough walking through it), but rather something suspended in air: more than just soft, it is insubstantial matter.

In these cases we would speak more properly of *complex fluids*, to distinguish them from simple fluids such as air or pure water. But things such as opals or, even worse, concrete, are surely neither soft nor fluids! Probably, to describe these systems effectively, we ought to recall that they are built from units that are much larger than molecules, and call them *supermolecular materials*. But although that is a more precise and general term, it's also a rather awkward and pedantic one, which has not caught on in the scientific community. In what follows I shall use any of these expressions without worrying too much one way or the other, for the real point is to grasp what they mean.

Conversely, a term I shall try to avoid as much as possible is “nanomaterials”, today as fashionable as “nanotechnology” not only in scientific literature, but also in newspapers, TV shows, and obviously science fiction. This is not because it is entirely incorrect, but because it is often an inaccurate and hackneyed word. “Nano” has a well defined physical meaning (for the curious, a nanometer means a billionth of a meter) and quite often the little blocks we are talking about are anything but “nano”. Even in science, luckily, fashions change or fade with time, and, in a sense, I hope this one will. Sometimes, indeed, I fear that desperately looking for “nanotechnology applications” is a dangerous attitude, which may possibly...dwarf (this is actually the original meaning of “nano” in Latin, and in my native tongue too!) a promising young scientist.

2.1 A big cast of little characters

As in a good drama piece, or an Agatha Christie crime story, we had better introduce right from the start the “microscopic characters” lying at the heart of soft materials, complex fluids, and all the weird things we shall talk about. Obviously, as in any decent thriller, I do not expect you to grasp right now the look, the temper, the pet manias of these characters (let alone who is the murderer). You will have to be patient, please, and wait for the plot to sort itself out. Take it rather as a shopping list, useful to tell us at least the trade names of what we are going to buy. Chapter by chapter, we shall get to know each of these personages, according to the following order of appearance.

Colloids and aerosols

Take a little fine dust, pour it into a glass of water, mix with care, and you get a colloid. That's all. A colloid, in its simplest form, is just a suspension of solid particles in a liquid. Actually, you don't even need a liquid. Candle smoke coiling and spreading in air is a colloid too, but one where the particles are suspended in a gas (since a colloid is also known as a “sol”, here we more properly call it an aerosol). This looks like rather tedious stuff, but we shall see that many pretty interesting materials are, at heart, nothing but colloids. Moreover, understanding how a simple particle suspension works

will provide us with the basis to understand much more complex systems. All things considered, most of what this book is about could actually be called colloids.

Polymers

This is a word you may already know, for instance because you have heard that plastics are made of the stuff. Polymers are in a way the exception to the basic rule that our building blocks are made of many molecules. To be precise, they are long chains made of many “basic units”, which in the simplest case are all identical, but can also be of different kinds. When dissolved in a liquid, these chains wind into little balls, similar to suspended particles in colloids, but much softer. When there are large numbers of chains, however, they no longer form separate coiled balls; instead, they grow intertwined into a kind of mesh, which is the fore-runner of what we know as rubber.

Micelles, vesicles, and emulsions

You are likely much less acquainted with these terms, but you are of course familiar with soap. Soaps, and in general what a chemist would call surfactants (don’t worry, it will be explained later), are made of very peculiar molecules, displaying a kind of double nature. Part of the molecule loves water, the rest cannot stand it. As a result, dissolved surfactant molecules huddle together to form large structures with the water-hating portions hidden in their midst, and these clusters are dubbed micelles. Surfactants are a typical example of a large class of chemicals called *amphiphiles* (amphi-, meaning both, here hints that they happily mix with both oil and water), having in common a readiness to organize themselves spontaneously into structures that exist *only* in solution (there is absolutely no way to take a soap micelle out of water). Not all amphiphiles form micelles. Some of them prefer to combine into more complex aggregates such as vesicles, which are, roughly speaking, water droplets surrounded by more water, but separated from it by a double layer of these particular molecules. If we add some oil, besides water and surfactant, the structures that form are stranger still. They are what we call emulsions, a stuff that, as we shall see, is abundant in any home.

Colloidal crystals, gels, and glasses

The characters we turn to now are not simple building blocks, but rather *structures* that the building blocks may form, and which set up the framework of what can be properly called soft matter. Unlike colloidal suspensions or polymer solutions which are liquids (complex, but still liquids), they are *solids*, which keep their shape without spreading around like fluids. In the simplest case of colloidal crystals, they are just a grand version of well-known solids

such as ice or diamond, reminding us in a way of the giant pencils or the elephantine baby-bottles once on sale at the fabulous “Think Big” shop in New York. In other cases, however, they are very special solids. While a “real” solid is made of atoms ordered in a simple geometrical arrangement (for instance, the atoms might all lie on the edges of tiny cubes), in gels or glasses the particles or the polymer chains are as randomly placed as molecules in a liquid. Yet, for some reason, everything holds together: our building blocks have produced a strong and stable house, although the architecture is a bit chaotic. The basic difference between glasses and gels is that the former are usually dense and hard, whereas the latter can be “almost empty”, standing out as the lightest solids imaginable.

Liquid crystals and granular matter

In between the Latin mess of liquids and the Prussian order of solids fit other materials, with an even more indecisive behavior: liquid crystals. We shall deal with them only briefly, since they are not usually made of large blocks but of small molecules. But at least we shall see that colloid science can suggest *why* they form. We’ll also say a few words about granular materials, stuff like sand, rice, or cereals, but where, unlike with colloids, there is apparently no “suspending medium” like oil or water between the grains apart. Nonetheless, many “packing” problems that we shall address for colloidal suspensions have a counterpart in granular matter, and are actually crucial in understanding their behavior.

Membranes, biopolymers, and biological machines

Here we are. Approaching what we call “life”, we shall reach the climax of our path, a summit where colloids, polymers, micelles, vesicles, and more elaborate structures dance together in a kind of rave party of soft matter. Even though, so far, we have grasped only some of the basic rules of this complex role-play game, one thing is certain: what marks biological structures out from their simpler lifeless forerunners is their *individuality*. For instance, proteins are just polymers, but polymers made of many (about 20) different basic units, the amino acids. Whereas a simple polymer in solution is a randomly coiled chain (so that, as we shall see, all simple polymers with the same length have the same structure, at least “statistically” speaking), every specific amino acid sequence gives a *unique* shape to a protein, and this in turn gives the molecule a single, well-defined function. Moreover, protein chains coil up much more tightly than simple polymers, which make protein coils more akin to rigid colloidal particles. Even DNA, the king of the biological jungle, and RNA, its faithful servant, are polymers, but with such a complex structure that the whole code that uniquely defines each living organism can be written inside them. Finally, the membrane enclosing a cell makes it similar to a simple vesicle, but it is a very special membrane that, aided by proteins, can

accurately decide the cell's shape and what it can trade with the outside. So vast a range of biological structures opens up countless ways for them to self-organize into proper “molecular machines”, whose operation we are still far from understanding in full. Really and truly, this is the stuff of dreams!

As you see, this is going to be a rather long journey, and we had better take our time to avoid tiring too soon. Let us then begin with the first and simplest item on the list, telling of the deeds and misdemeanors of the eternally suspended life of a colloidal particle.

2.2 When it pays to be superficial

For a first encounter with colloids, aiming to learn what is so special about them, let's start with a simple experiment. Imagine I give you a little block, of whatever stuff you like, with a cubic shape and a side of one centimeter. Suppose too that I provide you with a “magic lancet” allowing you, whatever material you chose, to cut it into tiny pieces. Then, begin our experiment by dividing the block in a thousand pieces (you guess how), so as to obtain 1000 smaller equal cubes with a side of one millimeter (if you guessed correctly, this should be obvious). Now repeat the same operation on each of these cubes¹, thus getting $1000 \times 1000 = 1,000,000$ tiny cubes with a side of a tenth of a millimeter. We have not finished yet. Let us repeat everything once more, to obtain one billion ludicrously tiny cubes with a size of a hundredth of a millimeter.

What is the net result of all this effort? If we think of the quantity of matter or, to put it differently, of the block volume, nothing at all. We started with one cubic centimeter of our stuff in a single piece, and now we have a billion tiny cubes, each with a volume of only one billionth of a cubic centimeter. Obviously, we neither gain nor lose anything. But let us think about the *surface* of these tiny cubes. Since a cube has six equal faces, our initial block had a total surface area of six square centimeters, about the size of a stamp. Now the surface of each tiny cube is only $6 \times 0.01 \times 0.01 = 0.0006$ square millimeters, yet, since we have a billion of them, the total area (try it with a pocket calculator, if you do not believe me) is 0.6 square *meters*, which is about the total area of 40 postcards. Every time we divide the cube size by ten, the total area increases by the same factor. Had we repeated our cutting operation twice more, obtaining “nanocubes” with a size of ten millionths of a centimeter, the total area would have increased up to 60 square meters, more or less the living area of a two-roomed apartment!

¹ I'd better supply you with a microscope too, to check what you are doing, hoping of course that you have a very steady hand. Which I do, for I thoroughly trust my readers.

Surprised? Welcome to the surface world of colloidal particles or, to use a more fashionable term, to the world of nanoparticles². By “particles” I do not mean electrons, muons, kaons, or any other of those unfamiliar things that (serious) physicists talk about. Rather, as in the original Latin meaning, I am talking about “small parts” of any material, whether they are solid, like dust grains, tiny glass beads, and metal scales, or liquid, like fog droplets, or even gaseous, like bubbles in a champagne flute. What matters is that they are pretty small and therefore have a lot of surface, even if, all together, they fill very little space. When a lot of nanoparticles are suspended in a fluid (usually a liquid such as water or oil, but sometimes a gas such as city air), we speak of a *colloid*³.

However, “small” is a rather vague term. For instance, I am certainly small if contrasted to Sun Mingming, China’s famous top basketball player, but not when confronted with a certain well-known Italian Premier. In physics, anything is big or small *with respect to something else*. To what extent can we call these particles large or small, then? We shall see later what is the maximum size a particle can have and still be “colloidal”, for this demands some thought. For the lower limit, we shall only ask that they are much larger than atoms and molecules. It is easy to see that a colloidal particle can be *really* small and still have a large volume compared with a molecule. To make a simple calculation without using too many decimals, let us recall that a thousandth of millimeter is called a *micrometer*, or simply *micron* (μm), so that $1\ \mu\text{m} = 0.001\ \text{mm}$. In turn, a thousandth of a micron is called a *nanometer* (nm). This is quite a small unit, but not yet small enough, for atoms and simple molecules are no larger than a few *tenths* of a nanometer⁴. For instance, since in water each H_2O molecule takes up a volume of about 0.03 cubic nanometers, it is not difficult to show that a droplet with a radius of just $0.1\ \mu\text{m}$ still contains almost 140 million H_2O molecules!

A large number of chemists and physicists (including myself) have spent much time and energy in trying to make and characterize colloidal particles and suspensions made of the most diverse materials, and with the most bizarre properties. Why so much interest in these miniature materials? The first and most important reason stems from the huge surface area that is a peculiarity of colloids, together with the observation that it is through the surface that something interacts with its surroundings. This is not too hard to grasp. If you have ever had a camping night in Norway, even in full summer (or

² A more concise but less precise term that, as already stated, I shall sometimes use *only* because of my laziness.

³ The word comes from the Greek $\kappa\omicron\lambda\lambda\alpha$, meaning “glue”. We shall see later what a colloid has to do with glue (very little indeed), but it is useful to point out that this word stands for the *whole* dispersion, i.e. the particles plus the fluid they are suspended in.

⁴ Because of its close relation to the atomic size, a tenth of a nanometer is given the special name of an Ångström, where that “dotted A” should be pronounced as a very closed “O” (although few scientists do so).

at least what the locals call summer), you may have realized that, to stay warm, it is worthwhile (and possibly pleasant) to huddle together as much as possible. More precisely, to limit the loss of heat, it helps to reduce the area you expose to the environment. To take another example, contrast the time it takes to dissolve raw sugar in water rather than refined (and, because “time is money”, more expensive) sugar. Again, when you notice the walls of a poorly aired bathroom moldering gradually and depressingly in spite of all the protective treatments you have applied, recall that all the biochemical reactions leading to mold growth occur on the wall surface, just like the iron oxidation responsible for rust formation takes place on the surface of balcony railings. The larger the contact surface, the faster that materials and energy can be exchanged with the surroundings, and in this matter colloids are speed aces. In addition, our nano-dwarves are so tiny as to slip into almost any space, hence some of us hope to manipulate these exchanges and reactions so that they take place just where and when it suits us. For example, we may think of inserting anti-cancer drugs into suitable nanoparticles, able to sail down the thinnest capillaries to the sick organ or tissue where the drug will be controllably released.

That is not all. There is a subtler but probably more basic reason to look at colloids with special interest. Until a few decades ago, to build new materials, we had at our disposal only those bricks that Nature or the ingenuity of chemists provided – that is, just molecules. Today things are different: nanoparticles can be regarded as the building blocks of a mesoscopic Lego that, with careful design of the framework and joints, allow us to make materials with totally new and stunning features that do still, in a way, stem from the properties that each single particle has already. So far, this statement may seem a bit mysterious, but in what follows we shall see how to do it.

2.3 Colloidal Waterage, an award-winning firm

Before venturing into the world of colloids, let us first face a situation where the huge surface of dispersed particles plays a simple but crucial role. In this “case study”, as a bonus, we shall get to know some colloids that Nature places at our disposal with no effort on our side.

The oil crisis (or the recurrent oil crises) has reopened the debate on the timeliness of using nuclear power. Sooner or later, no doubt, we will have used up all the extractable oil, although no one exactly knows *when*. Unfortunately, technologies based on renewable sources, in spite of developments that would have been unimaginable a few years ago, will hardly be adequate to grant our children the same comfortable life we enjoy today. Uranium is neither very abundant (thankfully, in some senses), nor particularly cheap (in the last few years, its price has risen much more than crude oil), but luckily we do not need a lot of it. From the experience obtained with existing nuclear plants we may also be able to draw inspiration for developing fusion power, which

would satisfy all our hunger for energy (so far, unfortunately, it remains the Holy Grail of physicists).

The word “nuclear”, however, unavoidably raises arcane fears in people, or at least substantial resistance. Having worked for a long time alongside nuclear engineers, I can swear that they are crazy about safety issues, and that nuclear plants, in particular those of the latest generation, are technology masterpieces, equipped with control systems that outshine most oil and carbon plants. So please don’t think of enrolling me in the NIMBY ranks which seem to find so many members worldwide.

However, a serious problem does exist: how can we dispose of all that radioactive waste that remains harmful for very long times and that, note carefully, not only includes the exhausted nuclear fuel, but also its container and everything that was contained in it besides the fuel? Actually, those countries (not mine) where reasoning is more common than quibbling have already seriously investigated this matter, outlining what sites are suitable for radioactive waste storage. However, to work this out, we must take into account the role that our colloidal particles may play. Luckily, many engineers are just doing that all over the world.

The story I wish to tell you can be summarized in a few lines. There is a very special place in the United States, the Nevada Test Site, where several (anything but peaceful) nuclear tests were made during the Cold War, which generated a huge amount of waste containing “radionuclides”, in other words radioactive atoms such as plutonium, cesium, and cobalt. The Nevada Test Site, like most of Nevada, is a desert zone, but concerns that these infernal dusts will spread around may cross our mind. After all, Las Vegas is less than 100 miles away! Yet, once the waste is stored, radionuclides have just one way to escape, and that is through underground waters. Luckily, these radioactive compounds are practically insoluble in water, so a simple calculation shows that they should stay close to the site for thousands, if not millions of years. Imagine therefore how astonished Annie Kersting and her geologist colleagues were to discover, in 1999, that plutonium had already spread around not by a few meters, but by more than *one kilometer*! What had happened? It’s simple: the radionuclides had taken the bus, or perhaps we should say the “colloidobus”.

Let me be more specific. A lot of colloidal particles, mostly minerals like clays with a flat particle shape and therefore a large surface, are suspended in underground water. Now, although they cannot be transported directly by water, radionuclides can ride the colloids by *sticking to their surface*, something that they readily do because, with all that surface at their disposal, hitchhiking is really easy for them. Thanks to their huge docking area, colloids can therefore assist in the transfer of stuff which would otherwise be totally insoluble in water. As we already mentioned and shall come back to later, this feature can also be exploited to carry around far safer and more useful substances such as drugs.

Was this the true story? Not all specialists agree. For one thing, underground waters flow through porous rocks, with very small pores. We shall see that these rocks, while letting water pass through, should in fact filter out most dispersed clay particles. Yet things could be very different for smaller particles, those made of lignosulfonates derived from lignin, the basic constituent of tree pulp. Whatever the truth of the matter, after the alarming observations made in Nevada, nuclear scientists and engineers consider this problem carefully whenever they have to plan a new depository for nuclear waste (which, I should mention, is also safely contained in massive watertight containers). This bears witness once more to their thoroughness and care for public safety. Trust them, for once; they are serious people!

2.4 Rock and roll in suspense

Colloids are therefore particles dispersed in a fluid of simple molecules, which we shall call, rather improperly, the “solvent”. Let us then see whether there is any relation between these particles and the solvent molecules. Now, particles are quite small on our usual gauge, but still very much larger than the molecules. We might guess that the particles simply ignore the latter, as we usually shrug off midges, at least if they are not too much of a nuisance. Is it really so? Quite the reverse! These “molecular fruit-flies” are bothersome to the point that they leave an indelible mark of their presence on the way the colloidal particles move. In short, solvent molecules have on particles the same effect that several pints of beer have on the drinkers at a bar. To see what I mean by this, let us jump back in time to 1827, and peep through the shutters of Robert Brown’s lab. Brown, please note, is not a physicist or a chemist, but an adventurous Scottish botanist who, after traveling all around the world, is observing under the microscope some grains of pollen of *Clarkia pulchella*, a close relative of fuchsias and primroses, suspended in water. The trouble is that these wretched specks do not seem at all keen to keep still under observation, but rather seem to suffer from a kind of Saint Vitus’ dance, stirring and jiggling madly about before poor Robert’s eyes.

At the time, it might have seemed easy to account for this. Most naturalists, in disagreement with physicists, believed that biological stuff possessed a kind of “spirit of life” that made it superior to inanimate objects, and *Brownian motion*, as we shall call the effect observed by Brown, could have been a direct manifestation of this⁵. After all, microscopists had already discovered that *animalcula* (“tiny animals”) such as sperm cells, though invisible to the naked eye, could move around at will. But Brown, who was no physicist, but no fool either, carefully avoided jumping to this conclusion. And he was right, since it was easy for him to show that even specks of humble

⁵ During the last century, most biologists have changed their mind. Not so certain philosophers, such as Henri Bergson.

and totally inanimate dust shared the same behavior. Nevertheless, Brownian motion remained a puzzle till the beginning of the twentieth century, when a personage you surely will have heard of, Albert Einstein, gave it a full and brilliant explanation⁶.

Now, you might regard this result as a trifle, compared with other ideas by the aforementioned Albert, but you would be wide of the mark. The explanation of Brownian motion produced a proof of the molecular nature of matter that could hardly be argued with. Actually, at the beginning of the twentieth century, not all scientists believed in the existence of atoms and molecules. Chemists obviously did, and they already knew a remarkable amount about how to play with them⁷. However, many distinguished physicists held the opposing view that there was no real need of these little things to explain how the world worked. That is to say, they somehow managed to stick to the old idiom “what the eye doesn’t see, the heart doesn’t grieve over”. Einstein’s theory, however, which so neatly explains Brownian motion, not only necessarily assumes the existence of molecules, but also allowed scientists to *calculate* how many of them are in a given volume, and this result matched the value used by chemists to make sense of the quantities of chemicals used in the reactions between these hypothetical constituents of matter. Since then, the atomistic view of reality has stood at the foundation of modern science.

At the time, this was anything but obvious, so much so that Svante Arrhenius, Chair of the Nobel Committee, while introducing Einstein as winner of the 1921 price for physics⁸, first took time to mention his contribution to the explanation of Brownian motion. So how did Einstein’s explanation work? At bottom, it rested on two assumptions:

1. Bodies are made of atoms or molecules (this is what I have already stated);
2. Each molecule has a kinetic energy, called *thermal energy*, which is proportional to the body temperature (and this I shall try to explain now).

If you have any faint memories of school, you may recall that we associate a form of energy to any moving body, dubbed “kinetic” energy, which is equal to half the body mass times the square of its speed. It should be evident why

⁶ To tell the truth, the same result was simultaneously obtained by a great Polish physicist, Marian Ritter von Smolan Smoluchowski; but he had rather too knotty a name to become popular, and certainly did not have a natural presence for TV shows (at least when compared with Einstein’s hanging tongue, as reproduced on a thousand T-shirts).

⁷ Just think that Alfred Nobel, to fund the peace prize that bears his name, had already invented dynamite some forty years previously. To make that, he clearly needed to be quite familiar with chemistry, at least if he wanted to save his own skin.

⁸ Which, as some of you may know, was not awarded to him for the theory of relativity, but rather for his work on the “photoelectric effect”, much less familiar to philosophers and scholars of the abstract, but fundamental for the future of day-to-day things such as solar energy or photography.

this quantity must be proportional to the mass: given that they travel at the same speed, would you prefer to be run over by a small motorcycle or by a trailer truck? To see why this energy is proportional not to speed, but to its *square*, we can observe that crashing into a wall at 50 mph is not just twice as devastating than colliding at 25 mph, but about *four times* (please don't try this at home).

The second assumption tells us, therefore, what it is that we measure when we check for fever with a thermometer: *temperature is a measure of molecular kinetic energy*, or of the speed at which molecules move about. Please note that I am not only referring to the molecules of a gas, where intuitively (or because they told us so) we expect molecules to wander around freely in all directions, unceasingly colliding with other like tiny, mad billiard balls. At a given temperature, the molecules of a liquid, or even of a solid, have the *same* kinetic energy as in a gas. The only difference is that in a liquid something else (we shall see what) keeps them together, forbidding them to escape from the container. In a solid, on the other hand, atoms can “vibrate” around a fixed position, even they cannot get too far from it, and vibration is a kind of motion too.

A little math now – but only a little. To express that kinetic energy is proportional to temperature, we shall write it as $E = k \times T$ or kT , where T is temperature measured in degrees kelvin, a scale which is identical in step-size to the common one (common if you are not American, at least) in degrees centigrade, but where “zero degrees” corresponds to the spine-chilling value of -273.15°C (about -460°F), and k is a multiplying factor called the *Boltzmann constant*⁹. This is just a rough figure, for some molecules actually move faster and others slower, but *on the average* the kinetic energy is about kT , so that we should rather write average energy $E \simeq kT$ ¹⁰. Compared with the figures we usually consider, the thermal energy of a single molecule is ridiculously tiny. To lift me (admittedly no featherweight) from the ground to a height equal to the size of a *single atom*, it would take all the thermal energy possessed at room temperature by something like *sixty thousand billion* molecules¹¹. However, the mass of a molecule is even more ludicrously small,

⁹ In honor of Boltzmann, founding father of statistical physics, this constant is usually indicated in serious scientific literature by k_B . For those of you more acquainted with the units of physics, its value is about 1.38×10^{-23} joules per kelvin.

¹⁰ The symbol \simeq (“almost equal”) means that here, as in other expressions, I am merrily neglecting small factors such as 0.7 or 1.5. I assure you this is not just a sign of the author's laziness, but rather the typical way physicists write formulas at a rough guess, so as to get to the crux of the matter without carrying along too many boring numbers (and to leave something for the engineers to do). Anyway, for the hairsplitter and the know-it-all, mean energy $E = 3/2kT$, at least for monoatomic molecules.

¹¹ This may seem a lot but, recalling what we said of the volume taken up by a water molecule, all these molecules could comfortably fit in a cube with a side

so that, with a kinetic energy of kT , its “thermal” velocity is some *hundreds* of meters per second. In a word, the molecular world is restless.

A grain of pollen, or more generally any colloidal particle, immersed in a solvent is then unceasingly bombarded by these shooting nano-bullets that transfer a little of their own energy to it, so that in a very short time the kinetic energy of the particle will also be equal to kT (neither more, otherwise the particle would give it back to the molecules, nor less, because then it would go on absorbing energy). This means that the particle, too, *must* be moving. But how? Each collision is a kind of “kick” (a feeble one, but still a kick) to the particle, kicks that come from the right, the left, above, below, in front, behind – in other words, from all sides. On average, all these nudges even out, so there is no a preferred direction for the particle to move. Yet, as Einstein realized, if we look at a very short time interval this is not *exactly* true. There will always be a little loss of balance, causing the particle to perform an extremely irregular zigzag motion, similar to the staggering walk of a drunkard.

Let us see whether the latter analogy helps us. For instance, imagine that we have drunk too much and that we get out on the street overlooked by the bar where we have been enjoying ourselves. We have no idea of the right way home, so we make a first move in a random direction, say to the right. Then we stop and think it over, and as a result we resolve to retrace our steps, or to keep going in the same direction, and so on. Where will we be after a certain number of steps? Intuitively, we may expect to find ourselves close to the starting point.

Quite sure? Then let us see whether the computer can give us a hand, asking it to trace the path of an inveterate drunk. To set the scene, suppose that our favorite haunt lies in the open countryside, and that our drunkard tries to set out for home across the fields. At any step (each one of the same length), the computer chooses a direction at random¹². To be surer, let us try with two heavy drinkers, each one of them taking 100 steps, just to see whether the paths they follow look alike. What comes out from the computer I am working on is shown in figure 2.1.

Surprise! Not only are the two paths extremely irregular (so much so as to be dubbed *random walks*), but they look remarkably unlike each other. Moreover, our first drunkard apparently does not have the slightest wish to come back to the bar (although he moves away from it by much less than 100 steps), and the second is rather reluctant too. What is happening? You may think that my computer has swindled us, and that this result is not to be trusted, but I can assure you that the single Brownian tracks of colloidal particles *really* do look like those shown in the figure.

of 0.01 millimeters. To compare it with the sort of energy unit we are used to hear about (and pay for), it would take all the molecules contained in about six gallons of water to get a total energy of one kilowatt-hour.

¹² If we had set this on a street, so that we only had to decide whether to move right or left, we could simply toss a coin. On a surface, the choice is a bit more tricky, but computers know their job!

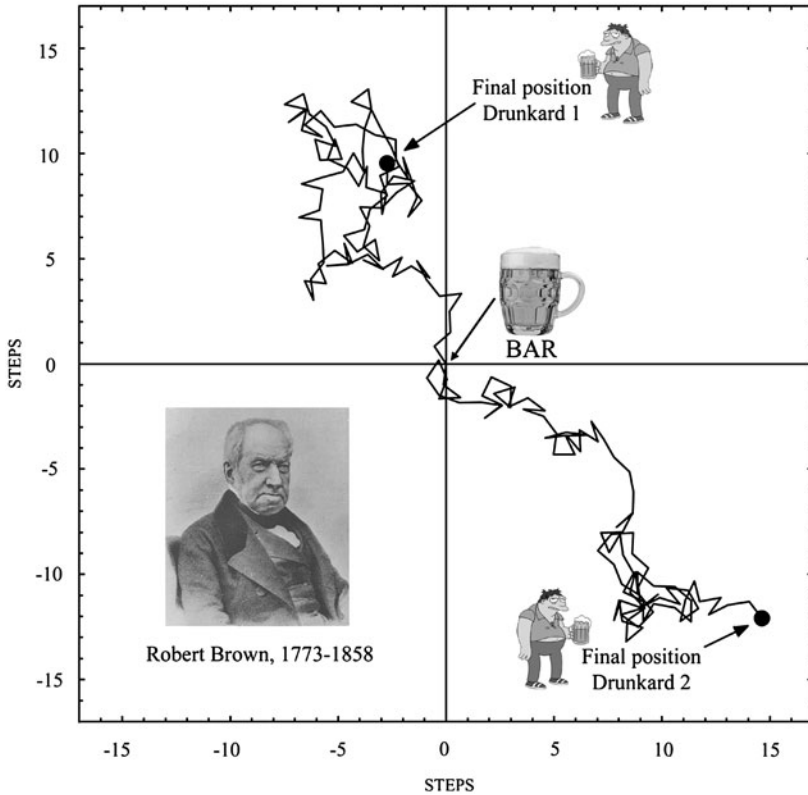


Fig. 2.1. Computer simulation of two random walks, each of them made up of 100 steps.

The point is that these paths are *so* random that actually, to grasp what is happening, we must resort to statistics, simulating the motion of a *large* number of drunks. The dotted “spots” in figure 2.2 therefore show, on squares with a side 200 steps long, the final points reached by 1000 drunks after each of them has performed a random walk of 100 steps (panel A), then 400 (panel B), and finally 900 steps (panel C). Note that the spots are actually centered on the drinking place. This means that, statistically speaking, we made a good guess. On average, our random walkers do remain trapped near the pub, although we find a smaller and smaller number of them who have managed to stagger longer and longer distances from its doorway.

There is another feature that is obvious in Figure 2.2. Although we multiplied the number of steps by four, the spot in panel B is about only *twice* as large as the spot in panel A. Similarly, the spot in C is only about three times as wide as the one in A, even though the drunks have taken nine times as many steps. I am sure it would take little effort to convince you that if

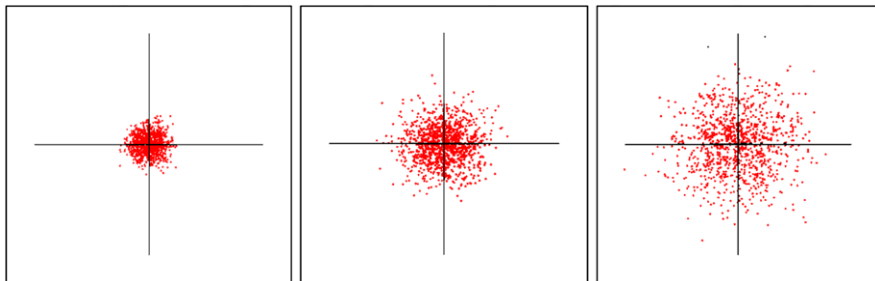


Fig. 2.2. Final positions of 1000 drunkards after 100 (A), 400 (B) and 900 (C) steps.

we had simulated random walks of 1600 steps, we would have got a spot four times the size. Now, since 4 is the square root of 16, as 3 is of 9 and 2 of 4, we can conclude that the spot size grows only in proportion to the *square root* of the number of steps. Assuming that our boozers take a step at fairly regular intervals, for instance once per second, this also means that the width of the region they “explore” grows as the square root of time.

It is worth pausing for a while to think about that result, for it is anything but trivial. Suppose for instance that after an hour our spot has a size of 100 meters. What we have found means that the spot would have reached a size of 10 m in under 4 seconds, whereas, to reach a radius of 1 km, we would wait for more than 4 days! Hence, Brownian motion starts like a torpedo, but then becomes slower and slower. It is easy to show that even a snail, no matter how sluggishly it proceeds, will sooner or later overtake even the most go-ahead of the drinkers (provided obviously that the snail is not tipsy too). Things get even more interesting if we note that what I called “spots” may actually be *real* spots. For instance, if we plunge a fountain pen into a glass of still water and release a drop of ink (which, as we shall see, is also a colloid), its size will grow only as the square root of time (which we could write as \sqrt{t}). Similarly, if we let a lump of sugar sit in a cup of tea without stirring, the size of the region sweetened by the sugar molecules grows only as \sqrt{t} . Phenomena such as these are called in physics *diffusion processes*. And it is not even necessary that there are particles or molecules to diffuse. The same thing happens with heat, the spread of energy from warm to cold bodies, provided that it is transported by diffusion and not by force, as for instance when we use a hairdryer.

This picture of Brownian motion allows us to get an idea of how large particles can be and still be called “colloidal”. In abstract terms, there are no limits to the size they could have. When immersed in water, even marbles, the sort we played with as kids, take on an energy equal to kT each. Yet we would hardly think of them as colloidal particles; we know that they would plummet under the effect of their own weight, ending up at the bottom of the

container¹³, and goodbye to the colloid! If they were much smaller, however, they would settle at a much lower speed. Just to give you an idea, if our marbles had a radius of just one micron (a millionth of a meter, if you remember), their *sedimentation velocity* (the more elegant term for settling rate) would be only 20 cm a day, low enough to allow us to study them while they are still suspended (and after that, a good stir is enough to put us back in business).

But the most surprising news is that, if they were really *very* small, they would not settle at all! Let us try to understand why. You may recall from your basic physics studies that, besides the kinetic part, there is another important contribution to the energy of a body, the *potential* energy. Without racking our brains for formulas or long-forgotten definitions, it is enough to say that it is the amount of energy a body stores when it moves against a force, a kind of investment the same force can give you back later as energy of motion (the kinetic energy). So, for instance, if you throw upwards from the ground a stone with mass m , giving it a certain initial speed and therefore kinetic energy E , the stone reaches (if we neglect air friction) a height h such that $m \times g \times h = E$, where g is the acceleration of gravity. The quantity $m \times g \times h$, or mgh , is exactly the potential energy the stone gains by moving against its own weight that pulls it down. Obviously, once the stone has reached the height h , it falls back, losing potential energy and regaining kinetic energy, until the kinetic energy reverts exactly to E when the stone is just touching down. This simple experiment shows that kinetic energy can be converted into potential energy (and the other way around) exactly as we can convert euros into dollars and vice versa. If there is no friction (which, to a small extent, is always present, just as a bank always takes some money off in currency exchanges), the *sum* (that is, the combined total) of the kinetic and potential energy remains constant. This is what we call the “conservation of mechanical energy”.

That is all we need, since we also know that a colloidal particle *always* has a kinetic energy kT . Therefore, even if it settles under its own weight, it will not necessarily end up at the bottom of the container, for it can harness this small amount of kinetic energy for climbing back to a height $h = kT/mg$. If we consider marbles once again, but this time with a radius of a *hundredth* of micron, it is easy to show that we can always find particles that rise to a height of at least 10 cm, even if we wait forever.¹⁴ Thus, there are always a lot of particles dispersed in the solvent and, in any case, it takes the particles a very long time to reach this final state, since their sedimentation velocity is just

¹³ Or the top, if they are ping-pong balls. What actually matters is comparing their weight to that of the fluid they displace (Archimedes’ principle, if anyone recalls this).

¹⁴ An accurate calculation shows that the particle concentration we would find at this level is about a third of the concentration at the bottom, and that almost 1% of the particles will rise by half a meter!

7 mm *a year*. We may summarize this digression¹⁵ by saying that suspended particles can be regarded as colloidal if they settle slowly enough, or if they are so small that, in practice, they never sediment out¹⁶. Obviously, it is also a question of viewpoint, since on the Space Station, in the absence of weight, even basketballs would be colloids.

We have spent quite a bit of time in describing how colloidal particles move, but it was worth the effort. As we shall see, all the microscopic world is subject to Brownian motion, including those chemical micro-plants, micro-motors, and micro-repair shops we are made of, which must work in the midst of a restless, jostling molecular crowd. There is really no such thing as a quiet job in the microscopic world.

2.5 Osmosis, the breath of a dispersed world

A well-known consequence of the fact that molecules have a kinetic energy is that a gas *presses* on the walls of its container (for instance on the inner tube of a bicycle tyre). Such a pressure is nothing but the overall push that the gas molecules exert on it through their collisions with the walls, divided by the total area of the container (or, as we shall say, the force exerted *per unit area*). If the gas is not too dense, this pressure P is simply equal to the molecular concentration c , expressed in molecules in a certain volume of air times (once again) kT , or $P = ckT$.

Getting back to our Brownian motion, we have already said that a Brownian particle in a liquid has as much kinetic energy as the solvent molecules. Is there anything paralleling the pressure in a gas that can be ascribed *solely* to the particles? Well, this quantity not only exists, but is also extremely useful for understanding the behavior of a colloid and of many other systems, both simple systems, such as a salt solution, and very complex ones, such as a neuron, one of our nerve cells. It is called *osmotic pressure*, from the Greek *ōsmós*, meaning simply “push”, so that, to recall its Hellenic origins, it is usually indicated by the Greek capital letter “pi” (Π).

What, then, is osmotic pressure and, above all, what visible effects does it have? In a gas, pressure exists because molecules push on the walls, which

¹⁵ Which is not totally useless. Remember for instance that many rocks were formed just by particles settling on the seabed. Hence sedimentation certainly does matter to geologists.

¹⁶ Clearly, that “enough” also depends on the density of the particles with respect to the solvent. Checking the results of a blood test, you may find for instance the sedimentation velocity of erythrocytes – your red blood cells, in other words. These are platelets with a size of a few microns, but they have a density comparable to water. Therefore, letting them settle under their own weight requires a ludicrously long time. To avoid a lifelong wait, we get them moving with a centrifuge, similar in principle to a salad spinner or the machines astronauts use to familiarize themselves with what they will feel at takeoff or landing).

in turn push them back¹⁷. That is, the walls *contain* the gas. If we wish to find a kind of pressure that concerns just the colloidal particles, we should therefore look for walls that confine *only* the latter, while they let the solvent pass through as freely as ghosts through the walls of a Scottish castle. The walls of many animal organs, such as the bladder or the bowels, have exactly this magic property, so that they are called *osmotic membranes* or, more commonly, “dialysis membranes”. Basically, the distinguishing trait of these membranes is that they have microscopic pores, large enough to let solvent molecules pass freely, but too small to allow colloidal particles through. Today, chemists and biologists can do much better without eviscerating too many animals. By means of structures we shall call “polymer networks”, indeed, we can make artificial membranes with pores of precisely the gauge we want, to hold back only those particles we wish to retain.

Usually, these membranes are shaped like hollow tubes and are rather elastic, a bit like a balloon, a feature useful for a little thought experiment. Let us fill a container with the solvent (no particles), then make a bag with a piece of dialysis tubing, fastening it up at both ends with a thread (like an old-style homemade sausage), and finally fill the bag with a colloidal suspension. If we now dip the bag in the container, we observe the bag swelling progressively as solvent gets inside from the external reservoir. The smaller and more concentrated the particles are, the clearer is this effect. Now, seeing the bag inflating like a balloon tells us that the pressure inside it has *increased*, to the point that, if we fill the bag completely without leaving any air space, the bag may even burst open. Somehow, the colloid “sucks in” solvent until, after some time, the swelling process ends. The osmotic pressure Π of the suspension is defined as the *extra pressure* within the bag at this final stage. How large is it? Well, if the colloid is not too concentrated one finds that $\Pi = ckT$, just like the pressure of a gas, but where this time c is the *particle* concentration in the bag (this is called the *van 't Hoff law*). Where does this excess pressure come from? It would be nice to find that it is just due to the “bombardment” of the osmotic membrane by the colloidal particles. In fact (though many colleagues of mine find this hard to believe) it is really so, but the way it works is rather complicated¹⁸.

What is important to stress is that the pressure increase stems only from the trapping of the suspended particles in the bag. To confine particles, an osmotic membrane may not be necessary. For instance, we have seen that

¹⁷ Another school memory. This is the notorious “law of reciprocal actions”, which you might remember, more prosaically, as the law of “an eye for an eye, a tooth for a tooth”.

¹⁸ For the most curious of my readers, the process takes place more or less in this way. To push back particles, the membrane has to apply a force. Since the particles constantly exchange energy with the solvent molecules, they transfer such a force to the solvent through collisions. Yet, when a fluid is subjected to an external force, its pressure must necessarily increase, and this can happen only if some extra solvent molecules pass from the reservoir to the suspension.

colloids settle out (some more, some less), meaning that *gravity* tends to confine them at the bottom of the container. The osmotic pressure must then be larger close to the bottom (where the suspension is more concentrated) than at the top. It was precisely by measuring the concentration profiles of settled colloids that Jean Baptiste Perrin managed to validate Einstein's model of Brownian motion, earning himself the Nobel prize for physics in 1926.

However, osmotic swelling effects are not limited to colloidal suspensions. Biological membranes too are capable of holding back simple substances such as salts or sugars¹⁹, and the osmotic pressure of a solution of small molecules (just because they are small and so, for a given concentration in weight, there are *a lot* of them) can be really gigantic. For instance, the osmotic pressure of salted water suitable for preparing good pasta (slightly less than 10 grams per liter, to my liking) is about *ten atmospheres*, which is the excess pressure you must bear underwater at a depth of 100 meters! This has important repercussions on physiology. For example, to prepare an intravenous shot or drip, we must use a “physiological” (or “isotonic”) solution, which is nothing but a salt solution at slightly less than 1% concentration (more or less the same as water for pasta). Why can't distilled water be used? Simply because we need a solution with an osmotic pressure comparable to that of our blood. As we said, the blood contains erythrocytes, small cells with a disk-like shape flattened at the center, and the membrane covering these cells does not allow salts to get through. So, if you add distilled water to a blood drop and look at what happens under a microscope, you will see the red blood cells swelling quickly, and then bursting like balloons. This is the same effect that takes place for our sausage, but strongly (and tragically, for the poor erythrocytes) amplified.

Even without a microscope at our disposal, we can make a simple and less bloody experiment using a couple of eggs. An egg is nothing but a huge cell, which has an outer membrane called the *amnion* (yes, it is really a caul), preventing outside agents from penetrating inside, but which we do not usually notice, for it is hidden under the shell. The eggshell itself is a chalky substance, and dissolves if immersed in an acid liquid like vinegar, or more easily in kettle descaler. The upper picture in 2.3 shows two eggs of similar size which I soaked in a descaler solution. Some hours later, the shells have gone and the eggs have become soft objects, just kept together by the external membranes. I then soaked one of the two eggs in a bowl full of plain tap water, and the other one in water in which I had dissolved as much common table salt as possible. The central picture shows the outcome after one night. The egg that was immersed in the salt solution (to the left in the picture) has slightly deflated, whereas the one in fresh water has swelled hugely. Even their visual appearance is different. While the amnion of the first egg looks whitish, the

¹⁹ Here, however, it is not a question of pore size. The reason these molecules cannot get through a membrane is a bit more complicated.

second one is stretched like a balloon, and so translucent we can make out the inside.

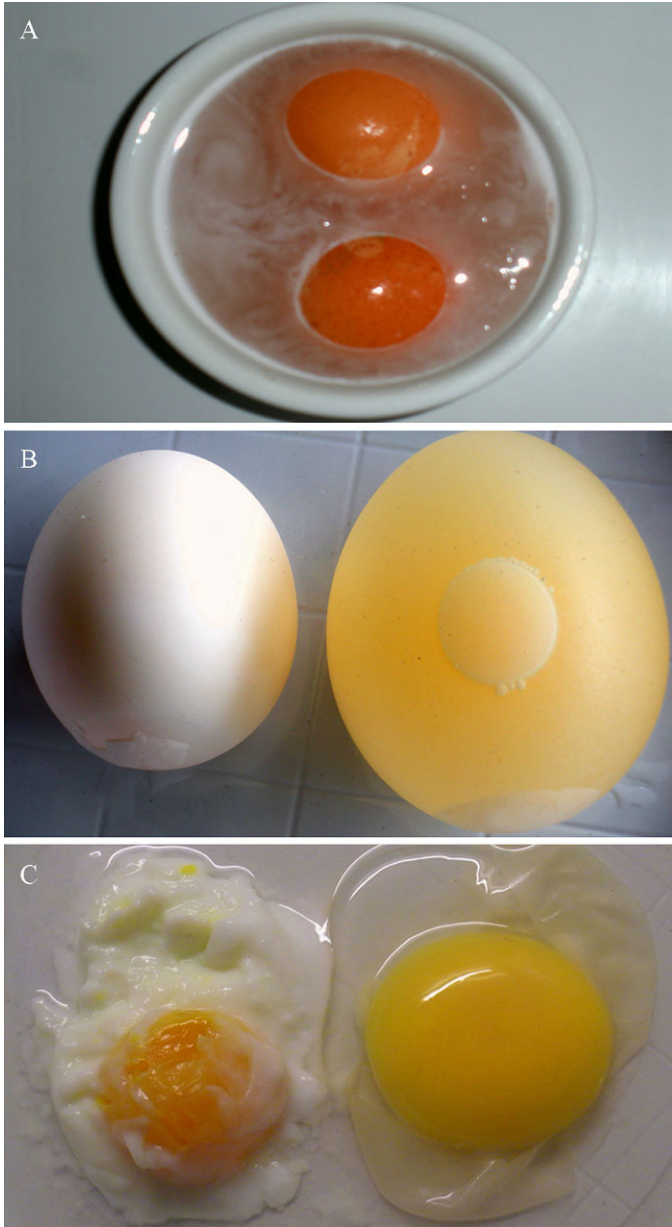


Fig. 2.3. A home experiment showing the effect of osmosis on eggs.

At this stage you should have guessed what has happened. An egg contains many substances like proteins that, for the good of the chick, should not escape from the amnion. Therefore, whereas water gets inside the egg soaked in fresh water by osmosis, diluting its contents, for the other egg the external salt concentration is so high as to favor the *exit* of some water, even if this yields an increase in the internal protein concentration. What is left inside is better appreciated by breaking the membranes (bottom picture)²⁰. While the white and the yolk of the first egg have remained liquid and thin, the content of the other egg has shrunk to a semi-solid jelly. Another home example, very familiar to Mediterranean people, is the way we usually remove the “bitter water” from eggplant, by covering slices of it with salt, maybe pressing to improve contact. Here two dialysis processes actually take place. On the one hand, part of the water seeps out from the slices by osmosis; on the other, there is an osmotic exchange between sodium getting into the eggplant, and potassium (which is mostly responsible for the bitter taste) coming out.

In the examples we have seen so far, the solvent flows spontaneously through a dialysis membrane to dilute a colloidal suspension or a salt solution. In some cases, however, it would be useful instead to take the solvent out from the membrane, in other words to make it flow the other way around. For instance, it would be very useful to use an osmotic membrane to extract fresh water from salt water. Because osmosis works in the opposite direction, however, it is clear that this cannot take place *spontaneously*. To do it, we should somehow pay, and in physics money always means energy. For instance, extracting fresh water from a salt solution is feasible provided that *we* apply a pressure (larger than the osmotic excess) to the solution, forcing the solvent through the membrane, whereas salts and other filth are retained inside (obviously this requires work, and therefore energy). This is the principle of inverse osmosis, used in many widely advertised domestic water purification systems²¹.

At this point, we should pause to do justice to biological membranes, which are anything but the simple dialysis bags we have been talking about. *Au contraire*, cell membranes, which we will discuss at great length in the final chapter, are masters of direct and inverse osmosis, since they manage to let through what they need when and how they like. Without these osmotic machines, I would not be here writing (nor you reading) this book, since our brains work just because of our nerve cells’ wonderful skill in this area.

²⁰ The “balloon” egg actually bursts, squirting all over the kitchen and triggering the rage of the experimenter’s spouse.

²¹ Technically, the method is a bit more complicated. Usually, pressure is applied *tangentially* to the membrane, which guarantees a much higher efficiency.

2.6 Colloidal Lego, matter made to measure

There is a sort of physicist who is perpetually unsatisfied: the condensed matter theorist, whom we shall dub in short a “theomad”. Probably the origin of their discontent is that, in their view, God or someone on His behalf has created too messy a world: had they been in His shoes, they claim, they would have made a much better job of it. To tell the truth, theomads are really good at creating ideal worlds and at examining in depth how they work – worlds made of billiard balls, rigid rods, equal coins, but above all worlds made of things that ignore each other or, if they do interact by means of some force between them, do so in a very simple way, as for instance balls connected by springs would. A well-known joke at the expense of theoretical physicists has them wondering how to increase milk production on a farm, and contains the immortal line, “Consider a spherical cow in a vacuum . . .”. Well, the bucolic world of a theomad is not only a place where all cows are spherical, but one where cows, in a first approximation, never get together at all (clearly there are no bulls around, at least).

Unluckily, the real world is quite different, not only because it is made of molecules, atoms, and “elementary particles” with, deep down, a split personality (somewhat like particles, somewhat like waves, as the ill-famed quantum mechanics says), which are anything but simple balls or sticks, but also because atoms and molecules, far from being lonely hearts, are related to each other by *very* complicated forces. Efforts to explain a world made of *these* things are likely to bring on a chronic headache, at the very least. Okay – you may say – but the real world is this one, and *that* is what you should try to understand, otherwise what do we pay you for? Nonetheless, many colleagues of mine keep on shamelessly designing worlds made of balls and sticks, and, in my opinion, they are perfectly right. Indeed, it’s only by studying these ideal worlds that some basic ideas, such as the difference between a fluid and a solid, or between order and disorder, can be fully grasped.

Obviously, till a few decades ago these colleagues of mine led a rather lonely life, for these worlds were only in their minds. Then computers came along, with their rapidly growing skill in simulating virtual worlds, including those all theomads dreamt of. Possibly this suits my kids and their friends, who are virtually PC peripherals, but an old (er . . . let’s say “full grown”) generation like mine prefers to see, smell, or touch something substantial (and this is obviously true for *any* kind of material). Luckily for us, colloids can often make our wishful thinking come true, because, using a kind of conjuring trick, we can to some extent *choose* the forces acting between colloidal particles, turning them into the bricks of a “mesoscopic Lego” that allow us to build the worlds the theoreticians long for. You may think that this is totally meaningless for, after all, a colloid is nothing but a bunch of large and complicated clumps of chemicals, immersed in a liquid like water which is anything but simple. Contrasted to stuff such as a salt crystal or a window pane, they must surely be harder to understand! Not so. This magic trick just consists in manipulating

the solvent (generally by some additive) and then neglecting it to care *only* about the particles and the forces acting between them. We shall now try to see how this gimmick actually works.

First, note that colloidal particles, compared with most other things around in the molecular world, usually have a much simpler shape. It is true that natural particles, such as clays flowing through water-bearings or dust grains suspended in air, are generally very irregular and varied in shape. Yet, over the past decades, chemists have learnt to create particles with very controlled size, shape, and material properties. Thus, it is not too difficult to produce spheres which are all more or less equal (just like the ideal cows we mentioned), with a diameter that can be as small as a few nanometers, made of glass, metals, and plastic materials. So far, making rods or disks has been less successful, but what we get is adequate for many purposes. Certain chemists and physicist have also been able to produce more elaborate shapes, such as little eggs, pyramids, or dumbbells: a paradise for theomads!

Yet, as we said, controlling the shape is not enough. Let us then see what kind of forces may act between colloidal particles. You might think that the term “colloid” gives us a clue, stemming as it does from the word for glue, but we should not be led astray. When the Scottish chemist Thomas Graham coined this word to set colloids apart from those solutions that were able to pass freely through a membrane (rather oddly, he dubbed these “crystalloids”), he chose it only because the first colloids were obtained from isinglass or sticky jellies. Nonetheless, Graham partly hit the mark, since colloids are often rather “sticky” by nature, and spontaneously tend to clump together. Why is that? All that can be said is summed up in the homeopathic maxim *similia similibus curantur*, or “like cures like” (this is actually the only situation, in my view, where such a claim makes sense). But what is this colloid disease that needs curing? It is precisely their peculiar property of exposing a huge surface area to the solvent. We shall see that building up a surface separating two different materials *costs energy*. After all, for a piece of metal or glass there is no better neighbor than another piece of metal or glass, rather than some solvent molecule that they may like but that is still alien stuff²²... For a colloidal particle, the easiest way to cut down costs (namely, contact area) is to join to a particle like itself, and then to another, and so on and so forth, till a single lump forms.

What I have tried to summarize in simple (and quite inaccurate) words corresponds, in serious science, to what are called *van der Waals* or *dispersion* forces, a concept that actually lies at the heart of physics²³ and plays a key role in everyday life. Just to give one example, without dispersion forces the

²² For some special particles we shall meet soon, which are quite “friendly” toward the solvent, things are rather different.

²³ That abstruse theory of quantum mechanics shows that dispersion forces magically stem from spontaneous “vacuum fluctuations”. In modern physics, a vacuum is not completely empty after all – so Aristotle was right, in a way!

great pyramids would not still be standing, since what we call friction, which is essential for keeping stones together, is strongly related to these forces. The important point is that these forces are *attractive*, namely they tend to make things stick together, and that they are strongest when they act between two objects made of the *same* material. Do you need proof? Just enter a glass-makers shop (although, unluckily, few of them are left) and look at the way glass panes are stored. Between any two of them, the judicious glass-maker inserts a paper sheet. Why? Well, take it out, stack the panes together, and then try to separate them, if you can. You will then realize that van der Waals force do indeed exist!²⁴

Therefore, when two colloidal particles, tossed about by Brownian motion, come near enough to each other, van der Waals forces make them stick together (or, as we should say, *coagulate*). “Near enough” actually means “very near”, since these attractive forces are felt only at the very short range of a few nanometers²⁵. Yet, during their random walk, sooner or later two particles do meet (the higher their concentration, the sooner this happens) and... game over.

Why then do colloidal suspensions actually *exist*? The point is that, besides dispersion forces, additional *repulsive* forces enter the game, pushing the particles apart and in this way *stabilizing* the colloid. A common origin of this repulsive interaction is that the surface of many colloidal particles is (for chemical reasons we won't go into) electrically *charged*. For instance, glass particles normally have a negative surface charge, whereas certain mineral colloids are positively charged. Do not worry if you don't remember anything about electric (or, more properly, electrostatic) forces. For our purposes, it's enough to keep in mind that:

1. *Like* charges, both with a positive or negative sign, repel each other, whereas charges with opposite sign attract.
2. Charges come by twos like cherries. If there is a certain amount of positive charge, the same amount of negative charge is around. Hence, a solution is always *electrically neutral*.

The second statement, in particular, tells us that if we have a colloidal particle carrying, for instance, 101 negative charges attached to the surface, somewhere there must be an equal number of positive charges. This opposite contribution is made of little charged atoms or molecules (which we call ions) going freely around in the solution. But the first statement tells us that these positive ions cannot be completely free. After all, there are 101 negatives attracting

²⁴ Separating microscope slides with tissue-paper is a good rule too, which unluckily my students have not yet learnt to follow.

²⁵ At extremely short distances, however, they become really strong, so much so that if the particles were perfect spheres, the forces would become infinite at contact. Perfection does not exist on this planet, but two particles made of a sufficiently soft and plastic material do sizeably buckle when they stick, showing the strength of dispersion forces.

them, so that, like the little Dalmatians, the positive ions are just waiting to...charge! So a little “cloud” of positive charges takes shape around the particle, a cloud of ions that may extend for tens or hundreds of nanometers. How many are there? You won’t be too surprised to discover that there are still *exactly* 101, as many as the charges bound to the surface²⁶. What happens then when two such particles approach? Before they get close enough to feel the fatal attraction of the van der Waals forces, the clouds surrounding them start to overlap and, since they have the same charge, to repel. As a consequence, particles and associated clouds are pushed away from each other, as if there were a spring between them. Ultimately, the surrounding ion clouds keep the particles so much apart that (sedimentation apart) a charged colloid can unhurriedly remain for years in a bottle, without coagulating and precipitating to the bottom as a dispiriting fine dust.

All this works in water, but surely not in *oil*. Water is what we call a *polar* liquid, where free charges, such as the ions that salts form when they dissolve, can exist. Oil is different. In oil, or in what is in general called a *non-polar* liquid, there is no way to separate a positive from a negative charge (have you ever tried to dissolve salt in oil?). So, colloids cannot be made stable by charge effects, and this is a pity, because for many purposes it would be quite useful to suspend particles in an oil. Moreover, electrostatic forces between charged particles are not so easy to investigate, and our theomads would prefer something *much* simpler, which is easier to obtain, as we shall see, in non-polar solvents. How then can we beat dispersion forces and avoid particle coagulation? The secret lies in coating them in little “hairs”, made of molecules in the shape of a rather long chain, but still short compared with the particle size. We shall talk at length about them in the next chapter. So far, it is enough to say that, when two particles approach closely, the “hair forests” covering them do not like to overlap. Once again, this mechanism keeps the particles far enough apart that van der Waals forces are too weak to make them stick.

Charging particles or covering them with hairs are not the only ways to stabilize a colloid. There are special particles we shall soon meet that remain peacefully suspended for ever, even if they are not charged or covered by hairs. The basic reason is that these particles just love to be surrounded by solvent. This may look strange. What happens if we take a lump of salt or sugar, substances that love water, and dip them into a glass containing this liquid? Obviously, they dissolve – in other words, their atoms or molecules slowly scatter around uniformly (by diffusion, remember). Why is it, then, that these special particles *do not* dissolve? There are two main possible reasons, either because they are actually long chains of tightly bound molecules (this is the case for the polymers we shall meet in the next chapter), or because the

²⁶ In this way, positive charges exactly “screen” the negative ones, and another positive ion has no more reason to approach, seeing from the distance the set “particle + cloud” as globally uncharged (“neutral”).

molecules they are made of are forced by their special nature to band together to form a particle, which is the case for the surfactants we shall encounter a bit later. In both cases, a thin solvent layer wraps around the particle, a bit like Linus' security blanket. Needless to say, it is just this beloved blanket that keeps particles far enough apart to avoid the ruinous effects of dispersion forces.

Analyzing colloid stability, we have therefore already seen at work those solvent manipulation techniques I mentioned earlier. Van der Waals forces can, for instance, be modified by changing the solvent and making it more favorable for the particles; additives that stick to their surfaces can make them more stable; or the same goal can be reached by charging them. We shall start from this last example to show that in fact we can do much more, adding *more* ions to fine-tune the forces between particles as we might tune a guitar.

2.7 Softness without limit: fractal aggregates

In discussing how a charged colloid behaves, I was very vague about the way the ion cloud surrounding a particle is actually made, and in particular about the size of this region, i.e., up to what distance it extends. This crucially depends on the *kind* of water we use to prepare the suspension, something which can be grasped with a simple experiment. Adding ordinary tap water to a suspension of charged particles, we would observe that the particles rapidly settle out as fine dust falling to the bottom of the container. This does not happen if we add distilled water instead. Quite the opposite: the suspension becomes even more stable. Now, we know that the main difference between tap and distilled water is that the former contains salts, mostly of calcium, sodium, magnesium, iron, and often chlorine. The total amount, usually abbreviated TDS (Total Dissolved Solids), is widely variable, but should not exceed a few grams per liter. Hence, it is the addition of salts that gets the colloid into trouble. Let us first get a general idea of why this happens. In the absence of salt, the cloud surrounding a particle, which is swimming in a kind of fresh-water lake, suddenly sees another similar cloud with the same charge. However, if we add a little table salt, mostly composed of sodium chloride containing a sodium and a chlorine atom (NaCl , as you surely know), things drastically change. As we said, salts in water split into electrically charged ions, such as Na^+ and Cl^- . Even if we add a small amount of NaCl , say a gram per liter, we get a huge number of ions in solution, about ten million Na^+ and as many Cl^- ion per cubic *micron*! At this stage, our particle is already swimming among *heaps* of ions. How could any difference ever be made by the additional few ions it finds around a playmate?

To put some numbers on this, theory shows that, by adding salt, both the size of the surrounding ion cloud (which is properly called the *Debye-Hückel length*) and the strength of the electrostatic forces considerably lessen, so that

repulsion is weaker and acts at shorter distances. For instance, in the presence of half a milligram of NaCl per liter the Debye–Hückel length is about $0.1\ \mu\text{m}$, but it shrinks to just 2 nm if we add 1 gram of salt per liter²⁷. At the same time, the repulsion force has decreased a few *thousand*-fold. You may picture the situation by regarding the repulsion due to the overlapping of the ion clouds as a kind of hillock the particle has to climb to get close to another one. If the particle succeeds, on the other side it falls into the bottomless pit of the van der Waals forces, and sticks to its companion. But climbing a hill requires energy, and we know that all the energy our particle has is kT . Therefore, if the required energy is much larger than kT , the particle will never make it. If we now start adding salt, the hillock shrinks and gets *lower*. Suppose that the energy goes down to just 2 or 3 kT . This value is still larger than the *average* particle thermal energy, but some more “gifted” particles may have enough energy to get over the hill, therefore sticking to another one. As we add more salt, the hillock progressively vanishes, and particle aggregation gets faster and faster. As soon as two particles meet they stick, and this happens the more often the higher is the colloid concentration.

To investigate better what happens, let us just consider a case where we have added enough salt to kill the electrostatic repulsion completely. Once two particles have stuck, a third one is more likely to bump into them, because now they are a bigger obstacle, and so on, till a bigger and bigger particle lump forms. What do these aggregates look like? Well, they have a truly special structure, which is related to one of the most original ideas mathematicians ever had. Although they can hardly be pictured on a flat surface (they are obviously immersed in space), these lumps look rather like I have tried to picture in Fig. 2.4. The first feature that catches the eye is that they are not compact objects, but are full of holes. Why? To understand this, let us see what happens to the particle at the top right, which is approaching the aggregate with its zigzag Brownian motion. There is a lot of room to fill within the aggregate, but the particle will almost never *get* there, for there is a high chance that, before getting into a hole, it bumps into one of those particles in one of the many “arms” protruding outside. And, remember, if it touches it sticks. You can easily see that this is a kind of avalanche process: the more particles attach to the arms, the more the latter branch off outside, the more difficult is for a newcomer to get inside the aggregate. The sketch I made conveys only a rough idea of what is happening, since we should take into account not only that single particles can stick to an aggregate, but also that two of these aggregates can meet and merge, generating even more holes. What results from all this, and can be explored with computer simulation, is really one of the emptiest objects one can imagine.

To see how “open” a colloidal aggregate can be, we have to go on a brief excursion into an abstract mathematical world, one of those only mathe-

²⁷ One can more rigorously show that the Debye–Hückel length is inversely proportional to the square root of salt concentration.

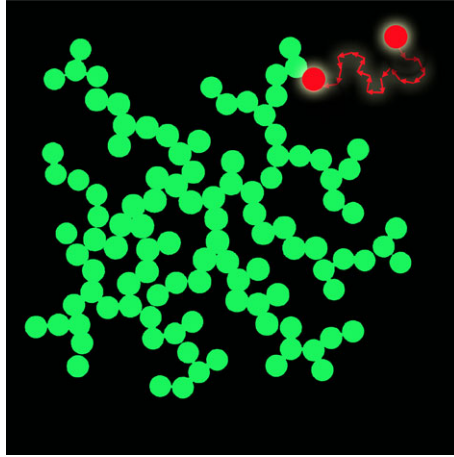


Fig. 2.4. Draft of a colloidal aggregate. Note the particle at the top right, which is just sticking to one of the aggregate arms.

maticians can conceive. We are used to regard everyday objects as “three-dimensional” , but what do we really mean by this? Well – you may say – everything, for instance the piece of furniture I just put in my living room, has a length, a width, and a height. True, but in the first decades of the last century a great German mathematician, Felix Hausdorff, thought of looking at this in a slightly different way. Take for instance three balls, made of the same material. The second ball has twice the radius of the first, and the third twice the radius of the second. I think you may agree that the second ball weighs eight times the first, and the third ball eight times the second, that is, 64 times the first²⁸. Let us then look at the two series of values to try and find a relation between them:

Radius (compared with the first ball): 1, 2, 4

Weight (compared with the first ball): 1, 8, 64

Not a big issue. The number in the lower series are just the *cubes* of those in the upper one. Thus, the weight (and therefore the quantity of matter) grows like the cube of the radius – or, as mathematicians would say, as the *third power* of the radius. But “three” is just the number of dimensions of our usual space. Hausdorff then had the apparently trivial but actually brilliant idea of stating that an object has three dimensions if, on measuring how much stuff is contained in a sphere of radius R placed inside it, the latter grows as R^3 . Common things obviously do have this property, but the astonishing fact is that, using this definition, there are objects that, though immersed

²⁸ If you accepted this claim without blinking, you are possibly not very well suited to experimental science, for I did not tell you that all three balls were *full*. Anyway, I’m telling you now.

in a three-dimensional space, have *less* than three dimensions. The colloidal aggregates we have just described are of this kind. Let us first recall that a number can be raised to a power that is not necessarily integer. For instance, we can write the square root of 5, $\sqrt{5}$, as $5^{1/2}$, or similarly $7^{2/3}$ means that we must square 7 and then take the cube root (or vice versa, it does not matter). These two examples may help you understand what we mean by $x^{a/b}$, or in general by x^c , where c is not necessarily a whole number. If we now ask a computer to make colloidal particles stick together, so that they generate a fractal aggregate (which is not too difficult), then to draw a sphere inside it, and finally to evaluate how the number N of particles contained in the sphere depends on its radius, we find that N grows approximately as $R^{1.7}$. Hence, not only is the aggregate dimension much lower than three, but it is not even an whole number! These weird objects are called *fractals*, and the power to which we must raise R (here 1.7) is called the *fractal dimension*.

Passed over in silence for almost half a century, fractals were rediscovered by Benoit Mandelbrot (who actually coined the word “fractal”) at the end of the sixties, and since then have been recognized by physicists in the shape of an incredible number of things, ranging from snowflakes to coastlines, lightning, river basins, even broccoli. In fact, without pointing it out, we have already encountered an example of a fractal. Consider the trajectory that a particle follows during its Brownian wandering. As we have seen, the radius of the explored region grows as the square root of the number of steps N . Turning this relation around, we see that the number of steps contained in a sphere of radius R is proportional to R^2 , which is like saying that the particle trajectory is so jagged as to be a fractal object with dimension equal to two.

Ultimately, maintaining that aggregates are fractals is a much more precise way of saying that they are full of holes. What’s more, it is easy to see that the larger a fractal aggregate gets, the emptier it is. Take for example two aggregates, one about twice the size of the other. The larger aggregate will contain $2^{1.7} \simeq 3.25$ times as many particles as the other (use a calculator to check, if you like). Yet its volume is *eightfold* larger, and therefore its density (the number of particles per unit volume) is almost 2.5 times *lower*. Therefore, the more they grow, the more colloidal aggregates become light, tenuous, made of almost nothing, filling a lot of room with very little stuff. These large objects are cumbersome, and this has noticeable effects on the properties of the solvent they are immersed in. In particular, they make it very viscous, meaning that the solvent finds it harder to flow, an effect that makes these aggregates particularly useful in many technological applications as *thickeners*. For instance, there is a good chance that particles made of silica (silicon dioxide, SiO_2 , the main component of what we usually call “glass”)

are present in the toothpaste you use everyday, making it in addition more abrasive (they are very common in “whitening” toothpastes)²⁹.

“Precipitated silica” (produced differently, but still in the form of aggregates similar to those we have described) is also used as an additive for many other purposes, not just as a thickener. For instance, it’s used to prevent clotting of granular materials such as table salt, which is particularly prone to clumping when damp, or to limit the formation of foams. I do not want to scare you too much, but the temptation of adding a bit of precipitated silica to some food to make it creamier is rather strong, and regarded as innocent in many countries³⁰. If *this* worries you, regard yourself as lucky in comparison to hundreds of thousands of workers in the mining, construction, ceramic, and obviously glass industry, who inhaled silica particles and have suffered the truly unpleasant side effect of this, silicosis. Luckily, many foods exploit natural colloidal aggregation to get that creamy taste that is so pleasant for the palate. A classic example is yoghurt, which is nothing but the outcome of the aggregation induced by bacteria of a very special colloid, milk, that we shall meet again when we encounter emulsions³¹.

Back to our aggregates, what happens if we let them grow more and more, avoiding allowing them to settle too fast (maybe using particles as dense as the solvent)? Well, within a short time they will join and form a *single* huge aggregate filling the whole container. We have thus obtained a very special material, a *gel*, or better a *hydrogel*, i.e., a material that behaves like a solid (if you carefully try to turn the container over, the gel does not spill over the floor), but that, in terms of quantity of matter, is made almost of nothing (once again, it has a fractal structure). These materials, which we shall amply discuss, have a large number of applications precisely because, although there is little stuff inside (apart from the solvent, of course), their internal surface is huge. To tell the truth, gels obtained by colloidal aggregation are very fragile. There are few contact points between the particles, and van der Waals forces are weak, so what we get is really a very “soft” material. In the next section, however, we shall encounter some very special relatives of theirs, which are anything but soft. On the contrary, they are about as hard as could be.

2.8 Concrete: united by charge

I have spent quite a bit of time in trying to explain why the presence of charges on the particle surface stabilizes a colloid so much that, to precipitate it, we must add salt to “kill” electrostatic repulsion. Is this always true? No, sometimes the opposite takes place, and particles bearing the same charge strongly

²⁹ If you think you can escape by saying goodbye to toothpaste and exchanging it for certain strongly advertized chewing-gums, you are mistaken. There really is a lot of silica in the latter.

³⁰ It is largely used in animal feeds, where it is officially known as additive E551b.

³¹ After all, the Turkish word *yoğurt* has the same root as the adjective “dense”.

attract each other. Don't worry, I did not lie; it was just a sin of omission. Everything I told you holds true if the surrounding ions carry a single charge or, as we shall say, if they are *monovalent*, for instance simple Na^+ or OH^- ions. But what happens when they are *divalent* (or even *trivalent*), meaning that they bear two or more charges each? Well, here even our theomads are partly groping in the dark. While in the former case we have a theory that works fairly well and justifies what we said on stability, here the problem becomes more challenging.

But there is at least one extremely important situation that clearly shows us that things can go the other way around. What I am going to tell you is the short story of a material, anything but soft at first glance, which has deeply marked the story of mankind and, moreover, contributed to the flowering of an empire of which my fellow countrymen and women are the progeny. Let us travel back to the distant past. We have said that friction is a blessing when building anything. Try to imagine how our ancestors could have erected their gigantic monuments if all they had were stones that slid over one another as if there were oil or an air cushion between them. Actually, what permitted them to build the great pyramids or the Mesopotamian *ziggurat* was their skill in wedging stones carved in masterly fashion or in making bricks of the right shape and solidity. But humans, who are (or at least were) not totally dumb, soon understood that it was worth giving friction a helping hand, by laying first some simple clay between the stones or bricks, and then mortars made of gypsum and lime, skillfully mixed. These "binders" were rather weak, and easily dissolved in water. Therefore, if something dating back to those old times is still standing, we mostly owe it to friction.

Until the Romans came, and with them a magic substance called *puteolana* made of volcanic pumice and ashes, which was abundant in the region around Pozzuoli, close to Naples. Indeed, it did not take them too long to discover that *puteolana*, mixed with lime, yielded a material that would set and hold firm even in water. Indeed, it actually *needed* water for hardening. This was the birth of the *opus caementicium*, a building technique that revolutionized architecture and made possible masterpieces such as the Pantheon or the great aqueducts. These vast structures used as binder mortar the ancestor of what we now call cement, or more precisely *hydraulic cement*³².

Then came the Middle Ages, during which the Romans' magic formula was completely forgotten, along with many other things, and Europeans reverted to using techniques that might have looked prehistoric to the Egyptians. A moderate awakening took place only with Humanism, thanks to the rediscovery of Vitruvio's *De Architectura*, and thus hydraulic limes slowly began to

³² Actually, it seems that even before the Roman times there were attempts to use "hydraulic limes", mostly made by the Greeks who (fancy that) also used volcanic ashes dug out of the wonderful island of Santorini. Yet, even if the Greeks may claim priority in many fundamental advances across all fields of knowledge (later duly copied by my old fellow countrymen), here they did not rival the Romans at all...

appear in buildings. Yet it was only at the beginning of the XIX century that, thanks to the development of high-temperature ovens, the advance took place that led an English kiln owner, Joseph Aspidin, to invent *Portland cement*, which is at the roots of most modern concrete binders. A full book would not be long enough to describe how modern concrete is made, or its properties and many different formulations and uses. Yet, bizarrely enough, even though more and more sophisticated concretes had already invaded the planet and gigantic skyscrapers already soared over many cities, until the end of the twentieth century no one had any sound way to explain *why* cement works so well. And this is because not only the chemistry, but also the physics of this wonderful material is extremely complicated.

What on earth have cement and concrete to do with colloids? Well, water (at least at the beginning) is there; it *must* be there. And then there are particles. Besides the large sand and gravel grains that make up the mixed matrix of concrete, the cement keeping it together is mostly made up of particles with a size between tens and hundreds of microns (a micron being a mere thousandth of a millimeter, remember), mainly (but not exclusively) composed of calcium silicate, a mineral containing silica, calcium, and oxygen. At the beginning cement is therefore a highly concentrated suspension, containing more than 40% particles. But the high adhesive strength of cement is due to smaller particles still. These are formed in a second stage of the setting process, as some of the original calcium silicates are dissolved and then crystallize back out of the liquid. These new particles are “platelets” with a thickness of about 5 nanometers and a diameter of a few tens of nanometers, made of hydrated calcium silicate hydrate (CSH for short), that, besides sticking to the original grains, rapidly form a gel similar to those we already met, but very much sturdier.

Why? It certainly cannot be van der Waals forces that keep them together so firmly; they would never manage it. Only electric forces can fill this role. Yet, since both calcium silicate grains and CSH particles are negatively charged, how can they attract each other? The point is that our ion clouds this time are mostly calcium ions Ca^{++} , which, as the double plus sign might suggest, are *divalent* – doubly charged. As I already mentioned, the reason why divalent ions can induce attractive forces between like-charged particles has only started to become clear in the past few years. To fully understand it requires very sophisticated concepts such as that of “ion-ion correlations”, but I shall try to give you at least a hint of a reason. Just picture a Ca^{++} ion as if it had two “little arms”, each one carrying a positive charge. These ions are obviously attracted by the CSH particles, having an opposite sign, but it may happen that these two limbs are attracted by two *different* particles. So, the ion becomes a kind of “little bridge” that holds two particles together at a very short distance. This is a very crude model, dangerously and superficially appealing to intuition (which is almost always misleading, in these tricky problems), but not totally alien to reality. On much firmer ground, in the past few years many proofs have accumulated in favor of a cement theory

based on colloidal forces, and not on real chemical bonds, as many formerly believed.

In fact, colloidal systems where forces of this kind are in action existed well before the invention of cement. These are the clays present in aquifers that were used as binders by our ancestors. Even more, in this case platelet particles (of a different kind) are already present, and do not require a precipitation process as in cement. The main differences are, first, that the particle charge is much lower and, second, that a lot of singly charged ions are there too. As a result, particle adhesion is much weaker and, moreover, water is a nuisance, since it just increases the normal electrostatic repulsion between the particles.

2.9 Particles spreading waves: colloidal light and colors

If you ever happened to stroll (not to drive, I hope) on a winter day through lowlands such as those surrounding my native town of Milano, you are surely familiar with the topic with which I want to start discussing the rich relation between colloids and light: fog. For on foggy days, when there is actually no cloud in the sky, nothing can be seen. I do not mean just houses, trees, or (worse) cars, but sometimes even your feet. Where does this weird (and dangerous) atmospheric effect stem from?

Let us start with saying that fog is a particle dispersion too, and to be precise a dispersion of water droplets in a “solvent” or medium which is not a liquid, but air, so it is an example of those suspensions called *aerosols* we shall deal with later. Actually, all fog does is to raise to a fever pitch what all colloids do, namely to scatter light. When illuminated, indeed, all kinds of particles pick up a little light and, instead of letting it pass straight on, scatter it in all directions. But they do not do this “democratically”. Instead, they prefer scattering blue rather than red light. To be more precise, every kind of “electromagnetic radiation”, which includes also forms of “light” that we cannot see, such as infrared, ultraviolet, X-rays, and gamma-rays³³, has a well-defined *wavelength*, usually indicated by the Greek letter λ (lambda).

Just picture a wavelength as the distance between two neighboring crests of the sea waves you see from the beach. Here, something more complicated than water is forming wave patterns, or “oscillating”, but the idea is the same, although for visible light these waves are very short, because λ ranges between $0.4\ \mu\text{m}$ for the blue-violet, to $0.7\ \mu\text{m}$ for deep red. We can therefore re-express what we have just said by stating that particles diffuse shorter wavelengths better than longer wavelengths. More precisely, a wavelength twice as long is scattered sixteen times (i.e., 2^4) less. To tell the whole story, it is not only

³³ Concerning the latter, we had better avoid staring at them for, even if they cannot be seen, we can certainly *feel* them. In any case, if there are a lot of gamma-rays around, you are probably witnessing an atomic explosion, and this could be the last of your problems. In all senses.

colloids that scatter light. Gas molecules scatter too, although to a much lesser extent. Indeed, it is atmospheric scattering that renders the sky blue and the sun red at sunset (this is the color that manages to reach our eyes, just because blue is scattered more). A crucial point is that, at least when the particles are small compared with the wavelength λ , the amount of light they scatter grows terrifically with their size: if we double its radius, a spherical particle scatters 64-fold more! When the particles becomes much larger than the wavelength, the growth with size slows down. Moreover, the particles tend to scatter preferentially in the forward direction and, to a lesser extend, backward, namely, in both cases along the direction of propagation of the light falling on them. A physical property on which scattering also depends, one you may be less familiar with, is the *index of refraction* of both particles and solvent. Without going into details, let me just say that this quantity is related to how fast the light moves in a material (the higher the refractive index, the lower the light speed), and also to how much the light is bent from its course (or better, *refracted*) when it encounters that material (the wonderful light effects in diamonds are just due to their high refractive index). For our purposes, it is enough to know that the closer the refractive indices of particles and solvent, the weaker is the light scattering. In particular, if a particle has the same refractive index as the solvent (a condition known as *index matching*), its scattering totally *vanishes*, and it becomes fully invisible³⁴.

Let us see some of the effects of these observations on light scattering by colloidal particles. Unless it contains very special particles (we'll come to these in a minute), a suspension of very small particles, for instance with a size of a few nanometers, looks pale blue for the same reason the sky is blue, and it is the more bluish the more it is concentrated. Yet, if we increase the particle size, all wavelengths get scattered more and more, and the suspension becomes whitish, like fog or milk. On the subject of milk, in the introduction I suggested you try a simple experiment. In Fig. 2.5B you can see the outcome I obtained with no special effort in my kitchen. It should not be too hard for you to reproduce it, provided that you use:

1. *Well-skimmed* milk, so to avoid the presence of large fat drops that, even at high dilution, will yield a whitish shade (we shall see later what the smaller “droplets” are that remain after milk skimming).
2. A flashlight producing a *really white* light, for instance made by an LED. In my case, it was my daughter's pig-shaped keyring flashlight, whose light-emitting nostrils are visible as a reflection in panel 2A (which shows a comparison with plain tap water, just to assure you I did not cheat). If you use a regular lamp, emitting a yellowish light, you can forget about the blue...

The weak blue halo in Fig. 2.5D shows that, as we suspected, a small amount of particles with non-negligible size is also dispersed in a solution of common

³⁴ This is basically the trick on which is based the famous novel *The Invisible Man* by H. G. Wells, which has been the subject of more than one movie.

table salt (which should not display any difference with pure water). This does not mean that additives such as silica particles are necessarily present (I checked on the packet that additives to avoid clotting are indeed present, but they are not colloidal particles), for these could simply be left over from the refining process. Anyway, something big is there, and we do not need any chemical analysis to discover it.

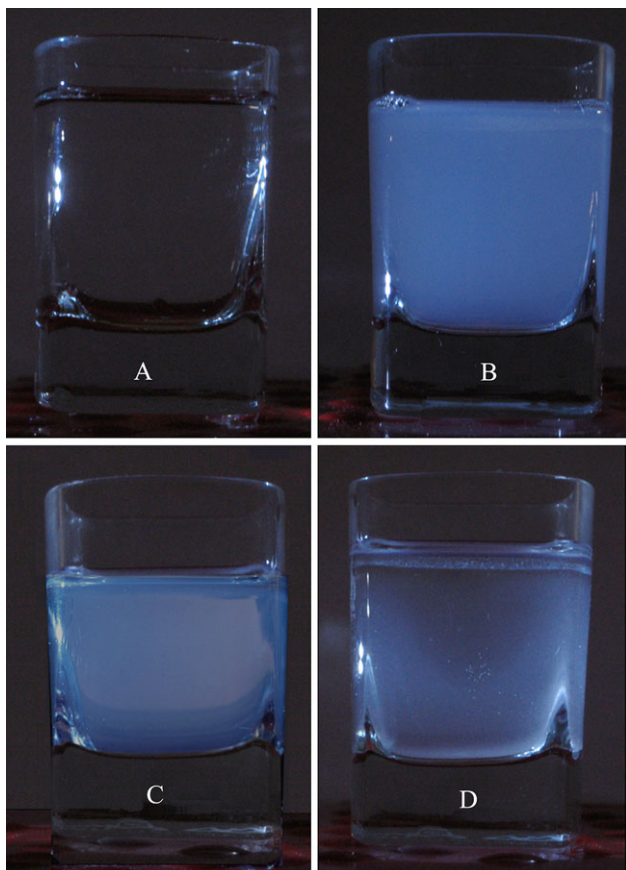


Fig. 2.5. Scattering of light from tap water (A), diluted skimmed milk suspension of colloidal particles with a size of 180 nm (C), and a solution of table salt (D). The light source is to the left.

We mentioned that large particles such as fog droplets, which have a size ranging between a few microns and some tens of microns, mostly tend to scatter forward, but also *backward*. This is the reason why using headlights

on a foggy day is definitely self-defeating³⁵. A related annoying effect takes places when the headlights of a car coming from the opposite direction fall on your windscreen covered, if the wipers are not working properly, by raindrops. There are not many drops, and they are much larger than fog droplets, but they scatter practically all the light forward (towards your eyes), appearing as bothersome shining little stars.

All in all, if colloids were just white or bluish, they would be rather boring chromatically. Actually, however, certain colloids are a riot of color, for colloids are a large fraction of the colors on an artist's palette – the *pigments*. Most of the colors appearing on the frescoes and canvases of the late Middle Ages and Renaissance, from ochre and verdigris to the wonderful ultramarine blue, were obtained by skillfully grinding soils (“earths”) and then dispersing them in a “binder”, generally egg yolk for frescoes and temperas, then linseed or poppy-seed oil with the revolution started by van Eyck in the XV century, which led to the predominance of oil painting. Hence, pigments are colloidal suspensions in every respect. Here, however, the colors do not arise from scattering, but rather because the particles chiefly *absorb* some specific wavelengths, reflecting just those we actually see. This is a very different way of producing color. Scattered light is only diverted from its original path, but in absorption, which for pigments usually comes from ions of metals such as copper, lead, or cobalt, the light loses energy that is turned into thermal motion of the molecules (so, on dog days, people prefer dressing in light colors, not in black). Anyway, even without calling in at a decorator's shop, we still bump many times a day into colloids that absorb light. Coffee and tea, for instance, are colloidal dispersions too. Just take a look at the ring that forms at the bottom of a cup of tea (green tea, for preference), caused by particles that clump together and settle out, or at the curious appearance of a coffee stain on clothing where, because of the surface tension we shall talk about later, particles gather together at the rim of the stain³⁶.

Coming back to pigments, you may have got the impression that their color is just a result of the chemicals they are made of. If so, you are on the wrong track. The colloidal state of the pigments has important effects on their color, for at least two reasons. First of all, particle size *matters*, as the Tuscan painter Cennino Cennini guessed, back in the early XV century. On pigment grinding, Cennini writes in his celebrated masterpiece *Libro dell'Arte*:

³⁵ Fog lamps, low-mounted because fog is generally weaker close to the ground, emitting a yellow light without any blue component, may help (you should now understand why), but only partially.

³⁶ By the way, both these drinks show interesting effects related to suspension stability. For instance, coffee with milk (or, if you prefer it, “espresso macchiato”) generally contains smaller particles, because some components of milk reduce aggregation, whereas lemon reduces the formation of scum on cooling tea, besides changing its optical properties.

“E tanto le macina, quanto hai sofferenza di poter macinare, ché mai non possono essere troppo; ché quanto più le macini, più perfetta tinta viene” [*And grind them as much as you can stand. For it is never too much. For the more you grind it, the more a perfect hue comes out*]

So much that, for vermilion:

“se il macinassi ogni dì persino a venti anni, sempre sarebbe migliore e più perfetto” [*Had I gone on grinding every day for twenty years, it would still improve and become flawless*]

Grinding brightens pigments mainly because, when we reduce the size of the dispersed particles, we decrease the scattering at all other wavelengths, which blurs the natural color. When a pigment is heavily ground, as we can do with modern techniques, our beloved “colloidal blue” peeps in once again. This happens for some hues such as “Mussini Transparent White”, which actually shows a light blue shade. But the appearance of a pigment also depends on the refractive index of the binder (i.e., of the solvent) used for dispersing it. For instance, when distempers for painting on canvas were progressively replaced by oil, which has a much higher refractive index than water, painters realized that some colors lose most of their gorgeousness. So the magnificent and expensive ultramarine blue becomes sadly dark, vermilion does not coat any more, whitewash looks almost transparent. When the goal is to obtain particularly brilliant and reflective white surfaces, the particle refractive index takes on a vital role. For instance, using pigments made of titanium oxide, which has a refractive index only 30% larger than zinc oxide, the fraction of light reflected by a painted surface grows from 20% to more than 80%.

Actually, scattering and absorption by dispersed particles are closely related. A suspension looks very different from a chunk of the same material, even when the latter is dipped into the same solvent. This difference may become sensational when the particles are *very* small (say, with a diameter of a few nanometers) and made of a pure metal, such as silver or gold. Obviously, particles of this size cannot be obtained by grinding (grinding a metal is not easy in any case). However, these particles can be made to grow *directly* from a solution of metallic salts. A pioneer of this technique was Michael Faraday, probably the greatest experimental physicist ever. When he wasn’t providing the basis for a coherent understanding of electric and magnetic phenomena – allowing James Clerk Maxwell to explain what light really is – Faraday dabbled in his spare time with the synthesis of gold particles by precipitation of a gold salt. Faraday was totally baffled by observing how the color of the suspension progressively changed from light yellow to orange and to ruby red as the chemical reaction went on. Stranger still, if the particles were aggregated by the addition of salt (Faraday did not know why, but he made a clever guess), the suspension could even turn blue.

Today we know that these effects arise because not only the purity and brilliance, but the *color* itself of the absorbed light depends on the size of

the particles, when they are very small compared with the wavelength³⁷. For instance, while growing, the color of silver particles shifts from yellow, to brown, to red, until they become grey and then completely black. Obviously, as in any scattering effect, the make-up of the solvent has a role too. Using some tricks of the trade, one can obtain mauve, purple, or violet colloidal gold, practically any shade between red and blue. Changing the optical properties of a suspension by controlling the particle size or solvent has its practical uses. Even more interesting, in the field of the so-called “nano-biotechnologies”, is the chance of deducing the particle size from the color of the suspension, as a technique, for example, to follow the progress of a biochemical reaction.

Optical properties apart, typical colloidal aspects of pigments are their stability and the way they disperse. Quite often, a pigment is made of particles that do not like water, or conversely oil, a problem making it hard to disperse them in these solvents without them aggregating. To do this, additives must be introduced to alter the particle surface and their interaction with the solvent. In ancient temperas, the egg yolk, besides being a very good binder with the painting surface, contained substances (similar, as we shall see, to soaps) that had exactly this protective action. Today, the formulation of industrial pigments is crucially related to the physical chemistry of colloids and surfaces.

I chose painting as a starting point to emphasize the relation between pigments and colloids, but what we said clearly applies to all the varnishes and enamels that the industrial world spreads on thousands of different surfaces, from building walls to car bodies. Just think of how many colloidal stability problems crop up in the production of a water-repellent paint, which must contain particles that “hate” water, but that, at the same time, must be dispersed in water-based solvents to be spread on a surface. And then there are most inks, which, since the first recipes based on soot particles, or made by precipitating iron salt with the tannin contained in oak galls, have been colloidal dispersions stabilized by the addition of gum arabic, a polymer that sticks to the particle surface.

Quite often, in particular in printing, it is important to spray an ink with high speed and accuracy through a nozzle, without the latter getting clogged. We shall later see that the presence of particles or other “big” stuff such as polymers or surfactant aggregates alters the way a liquid flows in quite remarkable ways (these effects are actually essential for paints to work properly). Here I will just mention a problem related to flow through a nozzle that has a marked practical importance. Suppose you fill a syringe with a colloidal suspension, but insert between the syringe body and the needle a filter containing a membrane with holes that are smaller than the dispersed particles (biologists use these a lot). If you now press on the plunger, you may expect the solvent to come out, while the particles remain inside, but this is not

³⁷ This is because absorption is due to the generation of a kind of collective wave effect in the electrons within the metal the particles are made of, whose frequency depends on the particle size.

the case. Unless the colloid is very dilute, the filter gets clogged in moments, and nothing more comes out the syringe. Now, this is not *too* strange. The particles collecting close to the membrane form a dense layer that blocks the filter³⁸. What is very surprising is that quite often the same thing happens, unless you press the plunger very gently, even if you use a membrane that has pores ten or twenty times *larger* than the particles you need filtering out.³⁹ Why and how particles, crowding to get through the membrane, hinder each other until they clog the pores (like a panic-stricken crowd trying to escape from a burning building) is still not completely clear, but you will appreciate that devising solutions that limit this effect is of great practical importance.

2.10 A very particular particulate ink

Pigments and inks are and will always be one of the most important technological uses of colloidal systems, but, in the Internet Age, information is more and more frequently spread electronically, and acquired by means of TV, computer screens, palmtops, and mobile phones. Just to put a figure on it, all around the world more than a square meter of liquid crystal displays (LCD) is produced every *second*. Will paper disappear? Probably not completely, for I believe and hope that none of us will give up leafing through the pages of a beloved book, I might almost say smelling them. But in many other cases using paper is really a waste. It does not make sense, for instance, that so much newspaper is sent every day for pulping, after a brief and partial fruition.

However, the reasons we are still so fond of newspapers are many. They can be read in any illumination, from full sunlight to dim candlelight; they are made of very thin paper, so much that they can be folded and pocketed, and above all no plug-in or battery is needed! Unluckily, from all these points of view, television or computer screens perform very poorly. Firstly, they require an *internal light source*, both when they are “back-lighted” as in liquid crystal display (LCD) screens, and when the elements that make up the image themselves emit light, as in the “organic LED” (OLED) screens which are coming onto the market (more efficient, and promising, but still a bit too dear). Keeping these light sources on obviously costs energy (and thus eats up batteries) and, moreover, the screen is generally not bright enough to be read in full sunlight. Things will be a bit better with OLEDs, but not too much. What probably will still improve is the maximum *acceptation angle* for reading, which for LCD screens is rather limited (but not for paper).

³⁸ This is the main reason why, in inverse osmosis, pressure is applied *tangentially* to the membrane.

³⁹ A practical consequence is that generally syringe filters are “disposable”, meaning that you get a little filtrate, and then you have to throw them away these rather expensive devices.

How nice it would be if instead we could make use of what Nature gives us for free, using a screen based on *reflection* of sunlight, as newspapers do all the time! A screen of this kind would do without internal light sources, and would be all the brighter in a better-lit environment. This really would be an ingenious application of solar energy. Moreover, if the screen uses energy only when it has to be “refreshed”, namely for *changing* type and not for *keeping* it, and were also thin and flexible, we could almost hail it as a miracle. Till a few years ago, all this seemed to be just a dream of science-fiction writers, but things are changing fast and, once again, it’s because of colloids.

To tell the truth, the first attempts to make electronic paper, or more accurately an electronic ink (*e-ink*) date back to the end of the 1970s. Yet, before a suitable and cost-effective material was obtained, we had to wait until the end of the millennium, when a group at the Massachusetts Institute of Technology, after duly creating a spin-off company (“E-ink”), started marketing the first e-paper displays. How do they work? As in any screen, they are made of pixels, each one containing a small capsule about a hundred microns across, filled with a colloidal suspension in oil of two kinds of particles. The first, made of titanium dioxide (TiO_2) and a few microns in size, scatter light strongly because of their refractive index. The others are made of the same material, but dyed with a black pigment. The gimmick devised by MIT researchers consisted in using a pigment that, by sticking to the particle surface, gives them a positive charge, whereas the original TiO_2 has an *opposite* sign. Thus, by applying a voltage between the upper (towards the reader) and lower side of the pixel using two transparent electrodes (electrical conducting plates), the white TiO_2 particles move to the top or to the bottom, depending on where the positive electrode is, whereas the black ones go the other way (see Fig. 2.6). What is very important is that the oil surrounding the particles does not conduct current. Thus, once a white or black pixel has been created, it stays that way with no need to supply further energy⁴⁰.

By dissolving a black dye directly in the solvent, the same trick was later possible using only non-modified TiO_2 particles. Using this method, it has been possible, from the first years of this century, to make high-contrast screens with a high resolution (thousands of pixels per square centimeter) and a thickness of a few tenths of a millimeter, very flexible (although not as bendy as paper yet) and, above all, with very low energy consumption. These so-called *electrophoretic displays*⁴¹ lie at the roots of those electronic book readers which are starting to be in high demand. Countries such as the Netherlands are already experimenting with these as substitutes for standard textbooks, something that will soon substantially lighten our children’s schoolbags.

⁴⁰ In physics, a system showing two “equilibrium states” of this kind is called *bistable*.

⁴¹ Electrophoresis is particle transport driven by an electric field. We shall come back to it when we deal with proteins.

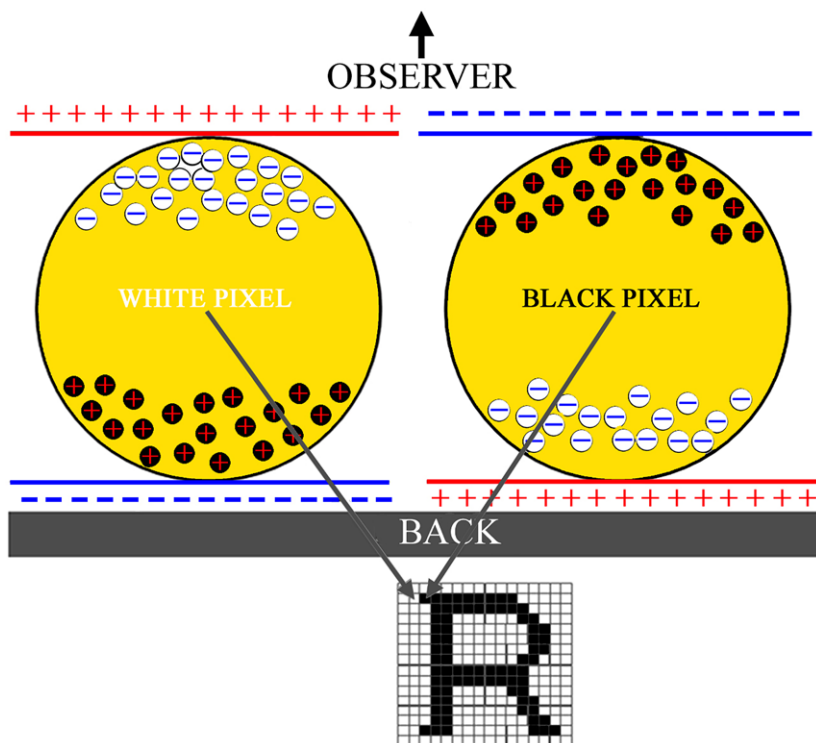


Fig. 2.6. Layout of an e-paper display.

Electronic displays still show some drawbacks when compared with LCD screens. In particular, since moving large colloidal particles is not as easy as aligning tiny molecular liquid crystals, they are quite slow. Refreshing a full page may take as much as a second. Moreover, black-and-white displays clearly do not meet the demands of the general public, by now accustomed to a profusion of colors that are easy to obtain on paper, but not so easy on a screen. To comply with this requirement, each single pixel in an LCD screen (or sensor in a digital camera) is actually made up of (at least) three elements, respectively fronted by red, blue, and green filters⁴², which can be turned on or off independently (each pixel on an OLED screen instead uses three different emitters with these colors). The same layout can be used for “electrophoretic” screens, but this means that the amount of sunlight reaching each colored pixel

⁴² Any other hue is obtained by “summing” these three base colors; red + blue gives magenta (a kind of fuchsia), blue + green gives cyan (a greenish-blue), and red + green, perhaps surprisingly, gives us yellow. Note that this method, which is called *additive synthesis*, is very different from that exploited with printing inks, where the apparent color is all that is left after “subtracting” what the ink absorbs (*subtractive synthesis*), and where primary colors are yellow, magenta, and cyan.

is reduced to one-third of the original, and that the brilliance, the main feature making e-paper so attractive, is noticeably penalized. Luckily, new methods to make electronic inks are currently being studied. These are no longer based on colloid transport, but rather on electrically altering the “wettability” of a surface, a concept we shall discuss in Chapter 4. Although still in its infancy, this technology promises both to render e-paper screens much faster, and to yield brilliant colors through a very different strategy, more like that used for generating them on paper with pigments.

2.11 Flying colloids: deceptive beauty of the aerosols

We close this chapter with some words on particle dispersions in a gas, in other words on aerosols. This is worthwhile, both because they have many technological uses, and since they have a lot to do with our health. We have already described fog as an extreme situation of airborne water droplets (clouds, obviously, are similar), but the air we breathe is always *full* of particles in any case. Just look at a sunray pouring through a loophole into a dark room. Those restless sparkling dots you see are nothing but scattering from suspended particles. Carefully note, however, that their frantic agitation is not due to Brownian motion (though it is there), but to unceasing air micro-currents dragging the particles. It is only thanks to these currents that the particles, which are *far* denser than air (and are not small at all), remain suspended and do not settle on the floor. To give some idea of this, the air in large urban areas typically contains tens to hundreds of micrograms of aerosol particles per cubic meter, with a size from a few tenths of micron up, which corresponds to tens of millions of suspended particles for each cubic meter of air we breathe.

There are obviously natural causes for the presence of aerosols in the atmosphere. Besides the noticeable uplift of sand from the desert and of water droplets from oceans due to wind and wave motion, the main ones are volcanic eruptions and forest fires (though these, in most cases, are not natural). Particles may be given off directly, or form by the “condensation” of gases into liquid droplets. For instance, volcanic eruptions produce a large amount of sulfur dioxide (SO_2), which is ejected to stratospheric height. In the stratosphere, the part of the atmosphere at a height between 10 and 50 km, sulfur dioxide condenses as droplets of sulfuric acid, which is the main source of cloud formation at these altitudes. The great eruptions, such as that of Mount Pinatubo in the Philippines in 1991, may actually increase the concentration of SO_2 in the stratosphere more than a *hundredfold*, with noticeable effects on the whole planet’s climate that can last for a very long time. Worse still, in polar regions, the surface of the droplets in stratospheric clouds is the site where chemical reactions occur that lead to the reduction of the ozone layer

(the notorious “ozone hole”, caused by compounds such as freon used until the 1990s in refrigeration and many other industrial applications⁴³).

In contrast, particles formed “at source”, such as powders, dust, water droplets, combustion products, and also “bio-aerosols” like bacteria, viruses, and fragments of organic matter, are the main components of the aerosols in the troposphere, the part of the lower atmosphere which extends up to a height of about 10 kilometers. On the whole, in normal conditions, the natural production of aerosols is a few *billion* tons a year, whereas those due to human activity are typically ten times less. But while the planet is used to coexisting with the natural aerosols, the manmade sort are a bit more troublesome. This stems both from their type and the fact that they are concentrated around urban areas. There are notorious events such as the “killer smog” of December 1952 that, owing to the wicked combination of “thermal inversion”, which generates fog, and the use of coal as major fuel in heating plants, caused more than 4000 deaths in a few days in London and surroundings. Yet anyone who lives (or at least survives) in a polluted city like Milano, as I do, does not need extreme examples of this kind to realize that particulate emission is one of the most pernicious side effects of the industrial society. The main components of aerosols deriving either from natural sources or human activity are summed up in Table 2.1. The last column is particularly meaningful.

	Oceans	Soil	Volcanoes	Fires	Transport	Industry
Carbon			X	X	X	X
Silica		X	X		X	X
Sodium	X	X	X	X		X
Chlorine	X	X	X	X		X
Calcium	X	X	X	X		X
Magnesium	X	X	X	X		X
Potassium	X	X	X	X		X
Aluminum		X	X		X	X
Iron		X	X	X	X	X
Sulfates	X	X	X	X	X	X
Nitrates				X		X

Table 2.1. Main components of aerosols, either natural or from human activity.

In urban areas, aerosols can be roughly divided into three groups, differing in both origins and particle size. First, there are the so-called “nuclei”, coming

⁴³ By themselves, these compounds are chemically inactive, but this is actually bad news. Since they do not react with anything, they rise without problems up to the stratosphere, where they are chemically split by “hard” ultraviolet rays (those that do not reach the ground), apparently triggering a devastating “chain reaction” that kills off the protective ozone layer (without which, I would not be here writing, nor you reading). Not all the experts agree on this mechanism, but the ban on freon and similar chemicals does not hurt, at least.

directly from combustion processes (industrial processes and domestic heating, but today mostly from vehicle emissions) or generated by gas condensation in a similar way to what we have seen for volcanic emissions. These particles have a very small size (lower than a tenth of a micron, $0.1\ \mu\text{m}$) and reach very high concentrations close to highways, for instance. Just because they are so concentrated, however, the nuclei have a short lifespan, and tend to combine rapidly into larger particles that make up the so-called “accumulated fraction” of urban aerosols, made of particles with a size ranging between 0.1 and $2 - 3\ \mu\text{m}$. The latter grow much more slowly and are small enough to remain suspended for a long time, so they make up the main cause of poor visibility in big cities. Just to give an idea, a few thousand particles per cubic centimeter cm^3 with a size of half a micron ($0.5\ \mu\text{m}$) will reduce visibility to less than a mile, whereas, owing to the strong dependence of scattering on size, a hundredfold larger concentration of $0.1\ \mu\text{m}$ particles has negligible effects. Coarse-grain particles with a diameter larger than a few microns (besides natural sources, these could be from construction or industrial activity or, in rural areas, from agriculture) settle much faster. An approximate distribution of the single components of urban aerosols is shown in Fig. 2.7.

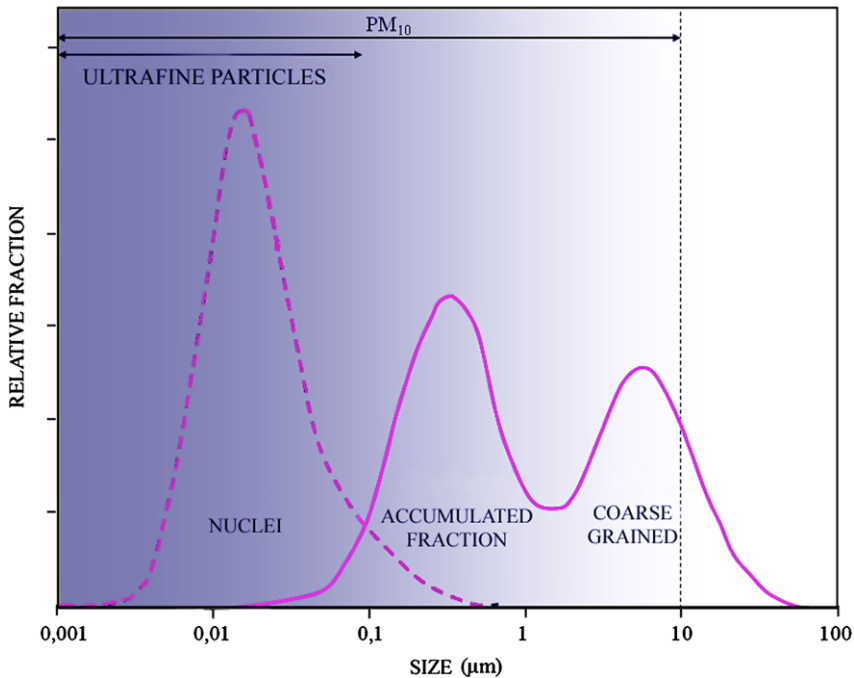


Fig. 2.7. Rough distribution of the three main components of urban aerosols.

For what concerns our health, the size of aerosol particles matters. It determines their power to reach different regions of the respiratory tract, and consequently their potential harmfulness. While larger particles, those more than about $5\text{ }\mu\text{m}$ across, settle into oral or nasal cavities, where they are rather easily removed, those with a size between 5 and about $1\text{ }\mu\text{m}$ penetrate deeper and deeper in the bronchi and, even though the mucus wetting the bronchial walls aids in getting rid of them, they can cause breathing troubles, asthma, and, in the long term, chronic bronchitis. Particles with a size smaller than about one micron are probably the most injurious, since they reach the lung alveoli, those tiny bags where oxygen is exchanged with the circulatory system, which have an overall internal surface comparable to a *tennis court*. There they remain trapped, because there is no “washing” mucus like in the upper bronchial tract⁴⁴. So far, we have not looked in detail at the processes leading to particle trapping (which are similar to colloid filtering), nor do we have a clear view of the ways in which they induce disease or trigger immunoreactions. However, surveys by the World Health Organization suggest that these fine particles may be responsible for at least one in every 200 deaths in large cities.

But this is not the whole story yet, because *tinier* particles (say, around 100 nm), known as “ultra-fine” particles, can pass from the alveoli *to the blood*, directly entering the body circulation. Note that this is the typical size of the particles, dubbed DPM (diesel particulate matter), emitted by modern diesel motors, which is strongly suspected of having cancerous effects. As I have said, there is still a lot to be understood concerning the effects of fine particles on health. What should be already clear to you, though, is that the simple “PM₁₀” denomination, which gathers together all particles with a size smaller than $10\text{ }\mu\text{m}$ to fix their highest legal concentration, is totally inadequate. The effect of ultra-fine particles (so far partially obscure) could be quite different from those with a diameter of $5 - 10\text{ }\mu\text{m}$ ⁴⁵.

Before leaving the not-so-pleasant topic of fine dusts, I just wish to point out that in some conditions, dusts can give rise to curious and aesthetically fascinating optical effects. Gorgeous sunsets where green, yellow, red, and violet mix in a chromatic fancy often arise from the presence of aerosols, which can generate countless color shades⁴⁶. Actually, chimneys, oil refineries, or Beijing buildings often provide a foreground for these gorgeous scenes. Personally, I am content with the more traditional colors that fabulous and pollution-free places such as Santorini island may offer. And my bronchi thank me for it.

⁴⁴ As we shall see, this is also, and not by chance, the typical size of viruses.

⁴⁵ On the pleasanter side for our health, suitable aerosols can be used, as you surely know, to carry drugs. Even in this case, determining the size of the droplets produced by an atomizer is useful to establish the region of the respiratory tract in which they will probably settle.

⁴⁶ Volcanic eruptions that send particles high into the stratosphere are the masters of this art.

The colors of aerosols can be due to the absorption of specific wavelengths by the suspended compounds. For instance, they are mainly nitrogen compounds which intensify “sunset red” or yield yellow and brown nuances. Yet, even in the absence of absorption, colors may simply stem, once again, from light scattering. Let us see how. As we said, for non-absorbing particles the intensity of scattered light soars as we decrease the wavelength λ , but this is true only if the particles are small compared with the wavelength⁴⁷. For larger particles, things are much more complicated. In particular, when the particle size is about the same as the wavelengths of visible light, say between a few tenths and a few microns, the scattered intensity may even *grow* with wavelength, so red is scattered more than blue.

This can generate very curious phenomena. Although the English idiom “once in a blue moon” originally meant one more full moon than the usual twelve in one year (something happening every two and a half years, approximately), in current language it is used to indicate something very rare⁴⁸. Yet, in very special conditions, one can *literally* see a blue moon (not necessarily full), in particular after volcanic eruptions or great forest fires. For instance, after the gigantic outburst of Krakatoa volcano in Indonesia in 1883, it was apparently possible to see the moon turning blue (and also greenish) for almost two years. This is because these events can inject tons of particles into the atmosphere⁴⁹ with a size and a refractive index that happen to reverse the usual scattering trend with λ . However, just because this effect is so sensitive to size, it also requires the particles to have a similar size. This is the reason it is so hard to see a blue moon, possibly more so than glimpsing the famous “green flash” at sunset.

Without looking for a blue moon, however, there is a wonderful atmospheric effect that has a lot to do with aerosols, and which I think any of you will have appreciated after a rainstorm, looking at waterfalls, or simply observing a water sprinkler. In all these (and in other) conditions, there is a large number of airborne water droplets that are large enough for their optical properties to be explained without resorting to the complicated theory of scattering. It is enough to use the simple laws of light reflection and refraction, which some of you may remember from schooldays. The light rays bumping into a droplet are partly reflected backwards, but a certain amount is refracted, penetrating into the droplet to be partly reflected again from its back surface, so that, after a further refraction, they come out again in the

⁴⁷ And if their refractive index is not too high. You actually need to take the difference between the particle’s refractive index and that of the suspending medium, multiply the result by the particle radius, and compare the answer with the wavelength.

⁴⁸ The Italian equivalent means “once in a bishop’s death”, which is rather unfair to the church hierarchies!

⁴⁹ As I am preparing this English edition, we are all realizing what silica particles emitted by a formerly unfamiliar volcano with the almost unpronounceable name of Eyjafjallajökull can do.

backward direction. The curious outcome of this “ping-pong” of reflections and refractions is that, eventually, much of the light is reflected only within a narrow cone forming an angle of $40 - 42^\circ$ with the direction of the original rays. Since water’s refractive index depends on wavelength, the exit angle is slightly larger for blue than for green, and for green than for yellow or red.

The outcome, of course, is what we call a *rainbow*. When we stand with the sun behind us and look at the clouds still building up near the skyline after a storm, the overall effect we see is an arc of a circle centered in the opposite direction to the sun (the *anti-solar point*), which is therefore always *below* the horizon and has an angular aperture of $40 - 42^\circ$ on the vault of heaven (a couple of hands’ breadth at arm’s length). Obviously, therefore, unless you are on a mountain top or on a plane, the rainbow can be observed only if that the sun is less than 42° over the horizon, since otherwise it is completely below the skyline (this is why rainbows are usually seen near sunset). The more observant of you may also have noticed that, in some cases, a *double* rainbow forms, with the colors of the additional outer arc *reversed* compared with the usual ones. This secondary arc is due to rays suffering a *double* reflection before escaping the droplets⁵⁰. The rainbow is only the most spectacular of many atmospheric phenomena such as “glories” and “halos” that are due to suspended water droplets or ice crystals, and which I recommend you to look for. However, the moment has come for us to temporarily leave our simple colloidal particles, either solid or liquid, and to devote ourselves to other systems, which are still in some sense “colloidal”, but quite different and more complex.

⁵⁰ If you are really observant, you may also have noticed that, between the two arcs, the sky is considerably darker. This effect, due to the fact that back-reflection is very low for these angles, is called “Alexander’s band”, after the Greek philosopher from Aphrodisia who first described it.

Soft Matter

The stuff that dreams are made of

Piazza, R.

2011, XIV, 280 p. 61 illus., 35 illus. in color., Softcover

ISBN: 978-94-007-0584-5