

## Chapter 2

# Controlled Synthesis: Nucleation and Growth in Solution

**Pedro H. C. Camargo, Thenner S. Rodrigues, Anderson G. M. da Silva and Jiale Wang**

**Abstract** The controlled synthesis of metallic nanomaterials in solution is central to realize many applications that arise from their fascinating properties. As properties in metal nanomaterials are strongly dependent upon size, shape, composition, structure (solid versus hollow interiors), and surface functionality, controlled synthesis is a powerful approach to tailor and optimize properties as well as to establish how they are dependent on the several physical and chemical parameters that define a nanostructure. In this context, this chapter focuses on the fundamentals of the controlled synthesis of metal nanomaterials in solution phase in terms of the available theoretical framework. Specifically, it starts by introducing the mechanisms employed for the stabilization of nanomaterials during solution-phase synthesis (Sect. 2.2). The basics of nucleation and growth in solution will be discussed in Sect. 2.3. After that, the shape-controlled synthesis of Ag nanomaterials will be employed as proof-of-concept example of how thermodynamic versus kinetic considerations, oxidative etching, and surface capping can be employed to effectively maneuver the shape of a metal nanocrystal in solution (Sect. 2.4). Finally, some of the current challenges and outlook regarding the controlled synthesis of metal-based nanomaterials will be presented (Sect. 2.5).

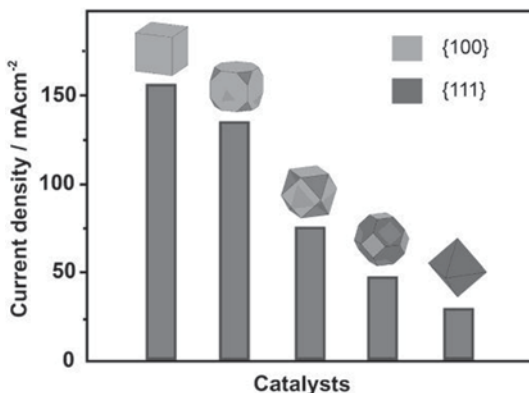
## 2.1 Motivation for Controlled Synthesis of Metallic Nanomaterials

The motivation for the controlled synthesis of metallic nanomaterials comes from the fact that their properties are strongly dependent upon size, shape, composition, structure (solid versus hollow interiors), and surface functionality [1]. Thus, the precise control over these parameters opens up the possibility of designing nanomaterials with desired or optimized performances for a given application. Taking catalysis as an example, in addition to small sizes (that are imperative to achieve high-surface areas), the control over the shape enables the exposure of specific surface facets that

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P. H. C. Camargo (✉) · T. S. Rodrigues · A. G. M. da Silva · J. Wang  
Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo,  
Av. Prof. Lineu Prestes, 748, São Paulo 05508-000, Brazil  
e-mail: camargo@iq.usp.br

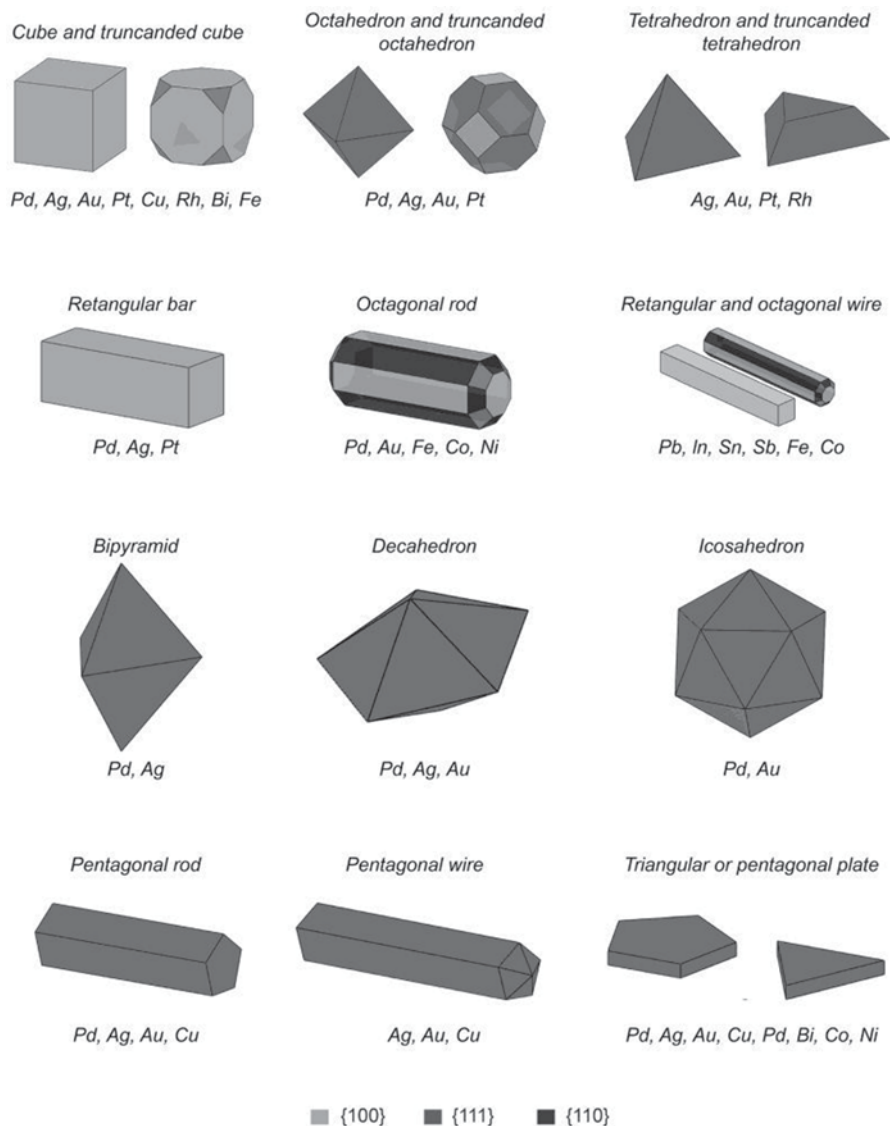
**Fig. 2.1** Maximum current densities for formic acid oxidation employing Pd nanocrystals displaying controlled shapes as electrocatalysts. The current densities (electrocatalytic activities) were strongly dependent on the relative exposure of {100} and {111} surface facets, decreasing as the shapes transitioned from cubes to octahedrons [3]. Copyright 2012 American Chemical Society



can be more catalytically active or selective for a reaction of interest [2]. The shape-dependent catalytic activity of Pd nanocrystals towards the electrooxidation of formic acid is shown in Fig. 2.1 and represents a notable example on how the control over shape can be employed for optimizing catalytic performance. As {100} surface facets are more active relative to {111} for the electrooxidation of formic acid, a gradual increase in the current densities was observed as the shape was changed from cubes to truncated cubes, cuboctahedrons, truncated octahedrons, and finally octahedrons, as these shapes gradually enable an increased exposure of {111} relative to {100} surface facets [3]. In addition to catalytic activity, optical, magnetic, and electronic properties have also shown shape/size-dependency [4].

It is noteworthy that, in order to reach its full potential, the controlled synthesis of metallic nanomaterials must meet several requirements that include monodispersity in terms of size, shape, structure, and composition. Among different methods for the controlled synthesis of metallic nanomaterials, solution-phase approaches offer many advantages that include the facile stabilization by the addition of proper capping agents, easy extraction/separation from the reaction mixture (by centrifugation, for example), straightforward surface modification/functionalization, potential for large-scale production, and versatility regarding the several experimental parameters that can be controlled during the synthesis (temperature, nature of precursors, stabilizers, solvent, reducing agents, their molar ratios, concentrations, etc.) [5]. Surprisingly, substantial developments on the solution-phase-controlled synthesis of metallic nanomaterials with a variety of shapes and sizes were made only recently. Figure 2.2 illustrates a variety of shapes that have been realized by the controlled synthesis of metal nanostructures [1]. Despite this progress, a detailed atomic understanding of the mechanisms of nucleation and growth stages during nanoparticle formation is still not completely understood, and most fundamentals are currently borrowed from classical colloidal theories [6].

In this chapter, rather than describing a variety of protocols for the controlled synthesis of different classes of metal nanomaterials, we will focus on the main fundamentals and concepts behind the controlled synthesis of metal nanomaterials in solution phase. Specifically, we will start by introducing the mechanisms employed



**Fig. 2.2** Different shapes that have been enabled for a range of metals nanocrystals by solution-phase synthesis

for the stabilization of nanomaterials in the context of solution-phase synthesis (Sect. 2.2). The fundamentals of nucleation and growth in solution will be discussed in Sect. 2.3. After that, the shape-controlled synthesis of Ag nanomaterials will be employed as proof-of-concept example of how thermodynamic versus kinetic considerations, oxidative etching, and surface capping can be employed to effectively maneuver the shape of a metal nanocrystal in solution (Sect. 2.4). Finally, we will

present some of the current challenges and outlook regarding the controlled synthesis of metal-based nanomaterials (Sect. 2.5).

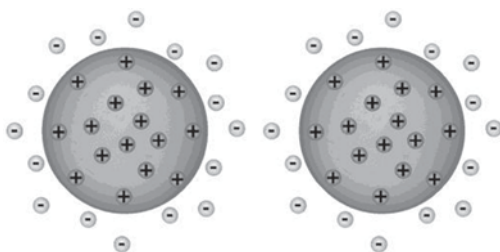
## 2.2 Stabilization in Solution-Phase Synthesis

The main feature that sets nanomaterials apart from their micro- and macro-counterparts is their large surface to volume ratios, which is responsible for many unique or improved properties that nanomaterials possess [7]. A large surface to volume ratio implies that nanomaterials display high-surface energies (as surface energy increases with surface area), which makes them thermodynamically unstable or metastable [8]. Consequently, the synthesis of nanomaterials in solution requires one to overcome their large surface energies and prevent them from agglomerating. Agglomeration is thermodynamically driven by the reduction in surface area and thus surface energy. In fact, the reduction of surface energy is also the driving force for other processes in solution-phase syntheses such as surface restructuring, formation of facets, and Ostwald ripening [5]. In the following section, we will discuss two main approaches that are commonly employed to stabilize metallic nanomaterials against agglomeration: the electrostatic and steric (or polymeric) stabilization. Interestingly, as will be discussed in Sect. 3 and 4, the steric stabilization can also be put to work for favoring the formation of nanomaterials with monodisperse sizes and controlled shapes.

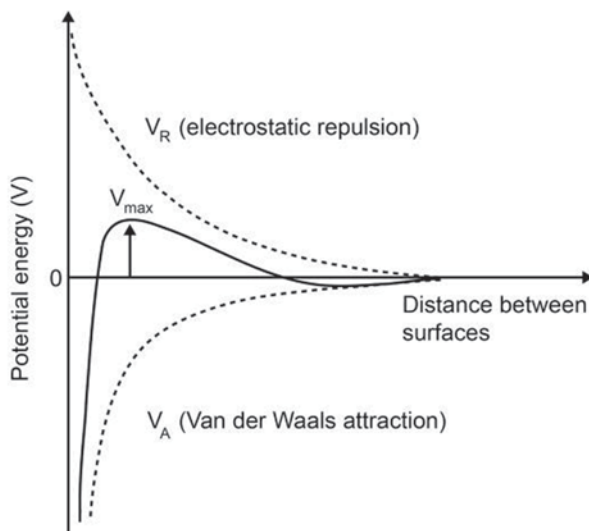
### 2.2.1 Electrostatic Stabilization

The concept behind the electrostatic stabilization is illustrated in Fig. 2.3 and it is based on the repulsion of electrical charges having the same sign present in the electrical double layers between neighboring particles [9]. The electrostatic stabilization can also be understood in terms of osmotic flow, in which solvent from the suspension flows into the region where the double layers overlap until the distance between the nanoparticles equals to or become larger than the sum of their individual double layers. As the overlap of double layers lead to a substantial increase

**Fig. 2.3** Electrostatic stabilization between two approaching particles: the electrostatic repulsion of like-charges drive particles apart as their double layers overlap



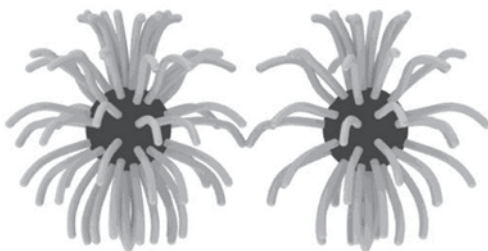
**Fig. 2.4** Overall potential energy ( $V$ , solid line) expressed as a combination of the attractive Van der Waals and repulsive electrostatic potentials ( $V_A$  and  $V_R$ , respectively, dashed lines) [9]. Copyright © 2002, John Wiley and Sons



in the concentration of ions in the inter-particle region, the osmotic flow works to restore the equilibrium concentration.

The formation of a double layer arises from the adsorption of charged species at the surface, dissociation of surface-charged species, and/or accumulation or depletion of electrons at the surface following the formation of a solid surface in a polar solvent or electrolyte. An equal number of counter-ions with the opposite charge will then surround the system to produce a charge-neutral double layer, as depicted in Fig. 2.3. In addition to the contribution from columbic forces, Brownian motion and entropy also contribute to the location of species in solution, resulting in an inhomogeneous distribution of surface ions and counter ions [10]. The DLVO theory, which was named after Derjaguin, Landau, Verwey and Overbeek, successfully describes how the electrostatic stabilization between neighboring nanoparticles in suspension works [11]. The DLVO theory assumes that the interaction between two electrically charged approaching particles in suspension consists of a combination of Van der Waals attraction and electrostatic repulsion arising from the neighboring double layers [12, 13]. Figure 2.4 shows a plot of the overall potential ( $V$ , solid line) illustrated as a sum of Van der Waals attraction ( $V_A$ , dashed line) and electrostatic repulsion ( $V_R$ , dashed line) as a function of the distance between the approaching particles. When the two particles are far away from each other (distance is large), both  $V_A$  and  $V_R$  tend to zero. As the particles start to approach each other, the electrostatic repulsion is stronger than the Van der Waals attraction ( $V_R > V_A$ ), leading to an increase in the overall potential ( $V$ ) with the decrease in distance until a maximum is reached at  $V_{MAX}$ , which corresponds to the repulsive energy barrier. As the distance is further decreased, the Van der Waals attraction surpasses the electrostatic repulsion ( $V_A > V_R$ ), and the overall potential becomes strongly dominated by  $V_A$ , which leads to the agglomeration of the particles. If  $V_{MAX} > \sim 10 kT$  ( $k$  is the

**Fig. 2.5** Steric stabilization between two approaching particles containing anchored polymers at their surface. Under both low- and high-surface coverage conditions, the polymer layers repel one another as they approach and/or interact



Boltzmann constant and  $T$  the temperature), collision from Brownian motion will not overcome  $V_{MAX}$  and agglomeration will not take place. On the other hand, if  $V_{MAX} < \sim 10 kT$ , agglomeration takes place and the particle suspension would not be stable.

It is important to note that these considerations indicate that electrostatic stabilization mechanism only applies to dilute systems, is dependent on the concentration of ions in suspension, agglomerated particles cannot be re-dispersed, and comprises a kinetic stabilization method. As an example, the widely employed synthesis of Au nanoparticles by the reduction of  $AuCl_4^{-}(aq)$  by trisodium citrate pioneered by Turchevich [14] and refined by Frens [15] is based on electrostatic stabilization, in which citrate anions (negative charge) bind to the surface of the Au NPs during the synthesis.

### 2.2.2 Steric (or Polymeric) Stabilization

The steric (also called polymeric) stabilization consists in preventing neighboring particles of getting close to each other in the range of attractive forces where Van der Waals attraction would lead to agglomeration by the presence of polymers at the particles surface [16]. In general, a polymer can interact with a solid surface by one-end binding (anchored polymer) or via weak interactions from random points along its backbone (adsorbing polymer) [9]. When two particles covered with polymer approach each other, the polymer layers from each particle will interact only when the distance between particles become lower than the sum of the thicknesses of the neighboring polymer layers. Figure 2.5 depicts two approaching nanoparticles presenting an anchored polymer at their surface. As the distance between the particles becomes lower than the sum of the thicknesses of the neighboring polymer layers, they can overlap or become compressed resulting in strong repulsion between the neighboring nanoparticles. When the polymer is at good solvent conditions and neighboring adsorbed layers can overlap (under low-surface coverage), stabilization occurs as a result of the unfavorable mixing of the adsorbed layers, as an increase in entropy accompanied by an increase in the Gibbs free energy results from the interpenetration of polymers (assuming the enthalpy variations are negligible due to the interpenetration). At higher coverage (and/or under poor solvent conditions),

the approaching adsorbed layers become compressed at the surface as the nanoparticles approach each other, and therefore, cannot interpenetrate. This process leads to an increase in the Gibbs free energy, driving the nanoparticles apart. Hence, steric stabilization emerges from the volume restriction effect (exclusion by space) due to the decrease in the possible configurations in the region between the particles and from the osmotic effect as the concentration of polymeric molecules in the region between the two particles becomes high [11].

It is important to mention that the steric stabilization is not so well understood in comparison to the electrostatic stabilization. Nevertheless, it is widely employed in the solution-phase synthesis of nanomaterials, offering many advantages when compared with electrostatic stabilization. For instance, steric stabilization is thermodynamic (agglomerated particles can be redispersed), it is not restricted to dilute systems, and is not sensitive to the presence of electrolytes, which is highly desirable for several applications. Moreover, it contributes to the production of monodisperse nanoparticles as the polymer layer adsorbed at the nanoparticle surface can also work as a diffusion barrier to the addition of growth species, favoring the diffusion-limited growth (Sect. 3.2) [5]. Polymers employed for steric stabilization can also play other roles in solution-phase syntheses such as serving as reducing agents, helping in manipulating precursor reduction rates, and interacting with distinct nanocrystals surface facets with different binding affinities, which is central in the context of shape-controlled synthesis [1, 17].

## 2.3 Fundamentals of Nucleation and Growth

The controlled synthesis of metal nanomaterials requires (and refers to) nanomaterials with monodisperse sizes and shapes. Therefore, all nanostructures produced from a reaction mixture must have sizes and shapes as similar as possible (narrow size and shape distribution). The controlled synthesis of metal nanomaterials from a homogeneous solution comprises two main stages: nucleation and growth. In this section, we will discuss the theory behind nucleation and growth stages in order to understand how these steps can be employed to obtain nanomaterials with monodisperse sizes.

### 2.3.1 *Homogeneous Nucleation*

Nucleation refers to the extremely localized building of a distinct thermodynamic phase and represents the first stages during a crystallization process. More specifically, it can be defined as the process by which building blocks (metal atoms in the synthesis of metal nanomaterials) arrange themselves according to their crystalline structure to form a site upon which additional building blocks can deposit over and undergo subsequent growth [18]. In this context, nuclei correspond to infinitesimal clusters consisting of very few atoms of the growth species.



Lamer et al. pioneered the study on the synthesis of uniform colloids and the related nucleation and growth mechanisms [6]. These studies date back from the 1940s and are still the basis of our understanding on the synthesis of uniform nanomaterials (including metallic, polymeric, semiconducting, and oxide systems) [19]. From these studies, the concept of “burst nucleation” has been established to be crucial for the synthesis of monodispersed particles. Burst nucleation refers to the formation of a large number of nuclei in a short period of time, followed by growth without additional nucleation. This allows nuclei to have similar growth histories and, therefore, yield nanoparticles with same sizes. This concept is normally referred to as the separation of nucleation and growth stages during the synthesis [19]. For instance, if nucleation and growth could occur simultaneously, the nuclei growth histories would be significantly different and heterogeneous size distributions would be obtained.

The supersaturation of growth species comprises the first requirement for the occurrence of homogeneous nucleation. In the synthesis of metal nanoparticles, supersaturation may be achieved via the in situ generation of the solute growth species (metal atoms) through the conversion of soluble precursors into metal atoms by reduction or decomposition reactions. Alternatively, supersaturation could be induced by the decrease in the temperature of an equilibrium mixture containing the growth species. Although nucleation can take place in liquid, gas, and solid phases, we will center our discussion on the liquid phase, as the fundamentals are essentially the same in all cases.

The reduction of the overall Gibbs free energy to generate a new solid phase from a supersaturated solution containing the growth species as the solute represents the driving force for homogenous nucleation. The change in Gibbs free energy per unit volume of the solid phase ( $\Delta G_v$ ) is dependent on the concentration of the solute and can be expressed as follows:

$$\Delta G_v = -kT / \Omega \ln(C / C_0) \quad (2.1)$$

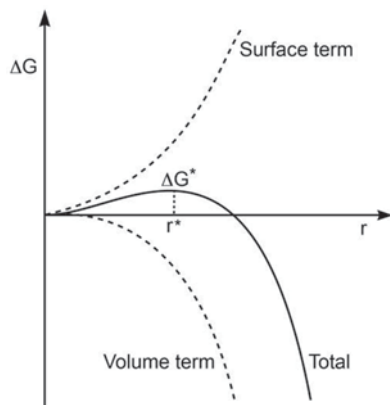
where  $T$  is the temperature,  $\Omega$  the atomic volume,  $C$  the concentration of the solute, and  $C_0$  the solubility or equilibrium concentration [20]. When  $C > C_0$ ,  $\Delta G_v$  becomes negative and nucleation is spontaneously favored. However, this decrease in the Gibbs free energy is accompanied by an increase in the surface energy per unit area ( $\gamma$ ) of the newly formed solid phase. Thus, the overall Gibbs free energy change ( $\Delta G$ ) for the formation of spherical nuclei with radius  $r$  from a supersaturated solution corresponds to:

$$\Delta G = (4/3)\pi r^3 \Delta G_v + 4\pi r^2 \gamma \quad (2.2)$$

where the first term corresponds to the change of volume free energy (volume term,  $\Delta \mu_v$ ) and the second to the change in surface free energy (surface term,  $\Delta \mu_s$ ). Figure 2.6 displays a plot of  $\Delta G$  as a function of  $r$  (solid line) [20]. The surface and volume terms are also shown as dashed lines. As  $\gamma$  is always positive and  $\Delta G_v$  negative as long as the solution is supersaturated, the plot of  $\Delta G$  as a function of  $r$  has a



**Fig. 2.6** Change in the Gibbs free energy ( $G$ , *solid line*) as a function of the nucleus radius ( $r$ ) as a sum of the volume and surface free energies [20]. Copyright © 2001, Elsevier



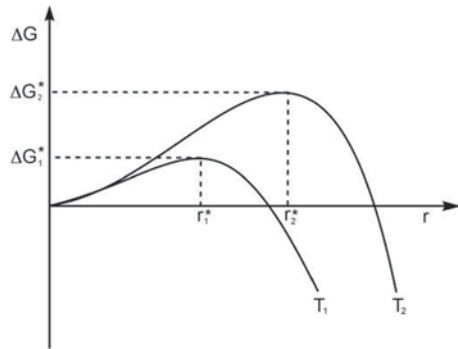
maximum that corresponds to the critical radius  $r^*$ . The critical radius ( $r^*$ ) can be defined as the minimum radius that a nucleus must possess in order to spontaneously grow from a supersaturated solution, or the minimum size required for the formation of a stable nucleus by precipitation from a supersaturated solution. When  $r < r^*$ , the surface term is higher than the volume term and any nucleus smaller than  $r^*$  will dissolve into the solution. In other words, the increase in the surface energy due to the nucleus formation is higher than the stabilization due to the formation of a new solid phase from the supersaturated solution, and nucleation is not favored. On the other hand, when  $r > r^*$ , the volume term exceeds the contribution from the surface term so that the created nucleus is stable and undergoes subsequent growth (the stabilization due to the formation of the new solid phase from the supersaturated solution becomes higher than the destabilization due to the increase in surface energy). Setting  $d\Delta G/dr$  allows us to find  $r^*$  and  $\Delta G^*$  according to the following equations:

$$r^* = -2\gamma/\Delta G_v \quad (2.3)$$

$$\Delta G^* = 16\pi\gamma/3(\Delta G_v)^2 \quad (2.4)$$

where  $\Delta G^*$  corresponds to the critical Gibbs free energy, i.e., the minimum energy barrier that must be reached for nucleation to take place. These equations illustrate that  $r^*$  can be decreased by lowering the  $\gamma$  of the new solid phase. Also, increasing  $\Delta G_v$  will lead to a decrease in both  $r^*$  and  $\Delta G^*$  ( $\Delta G_v$  increases with the supersaturation, Eq. 1). Surface energy, on the other hand, can be manipulated by changes in the solvent, temperature, and the use of “impurities” in the reaction mixture such as capping agents [19]. As an example, Fig. 2.7 shows how  $r^*$  and  $\Delta G^*$  for a spherical nucleus can vary as a function of temperature. It can be observed as an increase in both  $r^*$  and  $\Delta G^*$  with temperature. This is because supersaturation (and thus  $\Delta G_v$ ) decreases as the temperature is increased (Eq. 1) [5].

**Fig. 2.7** Change in the Gibbs free energy ( $G$ ) as a function of the nucleus radius ( $r$ ) for two different temperatures, where  $T_1 < T_2$  [20]. Copyright © 2001, Elsevier



The nucleation rate ( $N_R$ , per unit volume and unit time) is defined as the increase in the number of particles as a function of time and can be written as a function of  $\Delta G^*$  in the Arrhenius form:

$$dN/dt = N_R = \exp(-\Delta G^*/kT) \quad (2.5)$$

$N_R$  is also dependent on the number of growth species per unit volume (number of nucleation centers, which is determined by the initial concentration  $C_0$ ) and the jump frequency of growth species from one site to another. Thus,  $N_R$  can be written as:

$$N_R = \{(C_0 kT / (3\pi\eta d^3))\} \exp(-\Delta G^*/kT) \quad (2.6)$$

where  $\eta$  corresponds to the viscosity of the solution and  $d$  to the diameter of growth species. This equation shows that high nucleation rates are promoted by high initial concentration of growth species (high supersaturation), low viscosity, and low  $\Delta G^*$ . Moreover, in order to start the accumulation of nuclei for subsequent growth,  $N_R$  must be high enough to surpass the re-dissolution of nuclei. It is important to mention, however, that the thermodynamic model discussed above has some limitations when the synthesis of nanocrystals is regarded, as both  $\gamma$  and  $\Delta G_v$  should not be constant and vary with size [19].

Owing to their sub-nanometer sizes, there is actually little information and knowledge regarding the true identity of nuclei during the synthesis of metal nanomaterials due to the lack of experimental tools capable of precisely capturing and characterizing them. According to theoretical investigations and evidence from mass spectrometry as well as adsorption and emission spectroscopies, it has been proposed that the crystal embryos seem to be closely related to their corresponding metal clusters [1, 21].

Figure 2.8 depicts the Lamer plot, which shows the change in the atomic concentration of the solute (growth species) during the nucleation and growth processes as a function of time. This plot is also very useful for illustrating the concept of burst nucleation. In the synthesis of metal nanocrystals, the concentration of solute (metal atoms) is increased by the decomposition or reduction of the corresponding

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