

## Nanoparticles and Dendrimers: Hopes and Illusions

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Egon Matijević is one of the most inventive sculptors of colloidal particles. In our times, it has become fashionable to make these particles smaller and smaller: as usual, whenever we change scales, new features appear. My aim here is to discuss some of the hopes – deep or naive – and some of the difficulties which are met with these ultradivided colloids.

The very word »nanoparticle« is ambiguous. When spoken by inorganic chemists, it refers to objects of size 10–50 nanometers. When used by scientists interested in drug release, it means any submicron particle. In the present text, I shall follow the first definition; and I shall restrict my attention to hard, permanent objects (as opposed to, say, flexible polymer coils, or micelles).

### CHEMISTRY AND STABILITY

The chemical pathways which lead to such particles are numerous. Some start from high temperatures: *e.g.* the C<sub>60</sub> molecules, the carbon tubes; or the oxydes generated by laser evaporation of metals in the presence of oxygen (ZnO); or yet the products of flame oxidation starting from volatile chlorides (SnCl<sub>4</sub>). Other processes are based on precipitations in solution or

on solvent exchange: this will be described by experts in this book. My concern here is different. The first problem which we meet is stability. Nanoparticles in water aggregate more than expected. This may be due to the weakness of the overall charge, giving reduced Coulomb repulsions between neighbours: if the charge density  $\sigma$  is the same for all sizes, the overall charge of one particle (radius  $R$ ) is  $Q = 4\pi R^2\sigma$ , and the Coulomb energy  $U$  between the adjacent particles is:

$$U = \frac{Q^2}{2R\epsilon} = 2\pi \frac{\sigma^2 R}{\epsilon} \quad (1)$$

( $\epsilon$ : dielectric constant of water).

When  $R$  decreases, at some moments this  $U$  is not much larger than  $kT$ , and Coulomb stabilisation fails.

In actual fact, many nanoparticulate colloids are stabilised by special tricks – *e.g.* adsorption of nitrate ions on the surface of  $\text{TiO}_2$  particles: chemistry is much more important than physics for nanoparticles. This also shows up in the problem of Ostwald ripening: when we fabricate a population of nanoparticles in solution, we often face this classical difficulty: small particles manage to send a few of their molecules into solution – where they diffuse towards larger particles. This ultimately leads to an increase in particle size, and to a decrease in overall area: thus there is a thermodynamic force driving the process. Ostwald ripening is an important stumbling block for the fabrication of many colloids – but is even worse for nanoparticles (which are slightly less stable, and thus more soluble than the bulk solids).

## DENDRIMERS

There exists one family of nanoparticles which are automatically protected from that standpoint: the dendrimers, obtained by organic synthesis. Here, one starts with a small trifunctional molecule; reacts the three functions with new trifunctional units; and iterates the process, making sure that at each generation the reaction is complete. This stoichiometric build up can persist only for a small number  $n$  of generations: after that one has obtained a »molecular cauliflower« where steric effects blocked the exponential growth. By a suitable use of spacers in the basic unit, one can monitor  $n$  and the final radius. Making dendrimers is now a fashionable exercise, and many clever variations have been introduced into the scheme.

Will these sophisticated (expensive) nanoparticles be of practical use? Many possibilities have been quoted. I do not believe in all of them. Also, some of these applications do not really require the precision of a dendrimer

structure, and could be realised with statistically branched polymers – which are also rather compact, and much cheaper.

### SOME DREAMS ABOUT APPLICATIONS

Nanoparticles may become useful in drug delivery – dealing directly with rather insoluble drugs, or with fragile agents (antigens, DNA'S).

Another sector which is clearly tempting is catalysis, using inorganic particles or, in particular, dendrimers, where the analog of an active site can, in principle, be built on the outer surface. One major problem is to recuperate the particles from the reaction bath – or to lock them in gels, in porous structures, *etc.*

Modest but fruitful applications could possibly be found in cosmetics: *e.g.* with particles which are transparent for visible light (when they are much smaller than the wavelength, they do not scatter) but opaque for UV.

Magnetic nanoparticles have been used for long times in ferrofluids (*e.g.* cobalt particles protected by a surfactant and suspended in a hydrocarbon liquid). Here the small size is necessary: at larger sizes, the interactions between magnetic dipoles induce flocculation. Other applications (in solid matrices) are under way.

One possible use of nanoparticles is »quantum dots«: made of semiconductors, or metals, or (in the future) based on a large aromatic dendrimer. If we have a perfect, rigid box for electrons of this sort, many unusual electrical and optical properties can be expected.

I personally do not believe very much in making electronic circuits with linear, conducting polymers: but if we increase the diameter, and go to quantum dots, the situation is much better. If I force one electron through a molecularly thin wire (say a polyacetylene chain) I am making this chain locally very reactive, and thus very fragile. But if I add an electron to a quantum dot made of say 100 carbon atoms, the excitation is shared, the structure is less deformable and less reactive, and the hopes are more serious.

### JANUS GRAINS AND SELF-ASSEMBLED ORGANIZATIONS OF DENDRIMERS

Let me go now even deeper in science fiction: my starting point will be an object which we constructed long ago (at large sizes: 20 microns). This is a particle where one half of the surface is hydrophilic, where the other side is hydrophobic. We called this a Janus grain.

The nanoparticle along of a Janus grain can be constructed; two such particles in water will stick together by putting their hydrophobic side together, and make a dimer. But we can think of more complex structure. If our particle has, say, four hydrophobic spots in four tetrahedral directions, self assembly will lead to molecules which resemble carbon compounds. We can construct the analog of simple bonds, double bonds, *etc.* Could we imagine a new chemistry based on nanoparticles instead of atoms? Yes, if we could intelligently activate, or deactivate the various types of bonds: this could possibly be done by having on our patches, not simple hydrophobic functions, but more sophisticated groups who can be modified by selective optical absorption (*e.g.* one photon transforms one patch from hydrophobic to hydrophilic). This may be a future challenge for dendrimer chemists.

Let me end up by a note of humility: we are very proud of our ability to produce nanoparticles in various guises. But we should not forget that they have been already used over many centuries. The windows of some cathedrals are coloured with a beautiful deep red, based on gold nanoparticles. And far before, a special type of blue dye was invented by the Mayas. This is based on añil (indigo) which is a labile organic product: but here it is incorporated into a white clay (polygorshite). A recent study described in *Science* (1997) suggests that some mineral nanoparticles participate to the structure! Egon Matijević – a great amateur of graphic arts – certainly appreciates this point.

## SAŽETAK

### Nanočestice i dendrimeri: nade i iluzije

*Pierre-Gilles de Gennes*

Profesor Egon Matijević jedan je od najinventivnijih preparatora koloidnih čestica različitih kemijskih spojeva. U posljednje vrijeme zavladała je »moda« priprave što manjih i manjih čestica. Kada se nešto promijeni na ljestvici dimenzija čestica, dolazi se do novih spoznaja o koloidnim i površinskim svojstvima tih čestica. Pojam »nanočestica« dosta je neodređen. Anorganski kemičari pod tim pojmom podrazumijevaju čestice veličine 10–50 nm, dok istraživači u industriji lijekova smatraju nanočesticama bilo koju submikronsku česticu. U ovom prikazu razmotrena su koloidna i površinska svojstva čvrstih nanočestica. Fleksibilne polimerne zavojnice ili micelle, koje mogu također biti u području dimenzija 10-50 nm, nisu razmatrane.