

Chapter 2

Nanoparticles Dispersion and the Effect of Related Parameters in the EPD Kinetics

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Nomenclature

a	Particle radius
A	Hamaker constant
B	London constant
C_d	Deposit concentration
C_s	Solid content of the suspension
$C_{s,0}$	Initial solid content of the suspension
D	Particle diameter
E	Electric field
E_{ef}	Effective electric field
f	Efficiency factor or sticking parameter
I	Electric current
I^+	Electric current transported by the cations
I^-	Electric current transported by the anions
I_p	Electric current transported by the particles
i_0	Initial current density
i	Current density
K	Kinetics parameter
L	Electrode distance
m	Deposited mass
m_0	Initial mass of powder in suspension
R	Roughness
S	Deposition surface area
S_{WE}	Conduction surface area
t	Deposition time
V	Volume of the suspension
V_d	Volume of the deposit

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Greek Symbols

$1/\kappa$	Debye length
ε_d	Dielectric constants of the deposit
ε_s	Dielectric constants of the suspension
$\varepsilon_{r,l}$	Dielectric constant of the solvent
$\varepsilon_{r,p}$	Dielectric constant of the particles
ε_0	Vacuum dielectric constant
ϕ_d	Volumetric fraction of the deposit
ϕ_s	Volumetric fraction of the suspension
$\phi_{s,0}$	Initial volumetric fraction of the suspension
η	Solvent viscosity
μ	Electrophoretic mobility
v	Electrophoresis rate
ρ_s	Resistivity of the suspension
$\rho_{s,\infty}$	Resistivity of the suspension at infinite time
ρ_d	Resistivity of the deposit
ρ_+	Resistivity associated to the cations
ρ_-	Resistivity associated to the anions
ρ_p	Resistivity associated to the particles
$\rho_{s,0}$	Initial resistivity of the suspension
δ	Deposit thickness
σ_s	Conductivity of the suspension
$\sigma_{s,\infty}$	Conductivity of the liquid medium
τ	Characteristic deposition time
τ_0	Characteristic deposition time for initial conditions
τ_∞	The characteristic deposition time for final conditions
$\Delta\psi$	Potential drop and surface potential
$\Delta\psi_a$	Potential drop at the anode
$\Delta\psi_c$	Potential drop at the cathode
ζ	Zeta potential

2.1 Nanoparticles and Nanomaterials

In recent years the emergence of a new generation of high technology materials involving nanoparticles and nanocomponents has increased exponentially [1, 2]. Nanomaterials are used in many different domains, such as chemistry, electronics, magnetic materials, biotechnology, etc. The great interest of the nanomaterials deals with the new properties associated to the small size that can strongly differ from those of the bulk conventional material.

Feynman pointed out that the designing of materials atom-by-atom was a real possibility, as it would not violate any physical laws. However this prediction could not be demonstrated until the arrival of very sophisticated instrumentation capable

of viewing and manipulating materials at the nanoscale. The first use of the term “nanotechnology” was by Taniguchi in 1974 referring to “production technology to get extra high accuracy and ultra fine dimensions, i.e., the preciseness and fineness on the order of 1 nm (nanometer), 10^{-9} m in length” [3]. Although many definitions for nanotechnology have been suggested, NASA recently suggested the most thorough description: the creation of functional materials, devices and systems through control of matter on the nanometer length scale (1–100 nm), and exploitation of novel phenomena and properties (physical, chemical, biological) at that length scale [4].

A challenge of existing technology is to organize different functional components in two and three dimensions at the nanoscale. It is the cooperative interaction of different nanoscale components that allow the combination of desirable properties of single units into a larger integrated system [5, 6]. Nanoparticle assemblies have potential applications in photonic materials, advanced ceramics, and electronics, among other applications. Several approaches have been used to precisely position nanoparticles into two- and three-dimensional (2D/3D) structures, the most widely used being self-assembly processes, methods that utilize diblock copolymers, and nanoparticle infilling of colloidal crystals and other templates [7].

The progress in nanoscience has been associated with the elaboration of new methods for synthesizing, studying, and modifying nanoparticles and nanostructures [8]. In principle, there are two kinds of methods for synthesizing nanoparticles. The first group combines methods that allow preparation and studies of nanoparticles, and the second group includes methods that allow preparation of nanomaterials and nanocomposites, based on nanoparticles. This classification leads one to consider that particles can either be built from association of separate atoms through a chemical route (which constitutes the so-called *bottom-up* approach) or by dispersion or fracture of large units that are broken down through physical methods like milling (the so-called *top-down* approach). Figure 2.1 shows a schematic view of these two approaches to nanomaterials production.

For most ceramic processing techniques, the “bottom-up” approach is much more interesting, and this will be considered herein. The development of nanomaterials synthesis by this “bottom-up” approach has been determined by nanochemistry, which has two important aspects to be considered: on one hand, the different chemical properties and the reactivity of particles comprising a small number of atoms; on the other hand, its effect on the synthesis, modification, and stabilization of nanoparticles and the further assembly into more complex structures. Since the properties of synthesized structures directly depend on the size and shape of the original nanoparticles, the control of these parameters and their stability in a dispersing medium are critical for the manufacture of any nanostructured material. Nanochemistry studies the synthesis and modification of particles with sizes typically below 10 nm along one direction at least. Generally speaking, materials chemists efforts are devoted to the development of “bottom-up” techniques that afford the *self-assembly* of nanoscale species. There is also a parallel effort of nanophysics to allow nanoscale units by “top-down” routes.

There are two basic types of nanoscale building blocks that can be used for the fabrication of a device, zero-dimensional materials (0D, e.g. nanoparticles, nanoclusters, nanocrystals) and unidimensional ones (1D, e.g. nanowires, nanofibers,

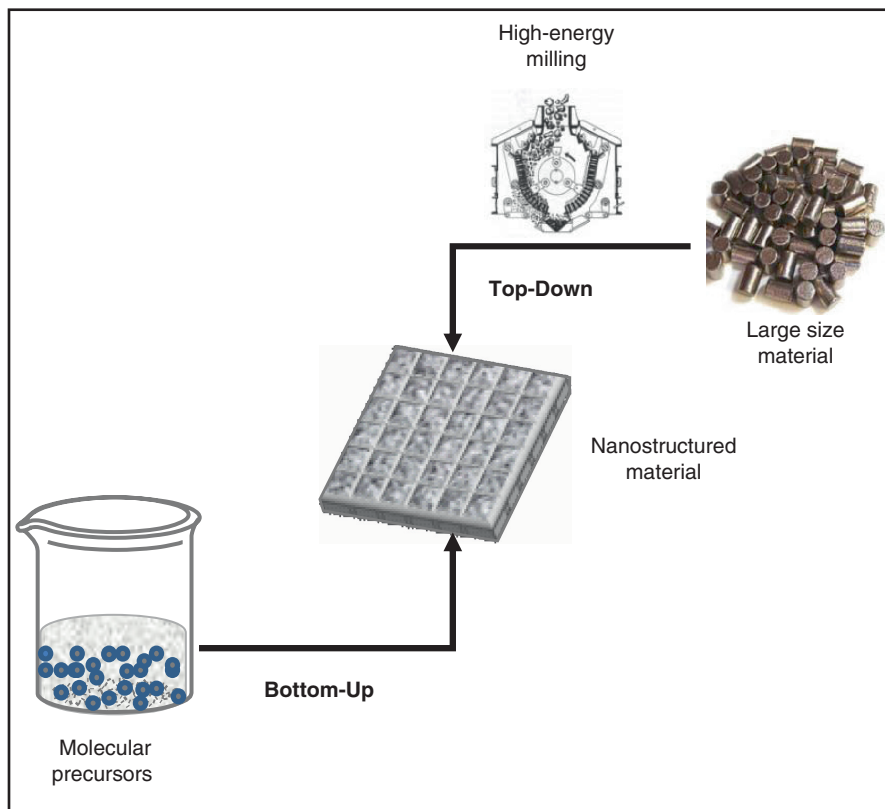


Fig. 2.1 The two approaches for the synthesis of nanomaterials

nanotubes). The assembly of these nanosized building blocks into 2D and 3D arrangements yields entirely new properties and functionalities. In this context it is important to make some basic definitions [8]. The term *nanoparticle* generally refers to 0D nanosized building blocks (regardless of size and morphology), or those that are amorphous and possess a relatively irregular shape; typical size in this case is >10 nm. For amorphous/semicrystalline nanostructures smaller in size (i.e., 1–10 nm), with a narrow size distribution, the term *nanocluster* is considered more appropriate. The agglomeration of noncrystalline nanostructural subunits should best be termed a *nanopowder*. The term *nanocrystal* is reserved to nanomaterials that are single-crystalline. A special case of nanocrystal that is comprised of a semiconductor is known as a *quantum dot*. The nomenclature of 0D nanostructured materials related to the typical size intervals are shown in Table 2.1.

There are different classifications of nanoparticles, proposed by different authors based on the diameter of a particle expressed in nanometers and the number of atoms in a particle. These classifications also take into account the ratio of surface atoms to those in the bulk. Figure 2.2 shows a generally accepted classification of

Table 2.1 Nomenclature of 0D nanostructured materials

Structure	Size (nm)		Typical name				
Nanostructures	<< 1		Clusters				
	1–10 ²		Nanoclusters and nanocrystals				
	10 ² –10 ³		Nanoparticles and nanopowders				
Microstructures	10 ³ –10 ⁵		Sub-micron particles				
Macrostructures	> 10 ⁵		Particulates (bulk powders)				
N° atoms	N=10	N=10 ²	N=10 ³	N=10 ⁴	N=10 ⁶	Bulk	
Diamteter (nm)	1	2	3	5	7	10	> 100
Chemistry	Nanoparticles						➔ Solid state

Fig. 2.2 Classification of particles according to their sizes

particles according to their sizes [9]. According to this classification, nanoparticles can be considered as intermediate entities between individual atoms and the solid phase, measuring from 1 to 10 nm and built of atoms of one or several elements.

In order to tailor a device property to its function, a good knowledge of the correlation between property and microstructure is required. Because the microstructure depends on the processing route, processing methods are decisive factors in developing new materials. While applications are most of the time well identified, material scientists continue to develop new processing methods that can produce components of a complex shape and high reliability with a minimum of machining and cost. These fulfillments have been already reached for submicron sized powders by wet processing through a colloidal approach [10, 11]. However, when moving to the nanoscale, there is an important problem because interparticle interactions are in the same range of particle size and spontaneous agglomeration occurs.

It must be remarked that the fraction of atoms pertaining to the surface increases as particle size decreases and hence, the contribution of surface atoms to the system’s energy increases. This has important thermodynamic consequences such as the fact that particle size is an active variable that determines the state of the system and its reactivity. That is, nanosized particles can enter into reactions untypical of coarser systems [12].

So far, we have considered the recent nomenclature related to nanomaterials and nanochemistry. However, it is also important to note the possible differences between nanoparticles and colloids, the last being known since the 1860’s. Although both types lie in the same nanoregime, some authors have considered the existing differences between them, mainly related with the lower control over composition and morphology. In general nanoparticles are considered to lie in the range of 1–100 nm, whereas colloids are typically larger than 10 nm. Other important differences with respect to colloids are that nanoparticles have reproducible syn-

thesis and physical properties and contain clean surfaces, while colloids contain surface-adsorbed species such as $-\text{OH}$, $-\text{X}$, $-\text{OH}_2$, etc. However, when introduced in a dispersing medium, as a liquid, the properties of the system become a function of the interactions among the different species in the system, including the interactions among particles and the interactions among particles and dispersing medium molecules. The dispersion in a liquid modifies completely the properties of the nanopowders that can be studied considering the laws of colloid chemistry.

2.2 Processing of Ceramics. The Colloidal Approach

Ceramic products have been used for more than 10,000 years. The term *ceramics* comes from the greek “κερασ” (keras), which means *clay*. This word proceeds from a radical of Indo-European languages “κεραμ” (keram), which in turn means corresponds to the verb to burn. Thus, ancient ceramics were clay-based products subjected to a thermal treatment. Although there are different definitions to ceramics, it is generally accepted that ceramics are inorganic, non-metallic materials that are subjected to a thermal treatment to reach their final characteristics. However, these properties are strongly dependent not only on the composition, but also on the firing temperature. Due to the special characteristics of the ionic-covalent bonding, ceramics exhibit excellent properties like thermal and chemical stability, hardness and corrosion resistance, among others. However, ceramics have a great limitation, their inherent brittleness consequence of the high directionality of the bonds, so that catastrophic failure occurs when the fracture stress is exceeded.

The strength of a ceramic material can be described by Griffith's equation,

$$\sigma = YK_{\text{IC}}/\sqrt{C} \quad (2.1)$$

where σ is the fracture stress, K_{IC} the fracture toughness, C the defect size, and Y a factor that depends on the position and shape of the defect. According to this law, there are two ways of increasing the strength of a ceramic material, by increasing the fracture toughness or by decreasing the flaw size. Toughness can be increased using composite materials, by the incorporation of secondary phases such as particulates, platelets and whiskers. Another approach to improve the toughness is through the design of materials with tailored microarchitectures, such as coatings, laminates and functionally graded materials, where the interfaces can arrest or even bifurcate the propagating crack. Toughness could be also enhanced by reducing the flaw size, C . This can be only achieved with a better processing control. Pores, inclusions, cracks and agglomerates can behave as flaws with a deleterious effect on the final properties. In all cases, the enhancement of toughness and the reduction of defects number and size are only possible if the reinforcing phase is well-dispersed in the matrix [13].

One major concern in the application of any material is the method of fabrication. Ashby et al. [14] have done a taxonomic classification of the types of materials and the types of processes for their manufacture. A summarized view of these

Table 2.2 Classes of manufacturing processes of materials

Classes of processes	Specific processes
Primary shaping	Deformation, casting, injection, powder processing, rapid prototyping, free-forming
Secondary processes	Machining, lamination and shaping, tempering, quenching
Joining & surface treatment	Adhesion, welding, fasteners Painting, printing, anodizing, plating

classes of processes is shown in Table 2.2. Polymers can be molded and ductile materials can be forged, rolled and drawn, but ceramics are brittle and must be shaped in other ways. Materials that melt at modest temperatures to low-viscosity liquids can be cast; those that do not have to be processed by other routes. Furthermore, shape influences the choice of a process, too. Slender shapes can be made easily by rolling or drawing but not by casting. Hollow shapes cannot be made by forging, but they can by casting or molding. The choice, for a given component, depends on the material, on its shape, dimensions and precision, and on the lot size [15–19].

Ceramics are mainly produced by powder processing techniques, which consist of four basic steps: (1) powder synthesis and/or preparation for further consolidation, (2) consolidation of powders into a self-supported shaped body, the so-called *green body*, (3) drying and burn out of organics, (4) sintering at high temperature to reach the final microstructure and properties, and (5) final machining and shaping, which is the most expensive step due to the hardness of ceramics. Maximum control at any stage is necessary since defects introduced in one step are very difficult to remove and will persist in the next steps.

A great effort has been devoted by ceramists to improve the quality of the starting powders [20], and to search novel forming processes capable to produce near-net shaped parts with high homogeneity and density and increased green strength in order to reduce as much as possible the machining step [21–23].

The exhaustive control of powders transformation (referred to as *beneficiation processes*, which include milling and mixing, washing, separation, filtration and granulation) has to be accomplished of a “clean” consolidation into bodies by non-conventional shaping procedures in which contamination by metal parts, high pressures or large concentration of additives is to be avoided. In this sense, colloidal processing methods have demonstrated their efficiency for producing complex shaped bodies with enhanced properties and increased reliability [10, 11, 24].

Forming methods can be classified according to three categories, depending on the relative content of liquid characteristic of the process: (1) dry pressing methods, where the liquid content is typically lower than 7%; (2) plastic forming, with typical liquid contents of 15–20 for extrusion or up to 30–40% in the case of injection molding, and (3) colloidal shaping methods that make use of suspensions, where the content of liquid is generally higher than 50%.

Suspensions have been used in ceramics from ancient civilizations, when it was observed that some water allowed clays to become plastic and to be easily handleable so that the first recipients could be created. During the decade of the 1980’s the wet forming of ceramics was in focus, and a strong development was possible when cera-

mists learned the importance of colloid and surface science and its great influence in ceramic processing. This knowledge allowed the development of different near-net shaping techniques in the 1990's. The basis for such shaping techniques was the well-known slip casting process [25], which consists of pouring a suspension into the cavity of a permeable mould that allows the liquid to pass through the porosity channels of the walls. This is a solid-liquid separation process, used also in other technologies like filter-pressing. Consolidation of the particles occurs as the liquid flows through the porous medium under a pressure gradient. In slip casting, the driving force for the consolidation is just due to capillary forces. The low casting rates can be increased by using an external aid, like microwaves, centrifugation and, most common, pressure. The family of casting processes have led to other related processes like tape casting, coagulation casting, gelcasting, etc. These processes have different consolidation mechanisms, although all of them have a basic requirement: they require the preparation of a concentrated and well-dispersed suspension of particles in a liquid, preferably water. All these processes involve the preparation of a stable suspension of the powders in a liquid with the aid of deflocculants, which maintain particles apart each other by either the development of electrostatic charges or through the adsorption of polymers that promote steric hindrance, and other additives such as binders, plasticizers, anti-foaming agents, etc. [26–28]. Colloidal processing allows the manipulation and control of the interparticle forces operating not only in the suspension but also in the consolidation step, where repulsive forces maintain still active, so that the formation of agglomerates is dramatically reduced. As a consequence, if a proper dispersion state is reached, green bodies with high relative densities can be obtained, which result in dense materials with fine microstructures and controlled grain sizes [29, 30].

Table 2.3 summarizes some colloidal forming methods typically employed for the manufacture of ceramic bodies [31]. One possible classification of the methods can be done considering the consolidation mechanism. Although both concepts are intimately related, the differences between forming method and consolidation mechanism must be emphasized. The forming method is the technique employed to obtain the body, e.g. slip casting, injection molding, tape casting, etc. Consolidation refers to the mechanism through which the particles arrange into a consolidated body with the desired shape and size. The main consolidation mechanisms are the following: (1) *filtration*, which is the basis of slip casting, as described before; (2) *deposition-evaporation* methods, which are those methods based on the deposition of a thin layer of suspension that undergoes fast evaporation, like in tape casting, screen printing, etc. One particular case is that of electrophoretic deposition (EPD) where particles are forced to migrate to the electrode with opposite charge to that of the particles under the influence of an electric field, which can be considered the

Table 2.3 Conventional colloidal shaping techniques

Filtration	Deposition evaporation	Flocculation coagulation	Gelation
Slip casting	Screen printing	Short range forces	Gelcasting
– pressure	Tape casting	Temperature induced	Injection molding
– vacuum	Electrophoresis	Coagulation casting	Thermogelation
– centrifugal	CVD, PVD...	Freeze casting	Protein casting
– microwaves	Dipping	Direct solidification	Starch consolidation
	Spin coating		

driving force for the deposition. Once the film is deposited onto the electrode material, coagulation occurs as a consequence of the rapid drying; (3) *Flocculation* and *coagulation* methods are based in the preparation of a stable suspension and its sudden destabilization after the formation of a physical gel formed by flocculation in a secondary minimum (when inorganic salts are added, for example) or coagulation in a primary minimum (when pH is moved towards the zero point of charge, and there are no repulsive forces that can overcome the attractive van der Waals forces); (4) *Gelation* methods are those based in the polymerization of small molecules (monomers or dimers) into long-chained macromolecules by either a chemical polymerization in the presence of a catalyst and an initiator or by thermogelation when the gel is formed as a consequence of a temperature change. In this case a chemical gel is formed that retains the ceramic particles in the developed network, while in the previous group the own particles are responsible for the development of a network structure that is considered as a physical gel.

Most of those shaping methods make use of moderately or highly concentrated suspensions, where sedimentation of large or dense particles is retarded while maintaining a flowing behavior. In general those suspensions are poured into moulds and the solids loading has to be the highest possible in order to minimize the drying shrinkage and the amount of liquid to be removed during drying. The main exception to this general rule is the case of EPD, where suspensions with low solids loading are normally used. It is mandatory, however, that colloiddally stable suspensions have to be used and that the particles must carry a substantial charge. That is, EPD requires stable suspensions like any other wet forming procedure, although the stability cannot be evaluated by viscosity inspection. The stability has to be measured considering other parameters, the most important being the electrophoretic mobility or the zeta potential, and the conductivity, which in turn depend on the pH, the type and concentration of deflocculants, the temperature, etc.

If the suspension is completely stabilized gravity can be neglected, but if the particles tend to settle gravity becomes an influencing parameter, affecting mainly layer thickness and deposit quality. If the suspension is well stabilized, a vertical configuration will be used. The stability of the suspensions and their effects in the EPD process and the deposit characteristics will be studied in the following.

2.3 Colloidal Stability of Ceramic Suspensions

2.3.1 Colloidal Dispersions

The term ‘colloid’ comes from the Greek word ‘*κόλλα*’ (*kolla*) for glue. It was originally used for gelatinous polymer colloids, which were identified by Thomas Graham in 1860 in experiments on osmosis and diffusion. The simplest definition of a colloidal dispersion is that it is a multi-phase system in which one phase (or more) is dispersed in a continuous one or medium. At least one dimension lies within the nanometre (10^{-9} m) to micrometre (10^{-6} m) range, so that colloidal dispersions are

Table 2.4 Types of colloidal dispersions

Dispersed phase	Dispersing medium		
	Gas	Liquid	Solid
Gas (bubbles)	–	Foam	Solid foam
Liquid (droplets)	Liquid aerosol	Liquid emulsion	Solid emulsion
Solid (particles)	Solid aerosol	Suspension/sol	Solid sol

mainly systems containing large molecules and/or small particles. The main factor determining the properties of a colloidal system are the particle size and shape, the surface properties, the interparticle interactions and the interactions between particles and dispersing medium. A fundamental issue of colloidal systems is that there is a well-defined separation surface between the dispersed phase and the dispersing medium. The interface plays an essential role in the surface properties, including adsorption, surface charge, electrical double layer, etc. There are many reference textbooks on colloid and surface science where the reader can find complementary information [31–39]. The colloidal dispersions may be classified considering the state in which either the dispersed phase or the dispersing medium are present (solid, liquid or gas). Table 2.4 shows the different types of colloidal dispersions.

To overcome the spontaneous tendency of particles to agglomerate by means of attractive forces (i.e. van der Waals), it is necessary to enhance the repulsive contribution to the interaction potential. This can be made by using dispersing aids, known as dispersants or deflocculants. Dispersants may be classified into several groups depending on the stabilising mechanism they promote, whose efficiency is a function also of the characteristics of the dispersing medium and the liquid/solid interface. In a polar medium, such as water, amphoteric ceramic particles develop an electrical double layer, whose thickness depends on the concentration of potential-determining ions (i.e. pH) that provides an electrostatic repulsion. The presence of a supporting electrolyte varies the surface charge and potential. Stability may arise also from the adsorption of surface active compounds or polymers, which provide a steric hindrance. They can be associated to electrical charge, thus providing an electrosteric stabilisation. Other possibilities are the use of alkoxydes that chemically react with the particle surface (coupling agents), but this is more properly a method for synthesising a coating material than a proper dispersing agent. Finally, non-adsorbing polymers could maintain the particles apart by means of a depletion mechanism. Table 2.5 summarizes the different kinds of dispersants used in ceramic processing.

Table 2.5 Kinds of dispersants used in ceramic processing

Substance	Mechanism
Potential-determining ions (pH)	Electrostatic repulsion
Electrolytes (inorganic salts)	Electrostatic repulsion
Surfactants (amphiphilic chains)	Adsorption + Electrostatic repulsion
Adsorbed polymers	Steric hindrance
Adsorbed charged polymers	Steric hindrance + Electrostatic repulsion
Coupling agents	Adsorption + Electrostatic repulsion
Non-adsorbing polymers	Depletion stabilisation

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