

# Nucleation, Growth, and Arrested Growth in Confined Space

## 2.1 Introduction

The separation of solid phases from liquid ones is a very old practice and, at present, it represents a pivotal step involved in many industrial processes. The optimization of this step is of utmost importance both for the quality of the final product, environmental impact, and economic reasons. To achieve this goal, a wide range of experimental procedures and a framework of theoretical principles have been exploited. The notions of solubility, solubility product, the common ion effect, homogeneous and heterogeneous nucleation, crystal growth, precipitation and coprecipitation, crystallization, saturation, supersaturation, and filtration are normally learned in elementary courses of physical chemistry. The thermodynamic, kinetic, and statistical aspects of nucleation, crystallization (slow separation from a liquid phase of a solid compound characterized by relatively high solubility), and precipitation (fast separation of a solid with small solubility) have been well established as well as the effects of temperature, pressure, and additives.

For completeness, it is worth remembering that, in addition to those occurring in liquid systems, some important processes involving nucleation and crystal growth are performed in various other environments such as vapour phases, glass matrices, alloys, solid surfaces, and interfaces. In addition to the same general criteria, the development of specific treatments is required for the analysis of these phenomena.

Generally, the main requisites requested to a suitable precipitation protocol in liquid phase are the purity and the recovery of the highest fraction of the total amount of the product. Moreover, this process often occurs in homogeneous liquid media. Only seldom the crystallization or precipitation are performed in microheterogeneous fluid systems, and the control of the crystal geometrical parameters is needed. However, the recent interest to synthesize nanoparticles by bottom-up chemical methods in confined space has given rise to the exigency to develop appropriate theoretical principles and experimental methodologies allowing the rationale control of their mean size and shape, polydispersity,

and structure. Obviously, the knowledge of the mechanisms controlling the formation and stability of nanoparticles in surfactant-containing systems and of those opposing their unlimited growth is of utmost importance to plan a successful synthetic route. With this aim, here will be presented a thermodynamic and kinetic treatment allowing to put into evidence the phenomena involving significant deviations with respect to precipitation in homogeneous systems and the processes underlying the formation, growth, and arrested growth of nanoparticles.

### 2.1.1. Thermodynamic Considerations

The thermodynamic stability of a substance A in a solution with respect to the pure crystalline solid phase depends on the difference ( $\Delta\mu$ ) between the chemical potential ( $\mu_A$ ) of A in both phases

$$\Delta\mu = \mu_{A, \text{ solid}} - \mu_{A, \text{ solution}} = RT \ln \frac{a_{A, \text{ sat solution}}}{a_{A, \text{ solution}}} \quad 2.1$$

If  $\Delta\mu > 0$ , i.e., if the activity of species A in the saturated solution ( $a_{A, \text{ sat solution}}$ ) in equilibrium with A pure is greater than that in the actual solution ( $a_{A, \text{ solution}}$ ), the substance will stay entirely and molecularly dispersed in the liquid phase. Moreover, the system will be monophasic and thermodynamically stable. On the other hand, if  $\Delta\mu < 0$ , a part of A will form a solid phase moving from the solution to the solid phase until  $\Delta\mu = 0$  and a condition of dynamic equilibrium between A in liquid and solid phases is realized. Given these properties,  $\Delta\mu$  is also called the driving force for crystallization. Taking into account the relationship between activity, concentration (C), and activity coefficient ( $\gamma$ ), the above equation can be rewritten as

$$\Delta\mu = RT \ln \frac{C_{A, \text{ sat solution}} \gamma_{A, \text{ sat solution}}}{C_{A, \text{ solution}} \gamma_{A, \text{ solution}}} = -RT \ln \frac{S \gamma_{A, \text{ solution}}}{\gamma_{A, \text{ sat solution}}} \quad 2.2$$

where S ( $S = \frac{C_{A, \text{ solution}}}{C_{A, \text{ sat solution}}}$ ) is the supersaturation ratio.

For sparingly soluble solutes,  $\Delta\mu$  is related to the molar enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of its transfer from the liquid to the solid phase by the equation

$$\Delta\mu = \Delta H - T\Delta S \quad 2.3$$

This equation emphasizes the interplay of energetic and entropic terms as controlling factors of the crystallization process.

Other thermodynamic equations allow to predict the temperature and pressure dependence of  $\Delta\mu$ . Besides, thermodynamics furnishes the relationships between  $\Delta\mu$  and the solubility of ionic and non-ionic solutes

through the knowledge of their activity coefficients in solid and liquid phases. The treatment of these aspects is quite cumbersome and out of the aims of the present book; for these reasons, the reference to standard physical chemistry textbooks is suggested.

These considerations can be formally extended to microheterogeneous systems taking into account that, at equilibrium, the chemical potential of species A in the various microenvironments marked by greek letters is equal ( $\mu_{A, \alpha} = \mu_{A, \beta} = \text{etc}$ ). Then, each microenvironment can be treated as a homogeneous system with the provision that the local concentration of the solute is generally different from the overall.

It is worth noting that, frequently, it occurs that the solute is practically solubilized only in a specific microdomain of the microheterogeneous system. In this case, the local concentration can be easily calculated from the overall without the need of the knowledge of distribution constants.

It must also be stressed that, due to specific and confinement effects, the solubility of species A in each domain of microheterogeneous systems can be found to be strongly different from that in bulk media, involving that the supersaturation value as well as all the thermodynamic parameters are different from those in homogeneous phase. Such consideration has important consequences on the thermodynamics and kinetics of nanoparticle formation in confined space. However, apart from direct experimental measurements, little help has been furnished by theory<sup>1</sup>.

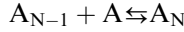
This is all that thermodynamics is capable to predict both for homogeneous and microheterogeneous systems. Further considerations require kinetic arguments.

### 2.1.2. *Kinetic Considerations*

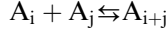
Generally, above the solubility limit, precipitation/crystallization happens very quickly in the presence of a solid phase constituted by the same (secondary nucleation) or different substance (heterogeneous nucleation). The presence of a solid phase contacting the solution offers, in fact, sites and/or a surface on which A molecules could nucleate and grow. In this case, the factors controlling the rate of the process are i) the arrival of the species to the surface of the solid phase and vice versa by thermal diffusion, convection currents, or mechanical agitation, ii) the area and the nature of the solid phase exposed to the solution, and iii) the incorporation rate of the precursors to the crystal lattice. The incorporation step includes the adsorption of the precursors, the partial release of solvating species, and the effective entrapment into the lattice. Generally, a more or less marked preference to be entrapped into certain crystal faces leading to anisotropic morphologies is observed.

However, in the case of homogeneous nucleation, i.e., in absence of a pre-existing solid phase, for statistical reasons the formation of that phase could not occur, and the liquid system will be described as kinetically stable. This because the formation of the crystalline phase is a multistep process requir-

ing the building up of molecular aggregates of increasing size according to the scheme:



and/or through agglomeration processes:



At the molecular level, the driving force of these processes is the Brownian diffusion of species allowing their haphazard encounters.

For this reason, the thermodynamic property that must be considered to know if the solid phase will be really formed or not from molecular or ionic precursors is the free energy of formation of a nucleus constituted by  $N$  molecules,  $\Delta G_f$ , given by:

$$\Delta G_f = N\Delta\mu + \Delta G_s \quad 2.4$$

This equation is constituted by the term  $N\Delta\mu = NkT \ln \frac{a_{A, \text{ sat solution}}}{a_{A, \text{ solution}}}$ , which takes into account the thermodynamic driving force for the aggregate formation, and another one,  $\Delta G_s$ , due to the formation of an interface between the aggregate and the surroundings. This last term is given by

$$\Delta G_s = A_N \gamma_s \quad 2.5$$

where  $A_N$  is the aggregate surface ( $A_N = K_N N^{2/3}$ ) and  $\gamma_s$  is the interfacial energy per unit surface.

From a molecular point of view, the interfacial energy  $\Delta G_s$  measures nothing more than the difference in the energetic state between species located in the surface and in the particle interior. This quantity must be necessarily positive, i.e., the energetic state of a species at the surface should be higher than that in the bulk, otherwise the interface would increase indefinitely leading to a molecular dispersion of the substance in the solution. In fact, while the time average of the resultant of all the forces acting on the molecules is zero independently if they are in the bulk or in the surface, the number and strength of chemical bonds formed by bulk species is larger than that of surface ones. This is the reason of the higher energy of surface species and that small-size crystallites (embryos) are thermodynamically unstable against an unlimited growth.

Here, for simplicity, only two states have been taken into account (surface and bulk species). However, it must be considered that, when two phases are in contact, an interfacial and not well-defined domain where the properties change proceeding from one region to the other is generated. This implies the existence of more than two states of species  $A$  in the particle.

For super-saturated solutions ( $a_{A, \text{ solution}} > a_{A, \text{ sat solution}}$ ), the first term is negative while the second is always positive. In such circumstances, the typical dependence of these contributions and of  $\Delta G_f$  upon the aggregation number  $N$  is shown in Fig. 2.1.

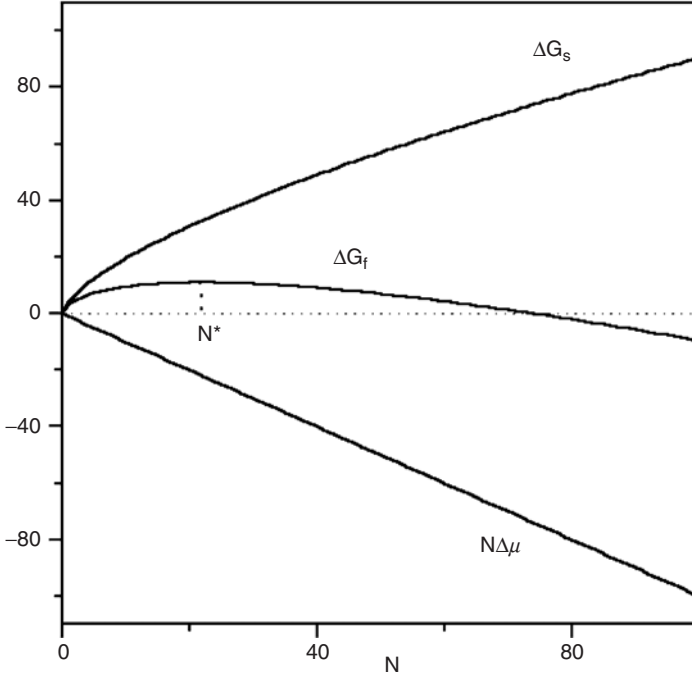


FIGURE 2.1.  $N$  dependence of the free energy of the formation of a nucleus ( $\Delta G_f$ ), the bulk crystal ( $N\Delta\mu$ ), and the interface ( $\Delta G_s$ ).

The  $N^*$  value corresponding to the maximum  $\Delta G_f$  is the critical aggregation number; when an aggregate of  $N^*$  molecules is formed, it is equally probable its growing as a bigger aggregate or decomposition in molecular precursors. The aggregates with  $N < N^*$  are called embryos and tend to decompose because a decrease of  $N$  is accompanied by a reduction of the system free energy. Aggregates with  $N > N^*$  are called nuclei and tend to grow spontaneously, because an increase of their size is accompanied by a decrease of the free energy. The  $N^*$  value can be calculated by considering the maximum value of  $\Delta G_f$

$$\frac{d\Delta G_f}{dN} = \frac{d}{dN}(N\Delta\mu + K_N N^{2/3} \gamma_s) = 0 \quad 2.6$$

i.e.,

$$N^* = -\frac{8K_N^3 \gamma_s^3}{27\Delta\mu^3} \quad 2.7$$

It can be noted that by increasing supersaturation, i.e., more negative  $\Delta\mu$  value, the  $N^*$  value decreases while higher interfacial energy per unit

surface shifts  $N^*$  towards greater aggregates. Moreover, supersaturation being generally the result of a chemical reaction achieved by mixing two reactant-containing systems, it can be regulated not only by the initial reactant concentrations but also by addition and stirring rates of the two systems.

The corresponding free energy barrier ( $\Delta G_f^*$ ) and the rate  $J$  of formation of aggregates of  $N^*$  molecules are

$$\Delta G_f^* = \frac{4K_N^3 \gamma_S^3}{27\Delta\mu^2} \quad 2.8$$

$$J = \Omega \exp\left(\frac{-\Delta G_f^*}{kT}\right) \quad 2.9$$

where  $\Omega$  is a factor correlated to the encounter frequency between the A molecules and consequently dependent on their diffusion coefficients<sup>2</sup>.

In the case of microheterogeneous systems, as a consequence of confinement effects, it occurs frequently that the diffusion coefficients of solutes is smaller than that in homogeneous solutions (the diffusion coefficient of a solute is that of the supramolecular aggregate where it is entrapped) while the residence time in a certain nano-size domain (cage effect) is increased. This involves opposite contributions to the  $\Omega$  value. On the other hand,  $J$  can be also influenced by specific surfactant/nanoparticle interactions involving changes of the  $\Delta G_f^*$  value.

It is worth noting that if  $J$  is very small, i.e., if the probability of the formation of a critical aggregate is negligible, the embryos in the systems are stable in supersaturation conditions against an unlimited growth. This can be obtained at high  $\Delta G_f^*$  and/or low  $\Omega$  values. A high  $\Delta G_f^*$  value is characteristic of particles with high interfacial energy and at low supersaturation levels, whereas small  $\Omega$  values imply a low diffusion coefficient. According to Eq. 2.9, it is generally believed that a  $\Delta G_f^*$  value of about 5–10kT represents a barrier adequate to avoid homogeneous nucleation only permitting the existence of short-living particles smaller than  $N^*$ .

On the other hand, if the probability of the formation of critical aggregates is significant, the rate of nuclei formation increases with the precursor concentration and consequently also the number of crystallites. In contrast, the induction time (i.e., the time required for the formation of an experimentally detectable solid phase) and the particle size decrease with precursor concentration<sup>3</sup>.

The various phases of the precipitation process are shown in Fig. 2.2. It must be stressed that these steps are not so well-disentangled as represented

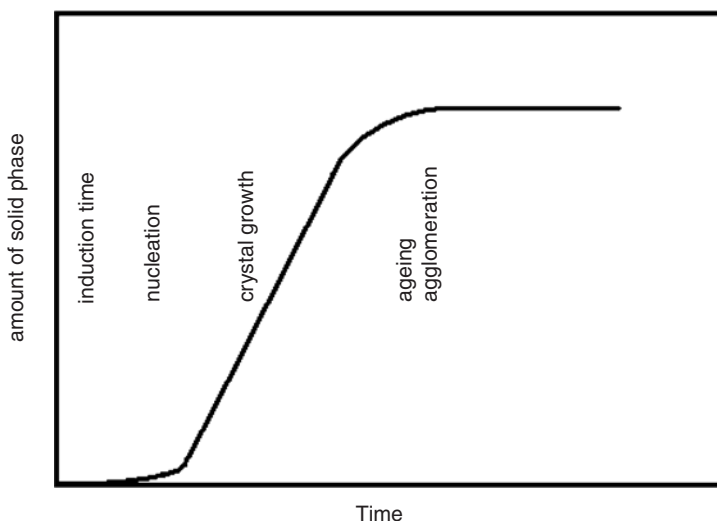


FIGURE 2.2. Processes involved during the precipitation process.

in the figure but, depending on the experimental conditions, more or less marked overlapping between the phases occurs.

## 2.2 Nanoparticle Growth, Growth Inhibition, and Size Control

According to the thermodynamic and kinetic premises, above the supersaturation threshold the unlimited nanoparticle growth is a spontaneous process whose rate can be controlled by altering some external parameters such as supersaturation degree, temperature, and additive presence. In order to inhibit this process, additional phenomena must come into play. Then, the appropriate use of the parameters regulating these phenomena could lead to the kinetic and/or thermodynamic fine nanoparticle size control. These features will be taken into account in the following subsections.

### *2.2.1. Time Dependence of Nanoparticle Size and Size Distribution*

In supersaturated solutions where the probability of formation of critical aggregates is significant, the crystal growth in homogeneous conditions can be described in terms of three distinct processes, i.e., nucleation, normal growth, and competitive growth. In addition to these processes, sometimes, other phenomena could occur such as solid-phase transitions, aggregation,

and recrystallization. All these steps are not well separated in time so that overlapping zones occur.

The total number of crystals ( $N_c$ ) formed by nucleation can be estimated by the equation

$$N_c = \frac{N_{Av} e^{\frac{-3\Delta G_f^*}{5kT}}}{3X_i^{0.2} V_m} \quad 2.10$$

where  $X_i$  is the mole fraction of precursors and  $V_m$  their molar volume. By rearranging this equation,  $N_c$  can be directly related to the supersaturation ratio  $S$  by

$$\log N_c = A - \frac{B}{(\log S)^2} \quad 2.11$$

where  $A$  and  $B$  are positive constants. It must be noted that, according to Eq. 2.11, an increase of the supersaturation value, i.e., higher precursor concentration, leads to a larger number of crystals meaning smaller nanoparticles.

The time dependence of the precursor concentration,  $C(t)$  can be evaluated by

$$C(t) = C_0 \left[ 1 - \left( \frac{t}{\tau} \right)^{\frac{5}{2}} \right] \quad 2.12$$

where  $\tau$  is the characteristic precipitation time, which can be calculated by the equation

$$\tau = \frac{V_m^{\frac{2}{3}} e^{\frac{2\Delta G_f^*}{5kT}}}{2DX_i^{0.2} N_{Av}^{\frac{2}{3}}} \quad 2.13$$

After the appearance of the first nuclei through the random formation of embryos of increasing size, their normal growth occurs by means of the incorporation of molecular precursors reaching the nuclei by diffusion. In this phase, nuclei agglomeration is neglected because their low concentration and diffusion rate make the probability of their encounters practically zero. During normal growth, the time dependence of the mean cluster size ( $\bar{r}$ ) is described by the equation

$$\bar{r} = (2DV_m C_0)^{0.5} t^{0.5} \quad 2.14$$

where  $C_0$  is the molar concentration of precursors, and the concentration of the precursors decreases with time. In stationary state condition, the radius distribution of nuclei is given by the Gaussian function



$$P(r) \propto e^{\frac{-K(r-r^*)^2}{kT}} \quad 2.15$$

where  $r^*$  is the critical radius. Generally, a sharp size distribution results when experimental conditions are set so that agglomeration is prevented and nucleation and growth are temporally separated processes. This can be achieved by realizing an initial high supersaturation followed by an inhibition of subsequent nucleation obtained by a dilution at selected time or by a change of some external parameter (pH, temperature, etc.).

When the precursor concentration becomes negligible, the competitive growth dominates the entire process. During this stage, a mass transfer from smaller particles to larger ones occurs, and the time dependence of the cluster size is described by the equation

$$\bar{r} \propto t^{0.33} \quad 2.16$$

It must be noted that equation 2.16 emphasizes the spontaneous tendency to an unlimited increase of crystal size.

Generally, when the particle size reaches a system-dependent value as a consequence of a growing process and/or of association of smaller aggregates, they tend conspicuously to separate from the liquid phase as an effect of the gravitational force overwhelming that due to the Brownian movements. In such circumstances, an upper or lower solid phase depending on the densities of particles and bulk medium is formed. It is also worth noting that precipitation of scarcely soluble substances from homogeneous solutions generally leads to a broad size distribution due to random crystal growth. Moreover, after precipitation, secondary processes can occur (recrystallization, ageing, aggregation) involving further changes of size, shape, structure, and defectivity of crystals.

### 2.2.2. Nanoparticle Growth Inhibition and Size Control

In some cases, the particle growth is arrested as a consequence of the occurrence of some phenomena. The physico-chemical processes underlying these phenomena and allowing a size control are

- charging of the nanoparticles
- passivation of the nanoparticle surface by adsorption of suitable species
- compartmentalization of nanoparticles in spatially distinct regions

It must be pointed out that each of these mechanisms has its peculiarity and limitations that must be taken into account in the selection of the nanoparticle appropriate synthetic method.

A well-known contribution to the stability of particles is given by the presence of a net charge and/or the formation of an electric double layer surrounding the particle. This phenomenon is quite frequent in polar solvents because the particle could adsorb ionic species of the solution and/or species

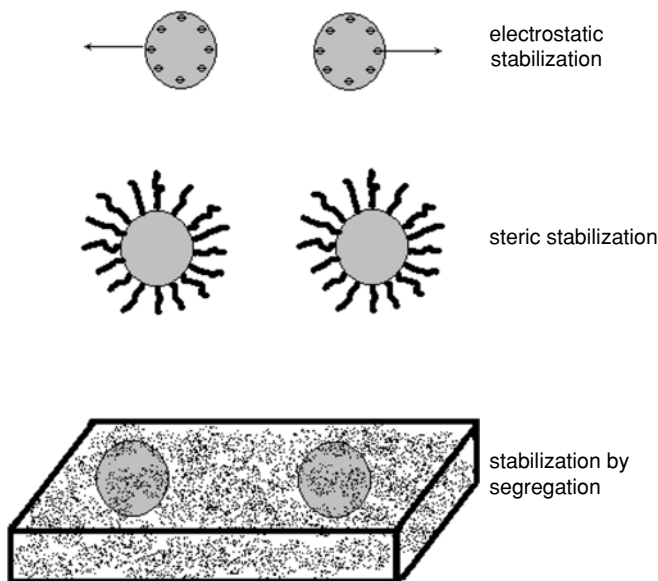


FIGURE 2.3. Mechanisms allowing nanoparticle size stabilization.

laying on the particle surface can dissociate, releasing ions on the surrounding medium. These processes together with the subsequent electrostatic effect on other nearby ionic species generate a double layer surrounding the particle.

Particles carrying the same charge and/or surrounded by an electric double layer repel due to electrostatic forces. In such conditions, a stable dispersion occurs when the particle-particle repulsive force arising by electric charges overcomes the attractive forces (van der Waals interactions, hydrogen bonding, etc.). Electrostatic stabilization is strongly sensitive to the presence of electrolytes, to their concentration and charge, and, generally, stable dispersions can be obtained at very low concentrations of nanoparticles. In particular, two opposite effects can be observed, i.e., ions coming from electrolyte dissociation can be selectively adsorbed, generating a charge on the nanoparticle surface or neutralizing pre-existent charges.

Moreover, it must be considered that when two particles approach each other, as a consequence of electrostatic forces and of the charge mobility on the particle surface and/or on the charged double layer coating the particles, the charge distribution around each particle is altered. The resulting charge distribution involves that the repulsive forces are decreased, the particles can move closer, and other distance-dependent interactions could come into play. Moreover, at sufficiently small distances, additional attractive forces such as the formation of chemical bonds and capillary forces can become operative<sup>4</sup>. For example, it has been observed that negatively charged silica particles readily deposit in presence of negatively charged polymer latexes<sup>5</sup>.

It is worth noting that not only in aqueous media but also in apolar solvents the stability of particle dispersions can be governed by the presence of a net charge on the surface or by double-layer electrostatic repulsions<sup>6,7</sup>. It has been suggested that surface charging in solvents with low dielectric constant could be sustained by specific mechanisms such as exchange of protons between particle surface and surrounding medium<sup>8</sup>.

Another phenomenon by which particles can be stabilized is the intentional use of appropriate capping agents. From a molecular point of view, the capping agents are molecules showing a physical or a chemical affinity for the species lying at the nanoparticle surface and forming a protective layer that makes the nanoparticle surface unreactive against agglomeration or precursor incorporation. Generally, the action of capping agents is based on their peculiar structure. In particular, they have a molecular moiety displaying an affinity to the nanoparticle surface and another unreactive moiety extending towards the environment that sterically prevents nanoparticle coalescence or precursor adsorption. As a consequence, the stabilization by surface capping is, generally, not sensitive to the presence of electrolytes and/or other unreactive additives. Capping with chemically bonded species is often contraindicated for nanoparticles to be used as catalysts.

Particles can also be stabilized against an unlimited growth by segregation or compartmentalization in spatially distinct domains. This strategy is based on the complete inhibition of nanoparticle encounters or material exchange process. This can be achieved by chemically anchoring particles on the surface of a suitable solid substrate or by dispersing them within a solid matrix. In such conditions, the freezing of the diffusive processes avoids the particle growth. This strategy is most frequently followed for the preparation of nanomaterials for optical applications or catalysis.

Stabilization of the nanoparticle size can also be achieved by performing their synthesis in microheterogeneous systems. This strategy has its distinct features even if it embodies all the above reported mechanisms. Thanks to the large difference of the diffusion coefficients of precursors and nuclei in microheterogeneous systems, in general the formation of nanoparticles occurs through two well-separated steps, i.e., the fast formation of nuclei and their slow growth. The separation is more evident at high reactant concentration<sup>9,10</sup>.

Specific stabilization mechanisms are observed in microheterogeneous systems. Such systems, in fact, allow the stabilization of nanoparticles most often because their nanoscopic domains act as a physical boundary that inhibits precursor and nanoparticle diffusion, encounters, and agglomeration. As a consequence, the rate of formation of nanoparticles in microheterogeneous systems is generally slower than it is in homogeneous media. This strategy is similar to that followed by biological systems to accomplish the control of mineralization process within small spaces such as biological membranes or liposomes.

When the molecular aggregates are confined in nano-size domains, further contributions to the stability of the system could arise from:

1. A change of the particle/surrounding medium interfacial energy due to the adsorption on the aggregate surface of a monolayer of surfactant molecules. Concerning this point, it must be considered if the aggregate surface is hydrophilic or lipophilic, because this aspect determines the orientation of the surfactant or of the micellar aggregate on the particle surface. If the surface is hydrophilic and the nanoparticle is dispersed in water, a second layer of surfactant molecules is generally formed, coating the first layer and forming a bilayer surrounding the particle.
2. A significant reduction of the encounter frequency due to the screening effect of the surfactant layer on the internanoparticle attractive interactions and to the dispersion of micelles in the solvent medium.
3. A decrease of the particle growing process due to the drastic reduction of diffusion rates, which gives enough time to other processes such as particle coating with specific molecules allowing stabilization and control of small-size particles.
4. An inhibition of the heterogeneous nucleation due to the coating effect of a monolayer of surfactant molecules on the possible solid surfaces or particles in the system.
5. A change of the microscopic processes leading to the formation and growth of particles.
6. A change of kinetic and thermodynamic parameters in confined space.

Concerning point 5, investigations on the growing process of ZnS nanoparticles in AOT reversed micelles allowed to point out that the time dependence of the nanoparticle size can be expressed by a power law whose exponent (0.074) is much lower than that expected for the same process in an homogeneous system (0.33)<sup>11</sup>. This was taken as an indication that the ZnS nanoparticles in AOT reversed micelles grow following a different mechanism. In contrast with homogeneous media where the particle growth is regulated by the diffusion rate of precursors, it has been found that in reversed micellar systems, the process is controlled by the intermicellar exchange of material.

From the analysis of the enthalpies of precipitation of calcium carbonate and calcium fluoride nanoparticles in various w/o micromulsions, it was suggested that their energetic state is strongly different from that in the bulk. The observed behavior was attributed to smallness of the nanocrystals, changes of the equilibrium constants, and nanoparticle/surfactant interactions<sup>12</sup>.

A generally overlooked question of all nanoparticle chemical synthetic methods is the destiny of secondary products that quite often accompany

the formation of nanoparticle precursors. Depending on the specific synthetic protocol, these substances could poison or dope the nanoparticle. This question is more important when the synthesis is carried out in confined space.

## 2.3 Internal and External Parameters Controlling Nanoparticle Formation and Stability in Microheterogeneous Systems

### 2.3.1. *General Considerations*

Size, shape, and polydispersity of nanoparticles can be regulated by selecting the appropriate system and experimental conditions. In the best condition, i.e., when the nanoparticle size and shape is controlled by that characterizing the structure of the microheterogeneous system, care must be taken for the suitable composition of the medium allowing selection of the dimensional parameters of the hosting space. It must be stressed that, in this case, important contributions to the control of nanoparticle structural parameters could arise by surfactant adsorption on their surface and strong reduction of diffusive motions.

More frequently, the size and shape of nanoparticles synthesized in microheterogeneous systems result from a fine balance between the tendency of the microdomains to maintain their original structure and that of nanoparticles to grow indefinitely. In these cases, the selection of the appropriate precursor to surfactant molar ratio could play a decisive role for a successful synthetic route. Because the formation of a nanoparticle requires the accumulation of precursors in a single nanodomain, the deformability of the surfactant layer, which controls the material exchange process among nanodomains, plays a pivotal role in determining the nanoparticle growing rate and its final size and shape. A lower material exchange rate involves a reduction of the precursor encounter frequency and consequently the formation of a greater number of nuclei and smaller nanoparticles.

Generally, the hindering to the diffusion process increases with the particle size, so that, when the nanoparticle reaches a critical size, it is stably entrapped in a single domain, and it can grow only by the arrival of further precursors in the molecular state. When all the precursors have been depleted, the nanoparticle reaches its final size. The flexibility of the surfactant layer is also involved if the nanoparticle size becomes comparable with that of the surfactant nanodomain because further growth requires an unfavourable swelling of the nanodomain. The final size is also influenced by the number density of nanodomains because an increase of their concentration involves an increase of the number of nuclei and consequently a smaller nanoparticle size.

Specific effects could also arise from the selective adsorption of surfactant molecules on certain crystallographic facets of the nanoparticles during their growth. It has been suggested that this phenomenon could significantly influence the nanoparticle shape<sup>13</sup>.

Sometimes, to enhance the microheterogeneous system capability to inhibit the nanoparticle growth and for a better control of their size and polydispersity, specific capping agents are added during the synthesis.

Summing up all the above considerations, the factors influencing nanoparticle size and shape are<sup>14–16</sup>

- structural and dynamical properties of the microheterogeneous system
- structure and composition of the water/oil interface
- surfactant layer flexibility
- surfactant nature
- size and shape of microdomains
- nature of the reagents and their localization
- distribution law of reactants among nano-size domains
- reagent local and overall concentrations
- diffusion and material exchange rates among microdomains
- reaction rate leading to the formation of nanoparticle precursors
- local solubility of the nanoparticle precursors
- presence of suitable additives such as capping agents or electrolytes
- nature of the solvent medium
- presence of specific capping agent

Taking into account the sensitivity of the structure and dynamics of microheterogeneous systems to the presence and concentration of additives, it is worth noting that both features must be considered in the presence of reactants.

According to the above-reported considerations, after choosing the appropriate microheterogeneous system, the most frequently employed external parameters to control nanoparticle synthesis are

- the precursor to surfactant molar ratio
- surfactant aggregate concentration
- the nature of the solvent medium
- the temperature
- the addition of specific capping agents

### 2.3.2. *Some Specific Examples*

Using w/o microemulsions as microheterogeneous medium, it has been found that, in some conditions, the nanoparticle size is controlled by the size of the water containing reversed micelle, whereas this does not occur if the synthesis is performed in different experimental conditions<sup>9,17</sup>.

It was suggested that many other factors can influence the final nanoparticle size, shape, and their distribution such as the number of reagent molecules per reversed micelle, the reversed micelle concentration, and the nature of the solvent medium<sup>18</sup>. This is because a change of these factors more or less affects the intermicellar material exchange, nucleation, and growth rates. It has also been found that an increase in the reagent concentration leads to an increase of the nanoparticle size.

The effect of various parameters on the synthesis of silver chloride nanoparticles obtained by adding an aqueous solution of  $\text{AgNO}_3$  to dioctyldimethylammonium chloride/n-decanol/isooctane microemulsions has been investigated. It was observed that i) an increase of the surfactant or water concentrations caused an increase of the particle size, ii) an increase of the silver nitrate concentration led to the formation of more nuclei and consequently smaller nanoparticles, iii) high n-decanol concentration or water to surfactant molar ratio induced destabilization of reversed micelles and consequently nanoparticle agglomeration and flocculation<sup>19</sup>.

The reshaping effect of silica-core gold-shell nanoparticles dispersed in aqueous solutions of cetyltrimethylammonium bromide has been investigated. In particular, it has been observed that nearly spherical nanoparticles are slowly transformed into elongated hollow toroidal gold nanoparticles with significant etching of the silica core<sup>20</sup>.

Microheterogeneous systems can also be employed to realize stable dispersions of particles. This is achieved by directly suspending finely divided materials. It has been found that the adsorption of the surfactant molecules at the particle surface plays a key role in the stabilization process. The dispersion process can be divided in the following steps: i) formation of sufficiently small particles, ii) formation of a compact surfactant layer on the particle surface, iii) dispersion in the medium<sup>21,22</sup>.

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