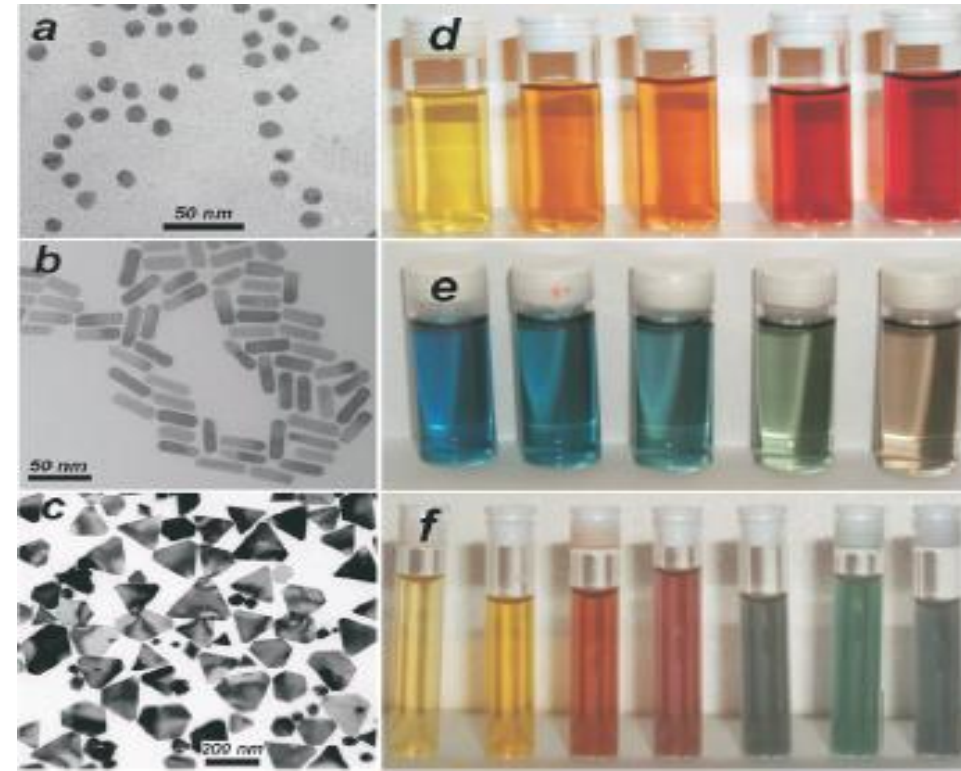
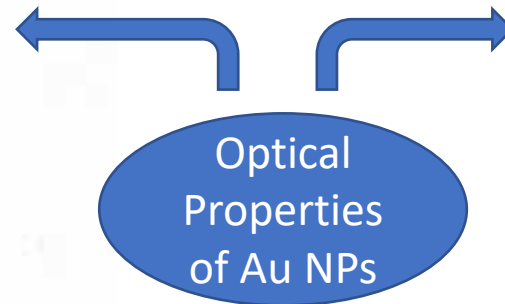


## **Size and Shape Control.... ...WHY and HOW?...**

- ❖ ***On the nanometer scale***, many ***material properties***, which are usually regarded as being intrinsic for bulk material, ***become extremely sensitive to its dimensions***.
- ❖ In other words, ***size and shape/morphology control become a new way of tuning the properties*** of nanostructured materials.
- ❖ Consequently, the ***synthesis of uniformly sized and shaped nanocrystals is critical***, because ***their size/shape uniformity is directly correlated with the homogeneity of their properties***.
- ❖ ***Major challenges in nanoscale science begin with the preparation*** of new nanomaterials with desired ***composition, monodispersed sizes, uniform morphologies***, and comprehensive and ***functionalized surfaces***.

# Size and Shape Control ...WHY?...

- Properties depend on the *size and shape of* nanomaterials.



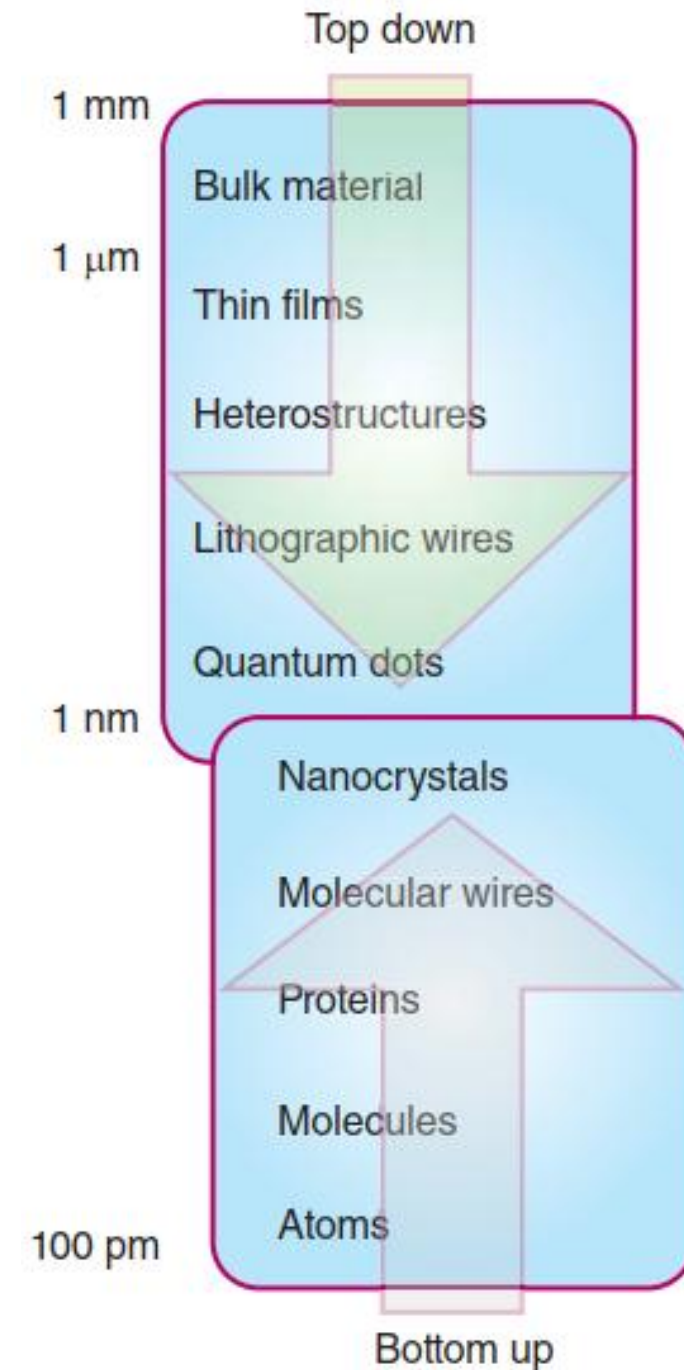
Nanoparticles showing size- and shape-dependent optical properties

- Synthesis of *controlled sized and shaped* nanocrystals is *critical*.

# BOTTOM-UP/TOP-DOWN SYNTHESIS APPROACHES

Nanomaterials synthesis can be broadly classified into the **top-down** and **bottom-up** approaches.

- In the **top-down approach**, one starts with a block of some material and machine a device or structure out of it. This is akin to conventional engineering using lathes and millers to machine a shape out of a solid block. The modern tools of nanotechnology, however, are able to machine structures with sizes of a few nanometers, so the size of components made with a top-down approach is not much different from the building blocks of the bottom-up approach.
- In a **bottom-up approach**, the building block (nanoparticle, molecular machine component, etc.) is identified and produced naturally and then assembled to produce the material or device required. The Chemical Synthesis of nanoparticles belongs to this bottom-up approach.



# Chemical Synthesis of Nanoparticles: Size and Shape Control Protocols

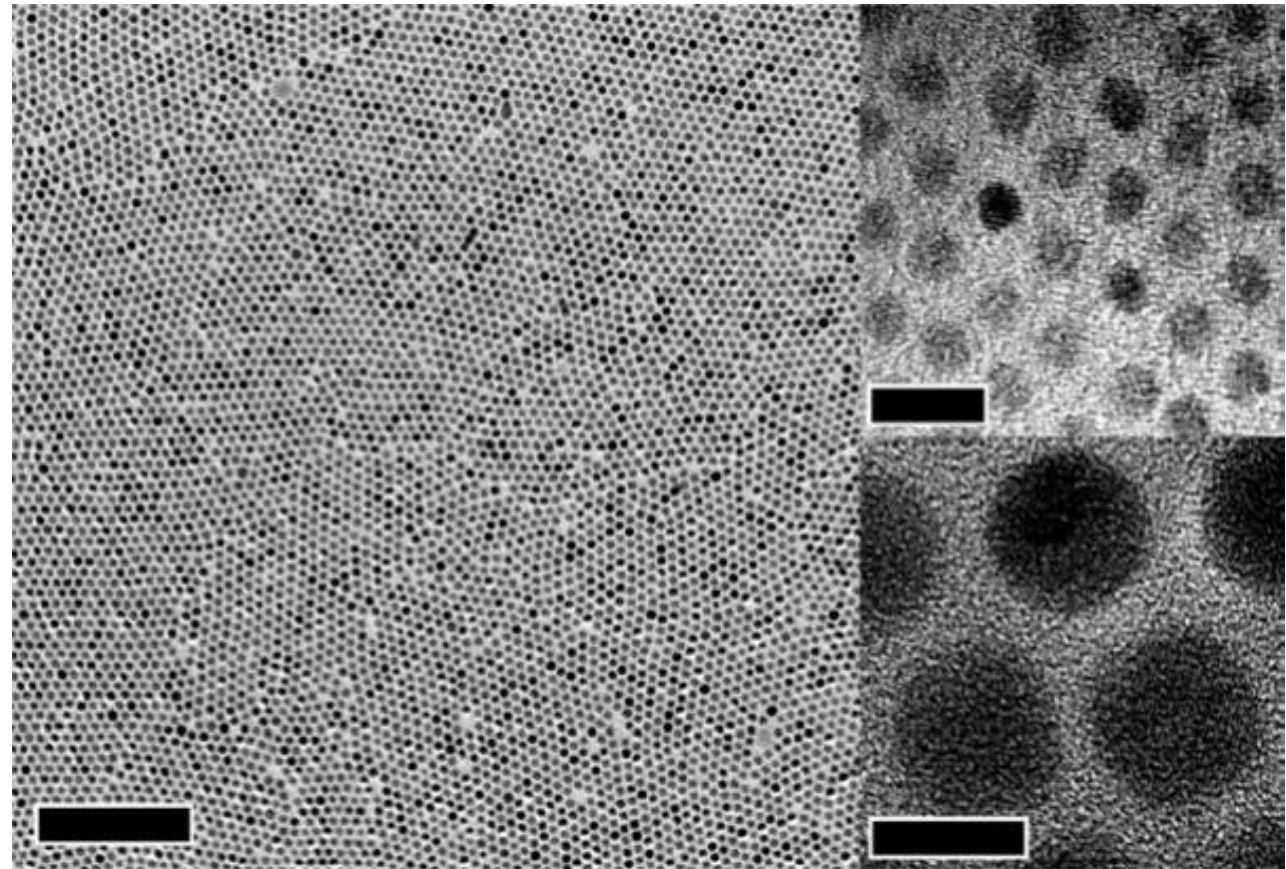
## Size Distribution Control

- It is **difficult to prepare the same sized nanoparticles.**
- As the physical properties depend sensitively on the size of the particles, one aims at obtaining **a narrow size distribution** in order to establish well-defined properties of the samples.
- Usually, nanocrystals with a **relative standard deviation ( $\sigma_r$ ) of the size distribution of less than 5% are said to be monodisperse**. (Some say,  $\sigma_r \sim 10\%$ .)
- Therefore, the synthesis of monodisperse nanocrystals is very much challenging.
- Low-cost routes capable of rapid **mass-producing** nanoparticles of desired dimensions are generally performed via **colloidal synthesis**.



➤ In recent times, several different chemical methods have been developed for the synthesis of monodisperse nanocrystals. Among them, **crystallization in organic media** has been most popularly used, and monodisperse nanocrystals of various materials, including II-VI semiconductors, transition metals, metal alloys, and metal oxides have been synthesized (Fig. 6.1). Studies on the crystallization mechanism have also been intensively pursued.

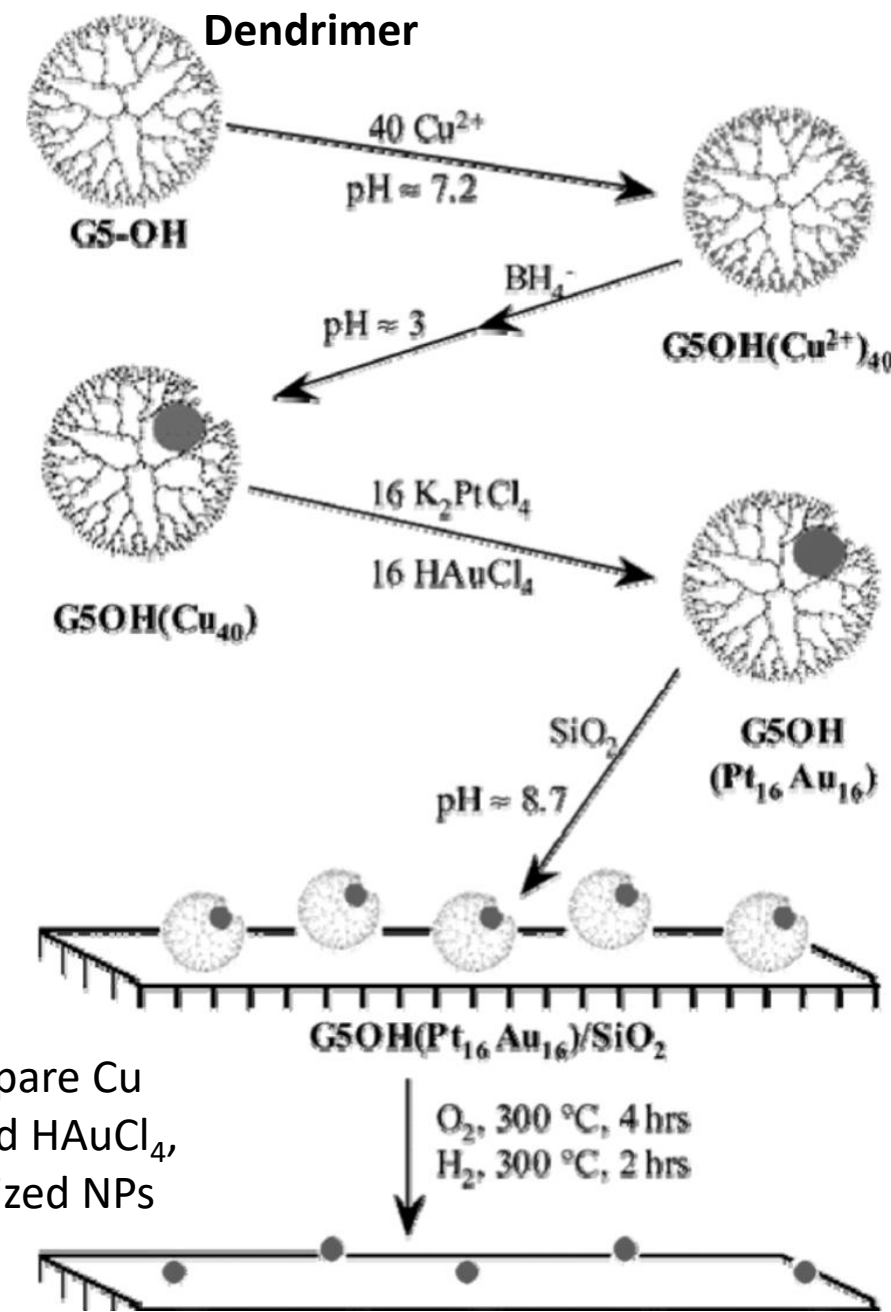
**Figure 6.1** Transmission electron microscopy (TEM) images of monodisperse nanocrystals. They are *iron oxide* nanocrystals synthesized by the heat-up method. The scale bar in the left picture is 2  $\mu\text{m}$  and the ones on the right are 10 nm.



## Size and Shape Control Protocols: Template-Based

- **Templates like micelles, reverse micelles, dendrimers, vesicles, and various other porous structures can also be employed during the synthesis of nanoparticles for the control of particle size.**
- For instance, the adjoining Fig. shows the use of dendrimers as templates for the synthesis of platinum and other metals. The nanoparticles were prepared by sequestering metal ions within supramolecular organic assemblies, namely polyamidoamine (PAMAM) dendrimers, followed by chemical reduction to yield the corresponding metallic nanoparticles. The dendrimers served *as both the template and stabilizer*.
- ✓ The dimensions of such particles also depend on the number of metal ions initially loaded into the dendrimer.

Fig.... Hydroxy-terminated generation 5 PAMAM dendrimers were used to prepare Cu nanoparticles (NPs). The Cu NPs were subsequently used to reduce  $\text{K}_2\text{PtCl}_4$  and  $\text{HAuCl}_4$ , resulting in stabilized bimetallic Pt-Au NPs with a 1:1 stoichiometry. The stabilized NPs were adsorbed onto a silica substrate and thermally activated to remove the dendrimers. Reprinted with permission from American Chemical Society publications.



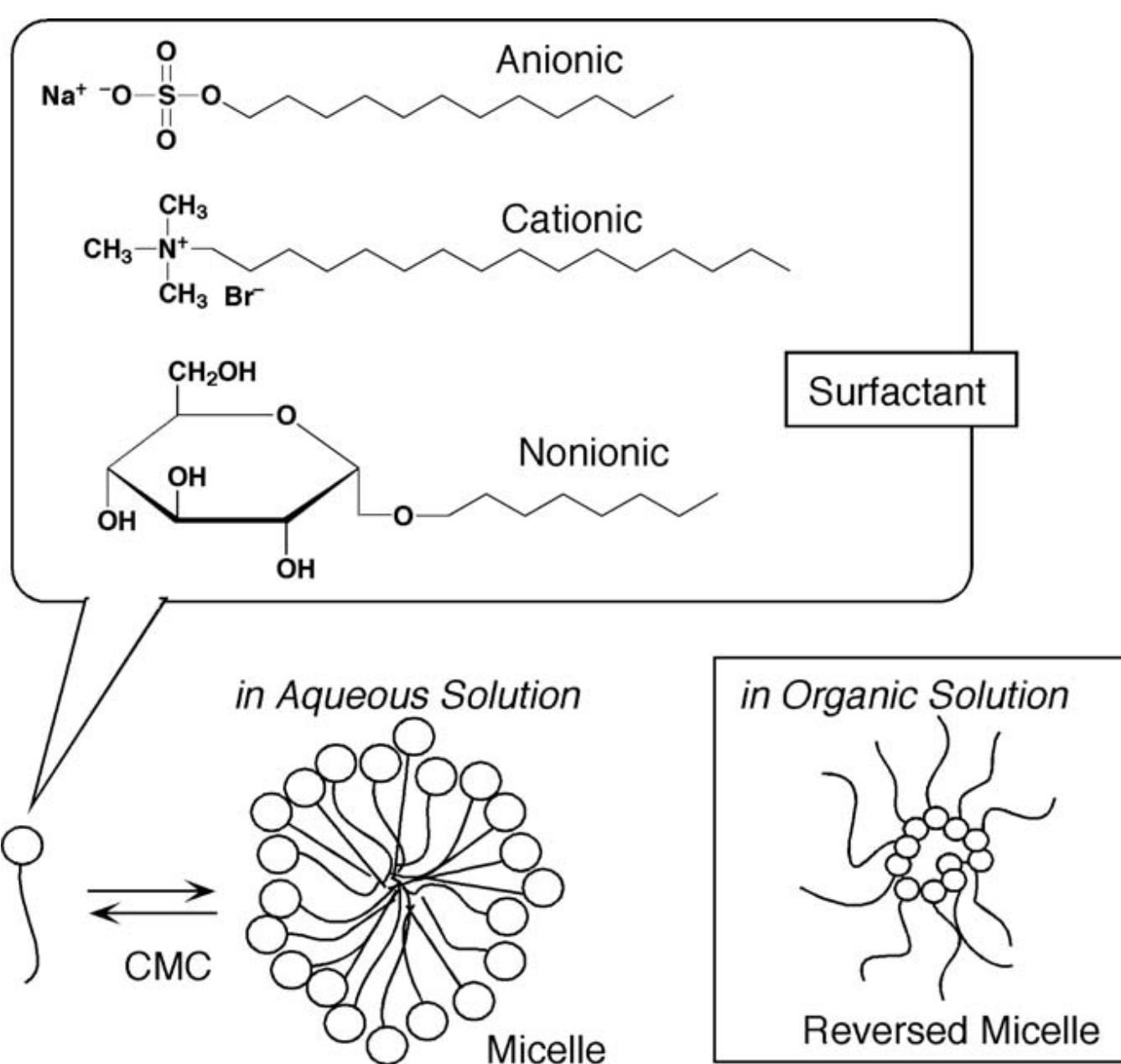


Figure .... Micelle and reversed micelle

- ❑ In a **micellar** structure, the hydrophilic part of the component molecule is located on the outer surface of the micelle, in contact with the aqueous phase, which minimizes the unfavorable contact of the hydrophobic part with water. Micelles can trap organic materials like oils in the inner hydrophobic core, so micelle formation is used in many cleaning agents.
- ❑ In a **reverse micellar** structure, the hydrophilic part of the component molecule is located inward in contact with the aqueous phase, the hydrophobic part points to the outer surface of the micelle.
- ✓ **Core size/volume is controlled by the ratio of water to organic solvent quantities .**



- The use of **reverse micelles** as nano-scale reaction vessels is one the most common methods in colloidal synthesis.
- After coming into contact, reverse micelles exchange their contents. This process has been used **to make nanosized materials via** either the chemical reduction of metal ions or **co-precipitation reactions**.
- ✓ An example is the synthesis of the CdS nanoparticle. CdS has a direct band-gap of 2.42eV and is widely studied for applications in both photoresistive and photovoltaic devices.
- ✓ In this process, **reverse micelles containing two different precursors are prepared:** one with *metal salts* and the *other with a sulfide source* (such as Na<sub>2</sub>S). The solutions are mixed, and nanoparticles are formed as the different micelles exchange their contents. After the formation of these nanoparticles, thiol molecules can be employed to stabilize them as they bond to the surface.
- **Templates** have also been used to control **particle shape**. For instance, *cylindrical pores* have been used to prepare *nanorods/wires*.
- Sometimes the **removal of the template** if not required **is problematic**.



# BASIC CONCEPTS OF SIZE DISTRIBUTION CONTROL

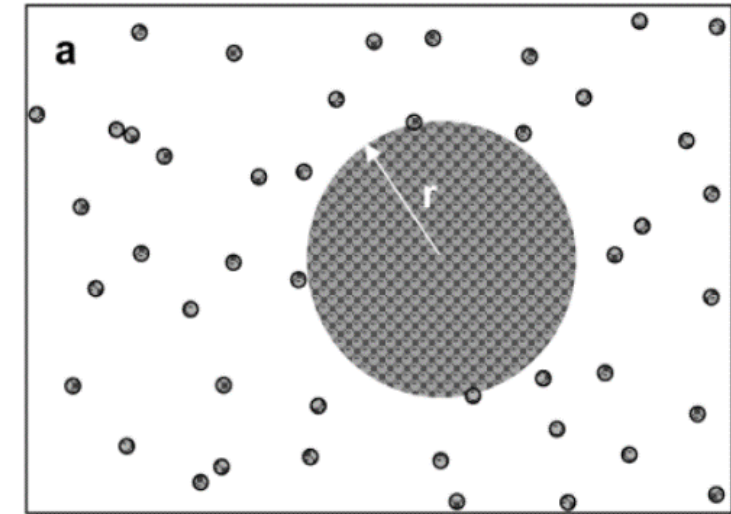
- ❖ The bottom-up solution-phase approach in essence consists of a “nucleation” step followed by the “growth” stage(s).
- Therefore, the chemical methods of producing NPs of controlled sizes and shapes require precise **control of the nucleation and growth steps**.
- *The size distribution control can be achieved in two ways:*
  - (i) nucleation control and (ii) size focusing.*
- ❖ Here, we will discuss how to **control particle size and shape** by controlling their *nucleation* and *growth* steps.
- *The strategy for the colloidal synthesis is rather simple:* the presence, in the system, of a reservoir of reactive molecular species, called “monomers,” that contributes to the particle formation.

- **Nucleation** is the process by which a metastable system such as *supersaturated solution* or a *supercooled liquid* initiates a *discontinuous phase transformation*. In the cases of solution-phase synthesis of metal NPs, the new phase is created by the clustering of the metal atoms that are generated in the solution through the reduction of metal ions (individually or in a cluster) by suitable reducing agents or through bond breaking of the precursor compounds.
- Based on the nucleation process, the **nucleation** can broadly be of **two kinds**: *homogeneous nucleation* and *heterogeneous nucleation*.

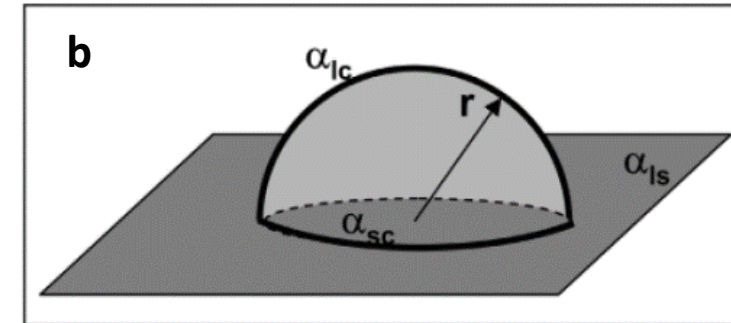
■ *Homogeneous nucleation occurs in the absence of any solid interface in the parent phase.*

■ *Heterogeneous nucleation occurs preferentially on pre-existing foreign bodies or solid structures.*

**Figure 6.** (a) Formation of a *spherical* nucleus of radius  $r$  from a solution.



(b) Heterogeneous formation of a *hemispherical* nucleus at a foreign substrate.



- ❖ *Homogeneous nucleation* occurs in the absence of any solid interface in the parent phase. Prior to initiation of homogeneous nucleation, concentration of the particle forming units (say, metal atoms or atom-precursor combined species, etc.) increases with time (due to their production) in the solution, eventually forming a 'supersaturated' solution. The supersaturated solution is not energetically stable (see below for energy-related further discussion) and will therefore tend to separate out the units. When the supersaturation reaches a critical value, the units begin to assemble in solution forming clusters like dimers, trimers, tetramers, and some of the eventually *critical-sized species called critical nucleus* (or *critical cluster* or *seed*).
- ❖ In the case of *heterogeneous nucleation*, nucleation occurs preferentially at special sites (e.g., grain boundaries, edges, and corners) on pre-existing foreign bodies or solid structures. For the growth of a crystal in solution, there must be a substance that acts as a seed onto which crystallization can occur. The *seed nuclei can be introduced externally or generated in the solution*. If the *crystallization proceeds with preexisting seeds, this process is called heterogeneous nucleation*.
- This terminology indicates that the reaction system is in the heterogeneous phase in the beginning. On the other hand, in homogeneous nucleation, the system consists of a single phase in the beginning and the nucleus formation takes place in the course of the crystallization process.

## A) Fundamentals of the *Size Control* in the Bottom-Up Synthesis

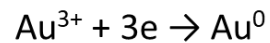
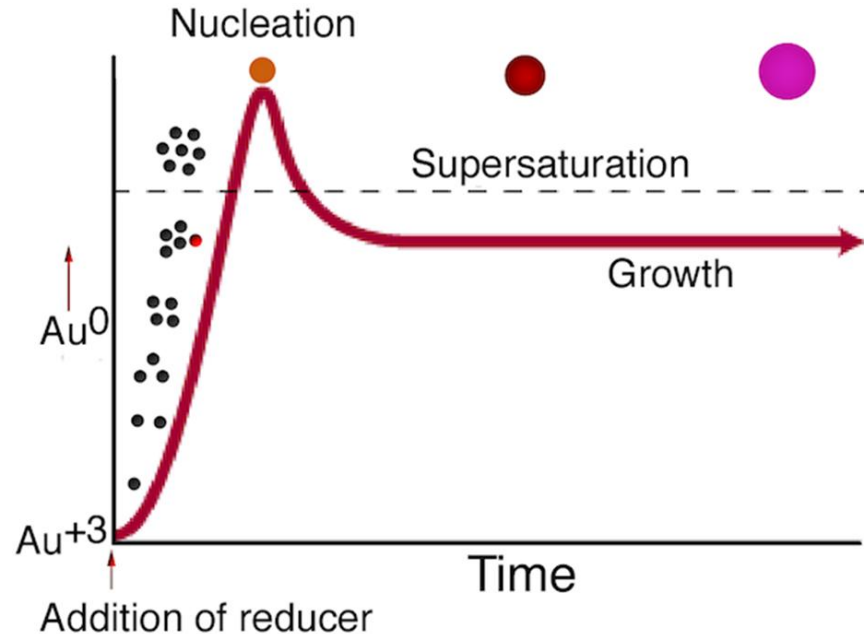
- The chemical synthesis in solution, the approach on which we will focus our discussion, actually offers the possibility of easily adjusting the size of the particles and thus tuning the physical properties.
- *A general description of the rationale of such a synthesis was established in the 1950s: A monodisperse sample, i.e., a sample with a narrow size distribution, can only be obtained when all particles in that sample nucleate quasi-simultaneously (nucleation burst) and no further nucleation occurs while the particles are growing (the separation of nucleation from the growth).*
- *In this understanding of the formation of colloidal particles, the reaction can be divided into three stages (along time or x-axis) as given by the classical LaMer model for the formation of uniform colloidal particles (see Figure 6.16): the prenucleation stage (stage I: induction period), the nucleation stage (stage II), and the growth stage (stage III).*
- At first, *the atomic constituents of the nanocrystals, the monomers, are generated (or introduced) in the growth solution.* Generally, this happens in the form of molecular precursors in which the monomers are bound to a larger molecule. *The binding strength or the equilibrium constant of this bond determines the rate at which the monomers become available. Also, the size of the precursors has an influence on their diffusivity and might strongly influence the synthesis. Over time in this first stage, the concentration of monomers increases and finally a critical supersaturation  $S_c$  is reached, at which the nucleation is induced.* At this point, the system enters into the second stage, the *nucleation stage*.



## Size Control in the Bottom-UP Synthesis

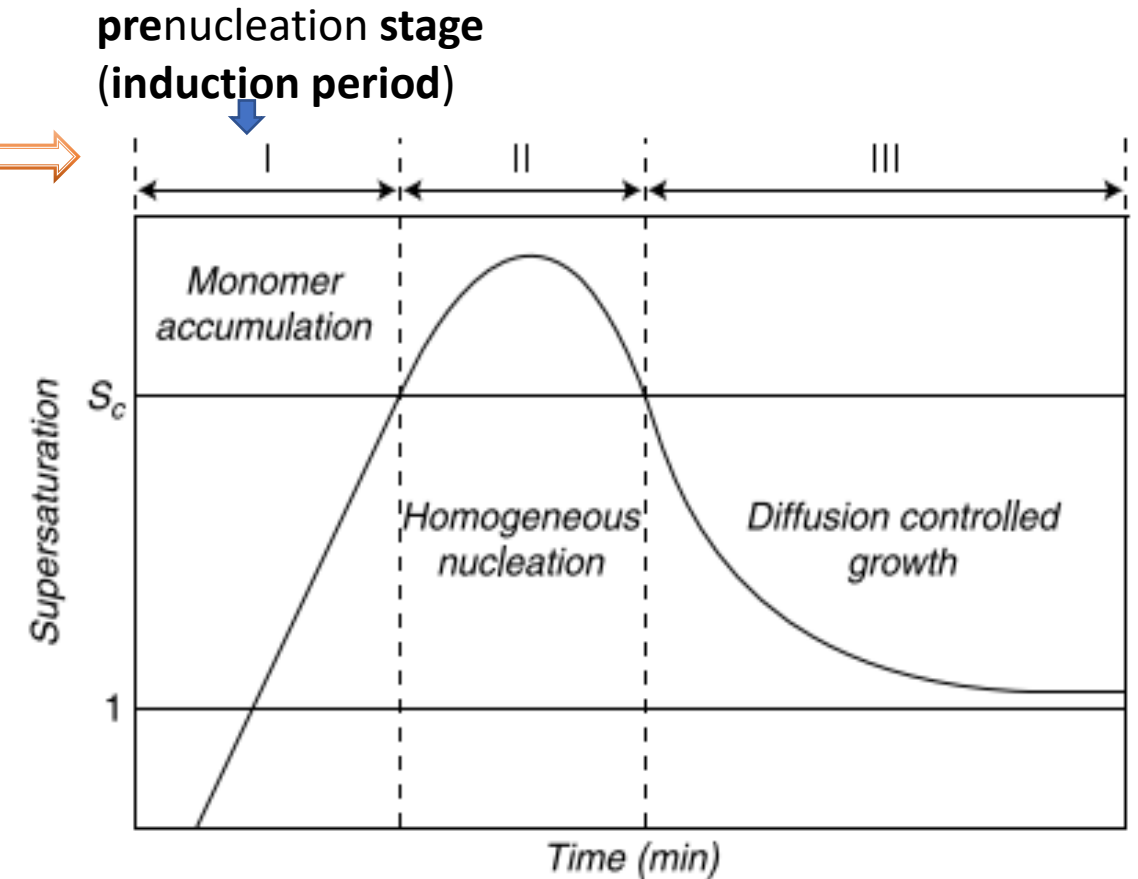
The classical LaMer model for the formation of uniform colloidal particles can help us in **understanding of the formation of narrow size distribution** colloidal particles in chemical synthesis in solution.

- The whole particle formation process is divided into three stages:



Producing gold nanoparticles from Au<sup>3+</sup> precursors

- Producing NPs of controlled sizes and shapes require precise **control of the nucleation and growth steps**.



**Figure 6.16. The LaMer diagram.**  $S_c$  is the critical supersaturation, the minimum supersaturation level for the homogeneous nucleation. 1 indicates saturation level.

- **In stage I (prenucleation stage),** the **concentration of atoms/molecules steadily increases with time to supersaturation levels.** The **state of supersaturation is essential for the nucleation.** Depending on the solute concentration levels, **three major zones are proposed (along y-axis or concentration axis).** The zone below the saturation level (i.e., the solubility curve) is called **stable (unsaturated) zone, where nucleation is impossible.** Ostwald introduced the terms “metastable” and “labile” supersaturation to specify *two stages of supersaturated solution.* The metastable (supersaturated) zone lies between the saturation level and the minimum critical supersaturation level (supersolubility curve) above which uncontrolled spontaneous nucleation commences. **In this metastable zone, spontaneous nucleation is improbable. However, seed-mediated growth would be possible in the metastable concentration zone.** The **labile or unstable (supersaturated) zone lies above the metastable zone, where spontaneous nucleation is probable.** The location of the minimum critical supersaturation level (supersolubility curve) is not as specific as the saturation level (solubility curve). **Many factors** affect the value of the metastable zone width, such as temperature, agitation, presence of impurities or additives, rate at which the supersaturation is generated, and so on. Therefore, the **induction period** is related to the metastable zone width and the nucleation rate.
- **In stage II,** atom concentration reaches a critical limit of supersaturation, and **rapid nucleation** occurs forming critical nuclei by **the aggregation of monomers.** With every nucleus formed, a certain number of monomers are withdrawn from the pool of monomers. Furthermore, **the nuclei start growing by consuming more monomers.** This eventually leads to a decrease of free monomers in the solution. Therefore, once the concentration of monomers has dropped below the critical supersaturation, the nucleation stops.
- In the **stage III,** the **growth** stage, the concentration of monomers constantly drops and thus the number of monomers **incorporated into the crystals increases.** As we will see later, at the beginning, this means that all nanocrystals grow homogeneously. At later stages, individual crystals dismantle to maintain a certain concentration of free monomers. Finally, only a few—macroscopic—crystals precipitate from the solution. If one wants to obtain a monodisperse sample of nanocrystals, the synthesis needs to be stopped well before that event.

- ***These three stages coincide with the accumulation of the monomers in the first period, the burst nucleation in the second period, and the size focusing in the third period, respectively.***
- *The relative durations of the three stages, especially of the nucleation and the growth stage, sensitively influence on the outcome of the synthesis.*
- ❖ The actual synthesis is initiated by the addition and activation of the atomic constituents of the crystal to a solvent. The atomic constituents can be presented, e.g., in the form of molecular precursors that are dismantled due to thermal activation or in the form of a salt the reduction of which is triggered by the addition of a reducing agent. Once these so-called monomers are present in the solution, they can spontaneously nucleate or be incorporated into the existing particles.

***Suggest ways to prepare monomers in the following cases to form:***

- (1) **Au nanoparticles from  $\text{HAuCl}_4$ .**
- (2)  $\text{Fe}_3\text{O}_4$  nanoparticles from Ferrous/Ferric Salts.
- (3) CdSe nanoparticles.

# BASIC CONCEPTS OF SIZE DISTRIBUTION CONTROL

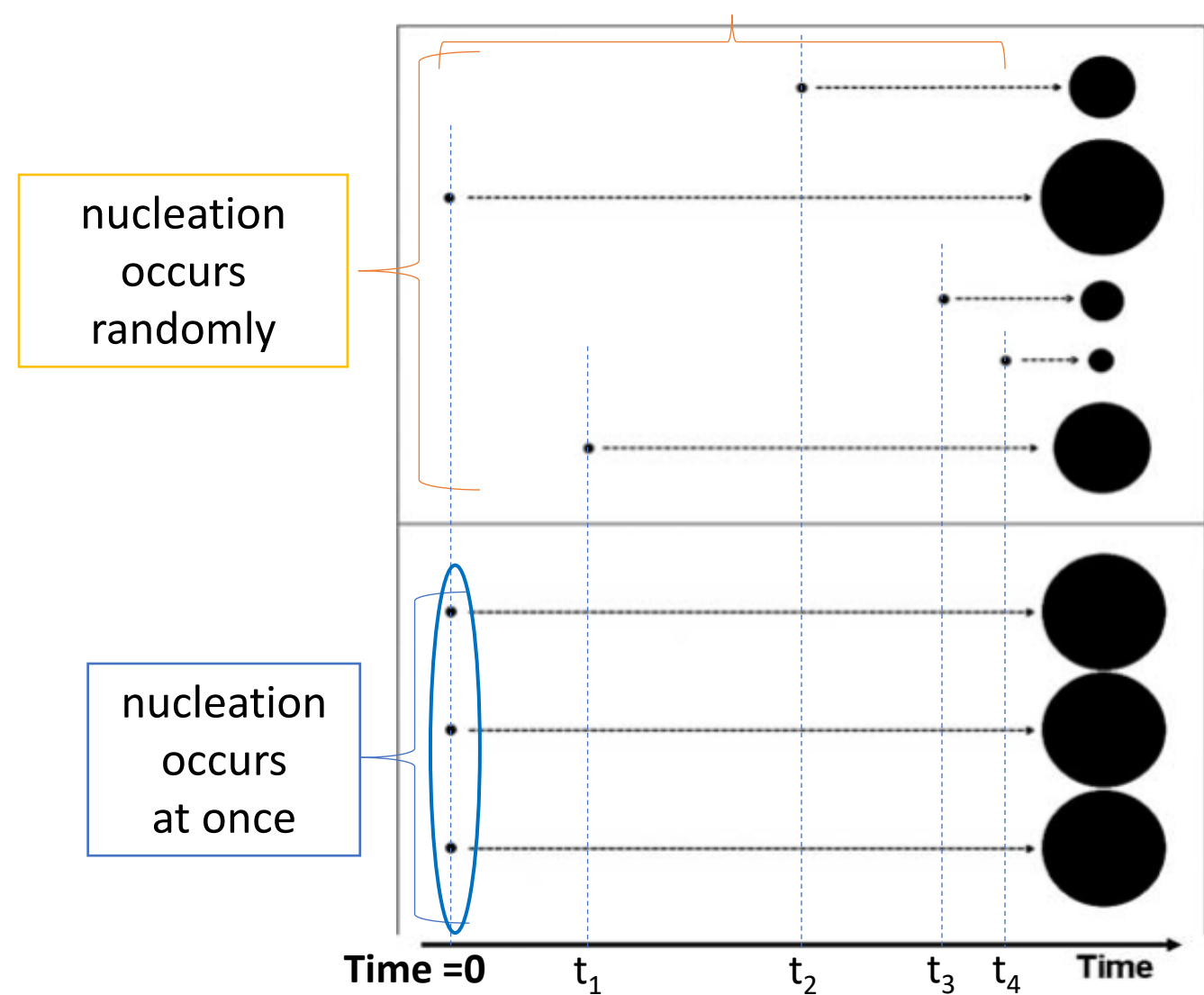
- ❖ The bottom-up solution-phase approach in essence consists of a “nucleation” step followed by the “growth” stage(s).
- Therefore, the chemical methods of producing NPs of controlled sizes and shapes require precise **control of the nucleation and growth steps**.
- *The **size distribution control** can be achieved in **two ways**:  
**(i) nucleation control and (ii) size focusing**.*



# Need for Nucleation Control...???

How the nucleation process influences the size distribution of the crystal particles?

- ❑ Upper part of the figure: the *nucleation occurs randomly* all the time during the particle formation process and all the *particles have different growth histories*.
- results in a *broad size distribution*.
- ❑ Lower part of the figure: an ideal case in which *all of the particles nucleate at once and grow under the same conditions*.
- size distribution would be *monodispersed*.



**Figure 6.2** Crystallization reaction systems in which homogeneous nucleation occurs randomly (upper) and at once (lower).

The **dots (•) to the left of the arrows indicate the formation of nuclei**. Each arrow and black circle show the growth of the corresponding particle and its size. Vertical dotted lines show time point of nuclei formation.

➤ *all the particles nucleate at once ...???*

❑ *Here are the substitutes for ideal single nucleation events....*

A) *Seed-Mediated (Growth) Synthesis*, &

B) *Burst Nucleation*

❖ *Seed-Mediated (Growth) Synthesis*

- ✓ Seed Mediated (Growth) Synthesis is a situation very similar to this idea.
- ✓ *Seed mediated growth method utilizes preformed uniform seed particles as nuclei.*
- ✓ *Heterogeneous nucleation* using these seed particles imitates the single nucleation event.
- ✓ However, *if the seeds themselves are not monodisperse, then seed-mediated growth does not guarantee monodispersity.*

## ❖ **Burst Nucleation**

- ✓ The short duration of the homogeneous nucleation process, or **“burst nucleation,”** is near to the ideal single nucleation event.
- ✓ The **homogeneous nucleation reaction has a very high energy barrier** compared to that of heterogeneous nucleation, and an extremely high supersaturation level is necessary to commence the **homogeneous nucleation process** in the solution.
- In fact, **violent “burst” nucleation is critical to obtain nanocrystals rather than microparticles.**

Let's consider the synthesis of monodisperse spherical iron particles from a solution containing  $1.0 \times 10^{-3}$  mol of iron precursor whose molar volume is  $\sim 7.0 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ .

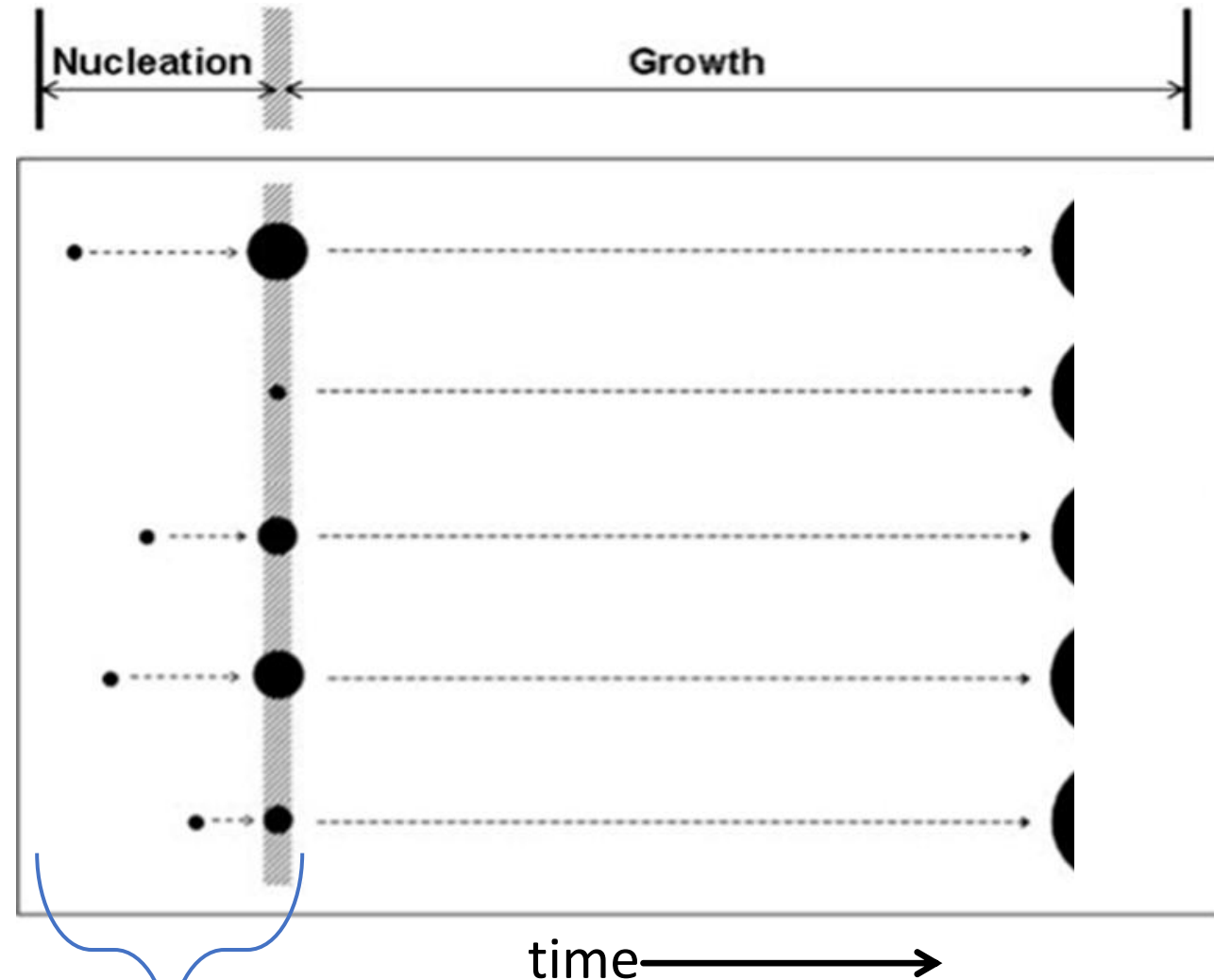
- ✓ When the number of particles in the solution is  $10^2$ ,  $10^6$ ,  $10^{12}$ ,  $10^{16}$ , and  $10^{18}$ , the particle diameter would be 510  $\mu\text{m}$ , 23  $\mu\text{m}$ , 240 nm, 11 nm, and 2.4 nm, respectively.
- Consequently, **it is very obvious that rapid and violent nucleation leading to the formation of large numbers of nuclei is critical for the synthesis of nanocrystals.**

**Figure 6.3 (upper part).** Schematic illustration of the size distribution generated during ***burst nucleation*** process.

The vertical thick line (shaded) indicates the point in time at which *the nucleation process is terminated*, dividing the nucleation and growth periods.

The ***dots (•) to the left of the arrows indicate the formation of nuclei.***

Each arrow and black circle show the growth of the corresponding particle and its size.



If  $\Delta t$  is very small,  
then it is *burst nucleation*.



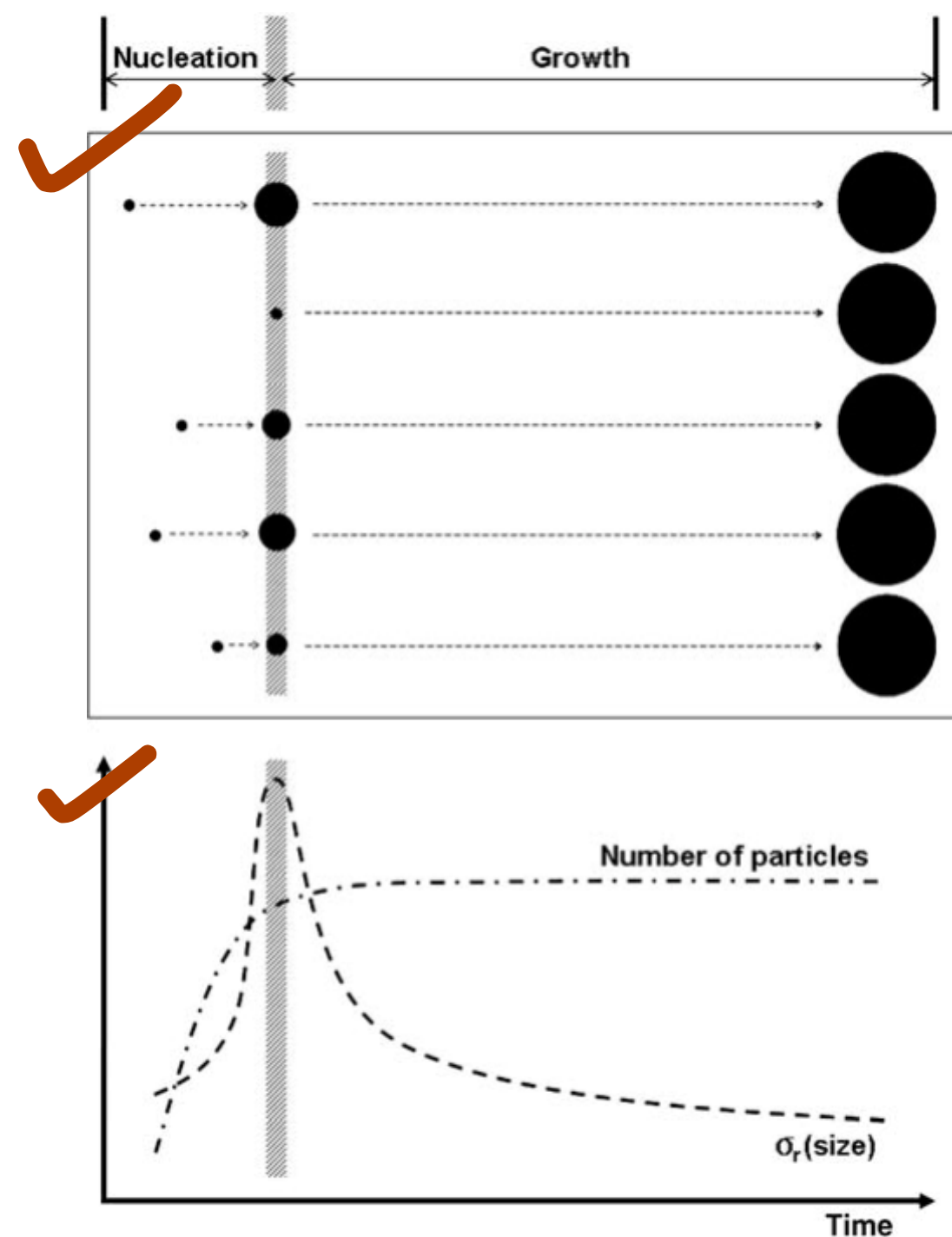
- Comparing the schematic of *burst nucleation* (Fig. 6.3) with that of the *single nucleation event* (Fig. 6.2, the lower part), it can be seen that *burst nucleation itself does not guarantee monodispersity*.
- In fact, ***however short the duration is, a broad size distribution at the end of the nucleation period is inevitable.***
- ✓ The explanation for this is as follows: The high supersaturation level promotes not only homogeneous nucleation but also crystal growth.
- ✓ Consequently, *in the course of the nucleation process, the nuclei formerly formed grow very fast, while those just formed retain their initial size.*
- ✓ As ***in the case of random nucleation, the size distribution broadens when the nucleation and growth reaction proceed simultaneously*** (note that not only nucleation but also the growth reaction occurs in the “nucleation” period in Fig. 6.3).

- **Given that burst nucleation does not guarantee the formation of monodisperse particles, why is it so important?** The answer has already been given above.
- **Burst nucleation satisfies the necessary condition for the size distribution control.**
- *If the duration of the nucleation process is much shorter than that of the growth process, the crystal particles share almost the same growth history throughout their crystallization.*
- The characteristics of burst nucleation are depicted in the lower part of Figure 6.3. In the nucleation period, the number of particles in the solution rapidly increases. *This increase is accompanied by the broadening of the size distribution, and the plot of  $\sigma_r(\text{size})$  reaches its maximum at the end of the nucleation period.*
- Then, the process goes into the growth period in which the number of particles remains stable, and the size distribution is narrowed. These changes indicate that the size distribution control mechanism works in the growth process, which is discussed in the next section.

# Burst Nucleation & Growth

- If one looks carefully at the schematic in the upper part of Figure, one can see that some *strange things happen during the growth period: **the small particles grow faster, whereas the large particles grow slower,** reaching the same size in the end.*

**Figure 6.3.** Schematic illustration of the size distribution control process. The vertical thick line (shaded) indicates the point in time at which the nucleation process is terminated, dividing the nucleation and growth periods. The arrows and the black circles share the same symbolism in Figure 6.2. In the lower part of the figure, the time evolution of the number of particles and the relative standard deviation of the size distribution,  $\sigma_r(\text{size})$ , are shown.



## Growth Control: Size Focusing

- The **curve for the** (diffusion-controlled) **growth rate vs. size ( $r$ ) resembles a hyperbola**, with **a negative slope: the larger particle grows slower** → **difference in the particle radii is reduced as the particles grow.**

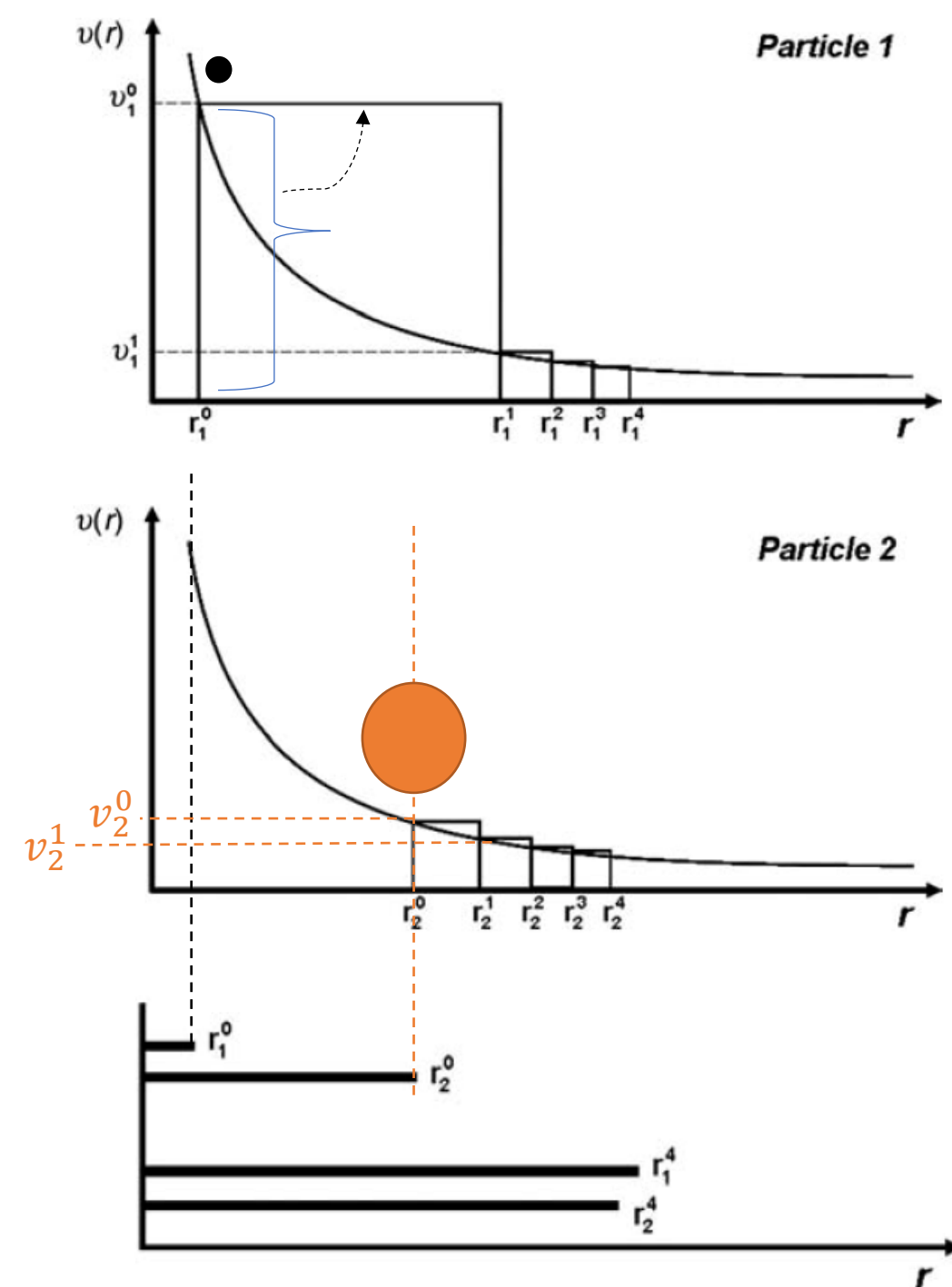
**Figure 6.4.** Plots for the growth rate,  $v(r)$ , vs. particle radius,  $r$  (upper and middle).

The graphs for  $v(r)$  in **both plots are identical.**

$r_1^n$  and  $r_2^n$  are the radii of particle 1 and particle 2 at  $n$ -th growth step.

In unit time, a particle of radius  $r$  grows by  $v(r^n)$  unit.

For the comparison, radii of particle 1 and particle 2 at the initial ( $n = 0$ ) and final ( $n = 4$ ) steps are shown together as a bar chart (lower).





Let's look at how a size-dependent growth process can achieve the desired monodispersity. Theoretical studies showed that, under certain conditions, the *curve for the growth rate vs. size resembles a hyperbola*, as shown in Figure 6.4. In this figure, the growth rate is defined as the increment of the radius per unit time. The *graph for the growth rate as a function of the radius has a negative slope*. That is, *the larger particle grows slower*, as they do in Figure 6.3. Using the plots in Figure 6.4, we can see how particles of different sizes, namely, particles 1 and 2, grow under this condition. The initial diameter of particle 1 is  $r_0^1$  and its growth rate is  $v_0^1$ . Then, during the first unit time step, particle 1 grows from  $r_0^1$  to  $r_0^1 + v_0^1$ , which is designated as  $r_1^1$ . Because  $v_0^1$  is the edge length of the first square on the left in the figure, the right bottom corner of this square locates at  $r_1^1$ . Similarly,  $r_1^1 + v_1^1$  is equal to  $r_2^1$  and its position can be found by drawing the second square on the right side of the first square. Consequently, the radii of particles 1 and 2 after four units of time are obtained by the graphical method, namely, drawing squares.

*The result is very interesting. In the lower part of Figure 6.4, it is clearly seen that the difference in the particle radii is remarkably reduced as the particles grow*. Moreover, following the same argument in this example, it can be easily shown that any negative-slope graph other than a hyperbola also yields a similar result. Generally, *the growth rate function of the negative slope induces the narrowing of the size distribution*, which is referred to as *size focusing*.

- In the following discussion, we explain why the growth rate has such a negative size dependency. Let's consider *a highly supersaturated solution, which guarantees the so-called diffusion-controlled growth process.*
- In this growth mode, the rate of increase of the particle volume is equal to the rate of solute diffusion from the solution onto the particle surface. The diffusion rate is written as  $dm/dt$  where  $m$  is the amount of solute. From *the principle of diffusion mass transport*, we know that  $dm/dt \propto r$  where  $r$  is the particle radius. On the other hand, *the amount of solute  $m$  required to increase the radius from  $r$  to  $r + dr$  is proportional to the particle surface area, so  $m \propto r^2$ .* In this condition, *the growth rate,  $dr/dt$ , of the larger particle is slower than that of the smaller one, because of the shortage of solute supply.*
- Here is an example. Let's consider two particles with radii of  $r$  and  $5r$ . To grow those particles to  $r + dr$  and  $5r + dr$ , it requires  $m$  and  $25m$  moles of solute, respectively. However, *the mass transport process dictates that, while the smaller particle takes  $m$  mol of solute from the solution, the larger particle gets only  $5m$  mol. As a result, the growth of the larger particle is retarded by the rate of solute diffusion, from which the name diffusion-controlled growth is derived.*

- According to theoretical investigations, *size focusing takes effect only when the crystal growth occurs in diffusion-controlled mode*. However, this mode is an extreme case of the crystal growth mechanism. *Normally, crystallization is a competition between two opposite reactions, precipitation, which is phase transfer from solute to solid, and dissolution, which is phase transfer from solid to solute.*
- On the other hand, in this growth mode, dissolution occurs to a negligible extent and all of the solutes that diffuse onto the crystal surface immediately precipitate. Therefore, *to sustain the diffusion-controlled growth mode, a very strong driving force for precipitation is needed. However, as the growth of the crystal particles proceeds, the driving force is exhausted, and the growth mode is no longer in the diffusion-controlled regime.*
- **Actually, in many synthetic reactions, size focusing continues for no longer than a few minutes.** *When the crystallization driving force is lowered, some of the crystal particles dissolve, while others keep growing, which leads to the broadening of the size distribution. This process is called (Ostwald) ripening.* Ripening is a slow process compared to size focusing. Therefore, the size distribution remains narrowed for a while even after size focusing ends. Usually, the synthetic procedure of nanocrystals is terminated at this point of time.

*Q. What are the two most important requirements (or conditions) for the formation of monodisperse nanocrystals?*

*Ans. (1) Burst nucleation: inhibition of additional nucleation during growth; complete separation of nucleation and growth.*

*(2) Diffusion-controlled growth (growth curve with negative slope): size focusing works.*

➤ *It should be noted that size focusing requires the absence of additional nucleation as the prerequisite condition.*

➤ *Continuous generation of new nuclei disturbs the focusing effect.*

➤ *This means that the sooner the nucleation period ends, the more beneficial it is for size focusing.*

➤ *This is often referred to as separation of nucleation and growth.*

## Homogeneous Nucleation and Growth:

**Finding** (A) **Nucleation Rate** and (B) **Growth Rate**

*(A) Nucleation and Nucleation Rate:*

There is an energetic barrier for the nucleation. We will now derive a simple mathematical expression for the nucleation barrier ( $\Delta G^*$ ). The derivation of is based on thermodynamic considerations.

In this section, we introduce a new terminology, the **monomer ( $M$ )**, which is the minimum building unit of a particle and can both be solvated in solution and precipitate to form particle. This monomer concept is more convenient and simpler than the conventional term, solute for the theoretical treatment of the nucleation process, because often the solute in solution and the constituent of crystal are not identical. In the following, the monomer is referred to as  $M$  in the equations.

➤ When **monomers bond with each other, a volume of matter is created, and energy is released (cohesive energy)** that **drives clustering** (inception of particle formation).

There is a difference in the chemical potential between the unbound and the bound state (i.e., monomers incorporated in the crystal) of the monomers, which is the driving force in the reaction. Obviously, the reaction takes place **only if the chemical potential of the unbound monomers is higher than that of the bound monomers.**

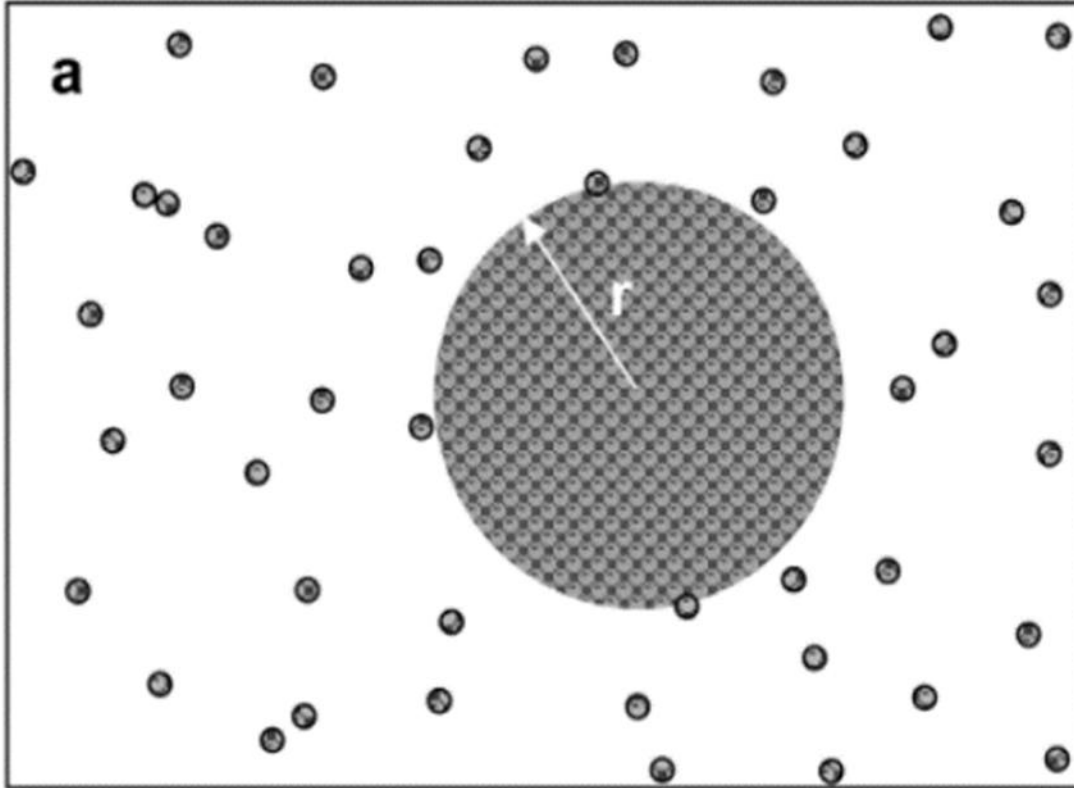


- On the other hand, *an interphase boundary area between the developing particle and the parent phase is created which requires energy (surface energy) and resists the particle formation*. When condensed phases form as a result of near-neighbor interactions, the surfaces of the condensed phases possess less numbers of neighbors and therefore a greater number of unsatisfied (dangling) bonds than their interior ones (at the initial stages, almost all particles are at the surface!). This raises the overall free energy of the system.
- Therefore, there is a competition between the surface energy and the volume free energy depending on the surface area to volume ratio of the developing particle.
- The other energy term that needs to be taken into account is the surface energy of the growing nanocrystal.
- As we will see in the following, especially at small sizes this surface energy is the predominant term. In other words, *the energy cost is more than the energy gain for particles of very small sizes*.

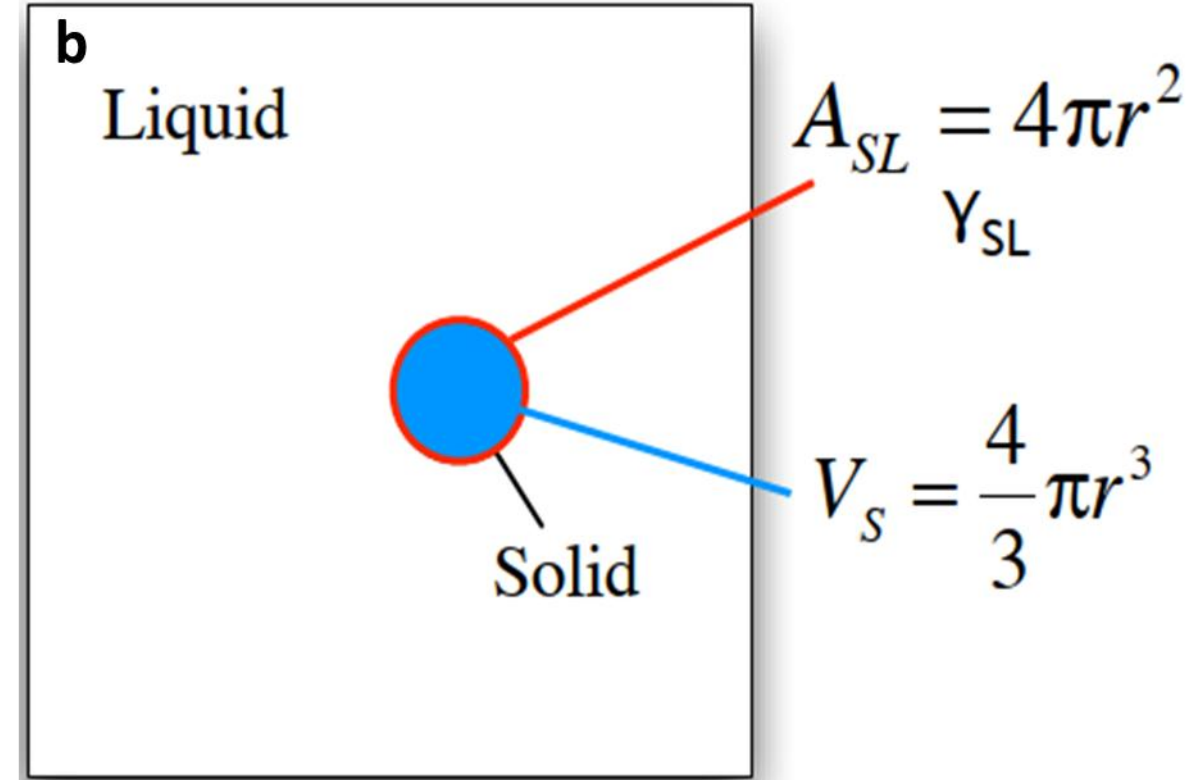
In this treatment, we will restrain ourselves to the very simple case of a spherical particles.

# Thermodynamics of Nucleation: Nucleation has an energy barrier. ....WHY?

Monomer-Monomer bond formation  
releases energy (**cohesive energy**)  
....*favors formation*



Surface formation increases  
surface energy  
....*not favors formation*



**Figure 6.** (a) Formation of a spherical nucleus of radius  $r$  from a solution leads to the surface and volume creations (hence corresponding free energy changes) as shown in (b).

➤ When a nucleus of radius  $r$  forms from the **homogeneous solution**, the change in the free energy  $\Delta G$  is:

$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_V \quad (\text{Eq. 6.1})$$

where  $\gamma$  is the surface free energy per unit area and  $\Delta G_V$  is the free energy per unit volume of crystal.

- ✓ In the simplified model that we have drawn here, we have in mind particles that are isolated from the surrounding. In particular, this means that there is no place to store/disperse the energy freed in the event of the nucleation.
- ✓ If two monomers form a dimer, they lower their energy, but this energy can only be transferred into an oscillatory energy of the dimer and as such it will lead to the instantaneous dissociation of the dimer.
- ✓ Therefore, this formation of dimers, and, similarly, the addition of monomers onto the particles, requires a third body to which the excessive energy can be transferred. This is actually another *role played by the solvent*.

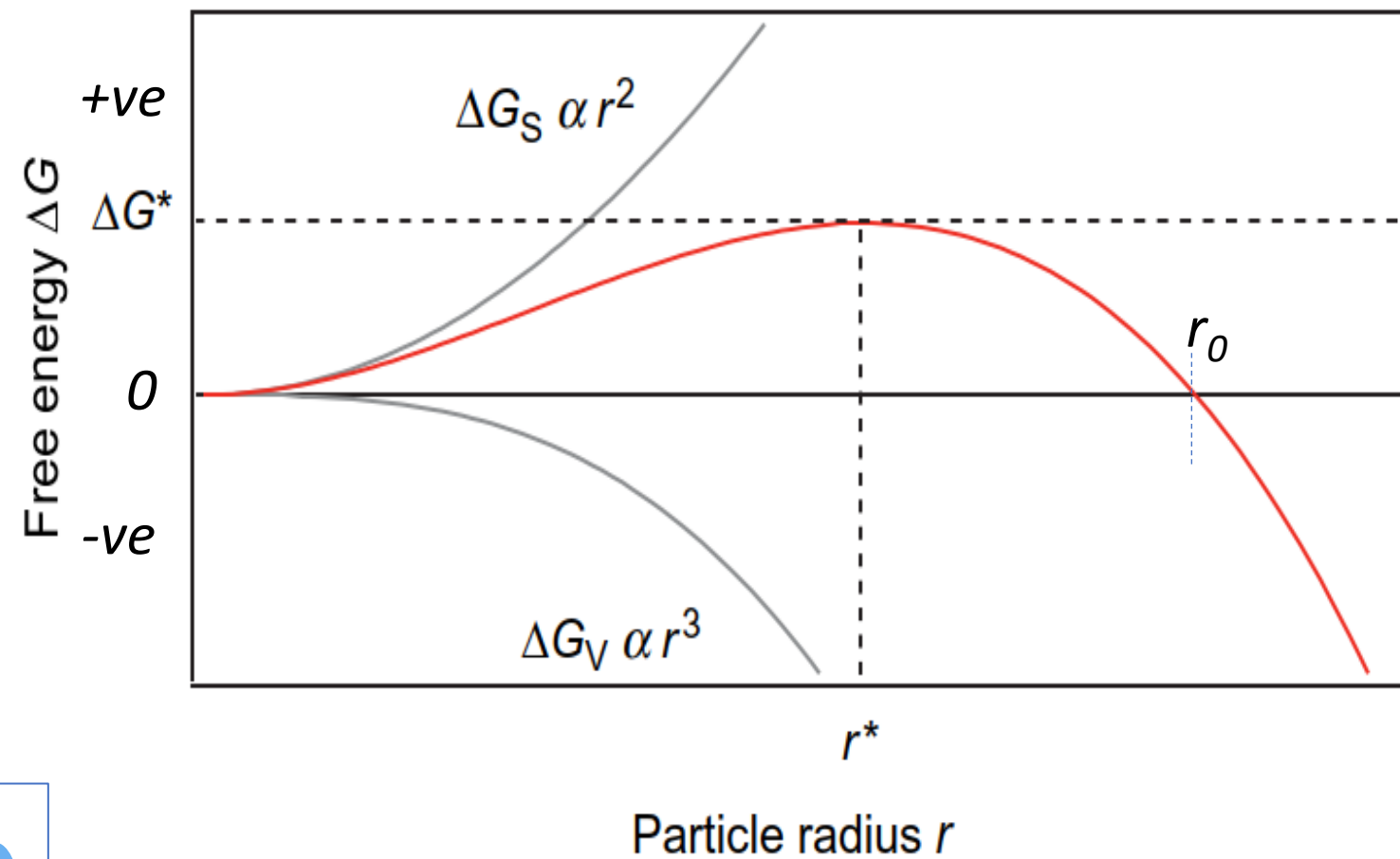
➤  $\Delta G_V$  is expressed as the difference between the free energy of the monomer in crystal and solution:

$$\Delta G_V = -\frac{RT}{V_m} \ln \frac{C}{C_0} = -\frac{RT}{V_m} \ln S \quad (\text{Eq. 6.2})$$

where  $V_m$  is the molar volume of the monomer in crystal.  $C$  is the monomer concentration in the solution, and  $C_0$  is the equilibrium monomer concentration in bulk crystal.  **$S$  is supersaturation ratio, which is defined as the ratio  $C/C_0$ .**

- ✓  **$S$  represents the *driving force* for both the nucleation and growth reactions.**
- ✓ As stated above, in the homogeneous solution, nucleation is accompanied by the ***formation of an interface*** between solution and particle at the cost of an increase in the free energy.
- ✓ On the other hand, the monomer in the particle has a smaller free energy than that in solution if the solution is supersaturated ( $S > 1$ ).
- ✓ Therefore, ***there are two opposite tendencies in the nucleation reaction*** (Figure 6.5). The **first** is the increase in the free energy caused by the formation of the interface, which is reflected in the first term on the right-hand side of Equation (6.1). **This term is always positive.**
- ✓ The other tendency is the decrease in the free energy caused by the formation of the crystal, which is shown in the second term, which is negative when  $S > 1$ .

**Figure 6.5.** The plot of the different contributions to the overall free energy of nucleation free energy (red solid line) as a function of the particle radius  $r$ . The contributions of the surface and the volume terms are marked in gray.  $r^*$  and  $\Delta G^*$  are the critical radius and the corresponding free energy, respectively.



$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta G_V$$

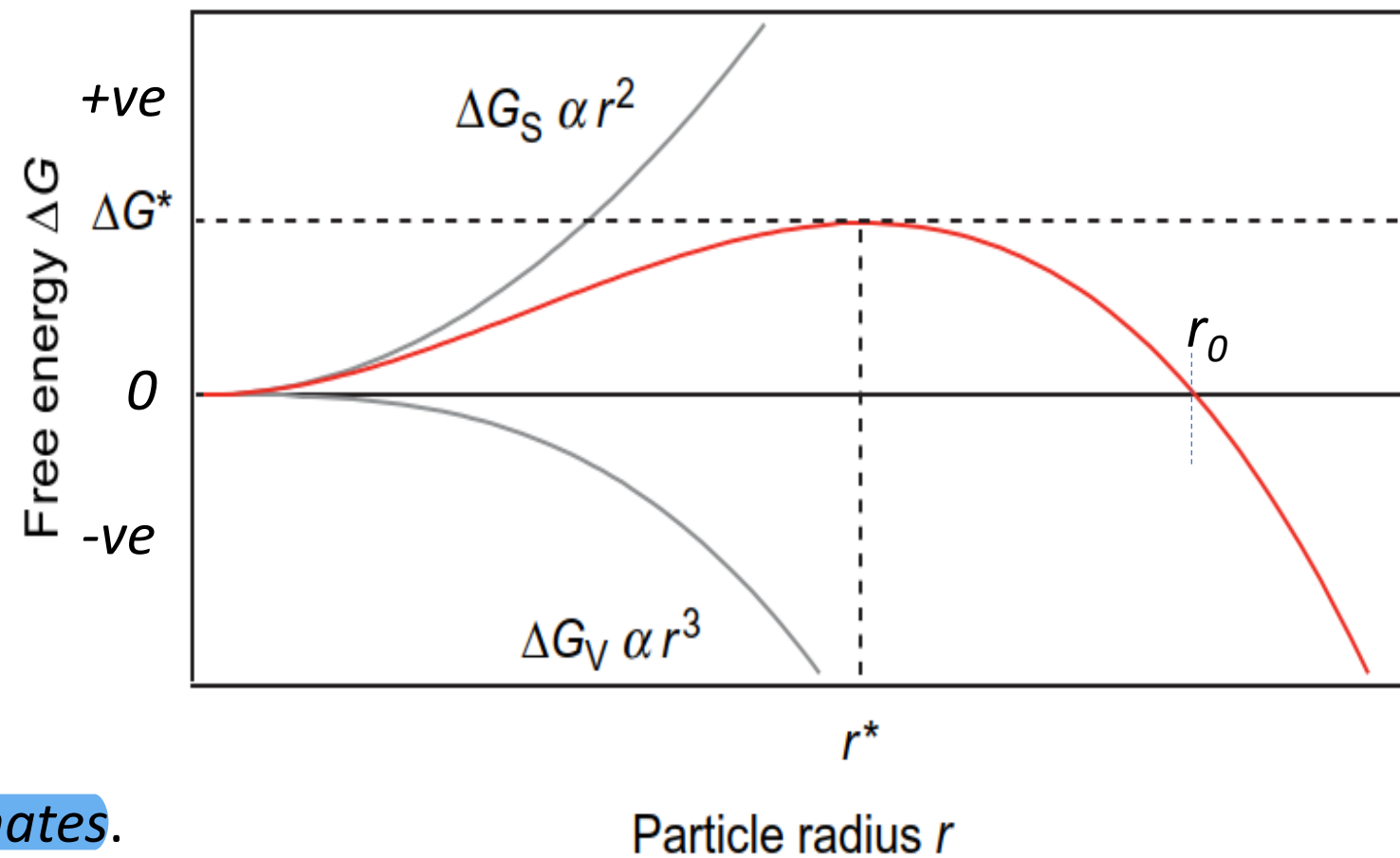
$$r^* = -\frac{2\gamma}{\Delta G_V} = \frac{2\gamma V_m}{RT \ln S}$$

$$\Delta G^* = \frac{4\pi\gamma(r^*)^2}{3} = \frac{16\pi\gamma^3}{3(\Delta G_V)^2} = \frac{16\pi\gamma^3 V_m^2}{3(RT \ln S)^2}$$

$$\Delta G_V = -\frac{RT}{V_m} \ln \frac{C}{C_0} = -\frac{RT}{V_m} \ln S$$



**Figure 6.5** The plot of the different contributions to the overall free energy of nucleation free energy (red solid line) as a function of the particle radius  $r$ . The contributions of the surface and the volume terms are marked in gray.  $r^*$  and  $\Delta G^*$  are the critical radius and the corresponding free energy, respectively.



- When  $r$  is small, *surface effect dominates*.
- When  $r$  is large, *volume effect dominates*.
- 1. When  $r$  is smaller than  $r^*$ , an increase in  $r$  leads to an increase of  $\Delta G \rightarrow$  *tendency to break away*.
- 2. When  $r$  is larger than  $r^*$ , an increase in  $r$  leads to a decrease of  $\Delta G \rightarrow$  *tendency to grow*.
- ❑ Unstable particles with  $r < r^*$  are known as **embryos** or **clusters**.
- ❑ Stable solid particles with  $r > r^*$  are referred to as **nuclei**.

In Figure 6.5, the graph for Equation (6.1) is shown. Because the contributions from the surface and the volume of the nucleus are second- and third-order curves, respectively, their summation has a maximum point at  $r = r^*$ .

The physical meaning of this graph is as follows:

- 1) In the region where  $r < r^*$ , the only direction in which the free energy is decreased is that corresponding to the reduction of  $r$ . Consequently, any nucleus smaller than  $r^*$  dissolves away spontaneously.
- 2) However, if a nucleus is larger than  $r^*$ , its growth may be favored.
- 3) As a result,  $r^*$  is the minimum radius of a nucleus that can exist in the solution.
- 4) The value of  $r^*$  can be found by using  $d\Delta G/dr = 0$  at  $r = r^*$ .

$$r^* = -\frac{2\gamma}{\Delta G_V} = \frac{2\gamma V_m}{RT \ln S} \quad (\text{Eq. 6.3})$$

- *It is to be noted that monomers as well as their clusters are not thermodynamically stable and thus transient in nature. Therefore, nucleation requires sufficiently large localized fluctuations so that the chemical driving force is large enough to offset the resisting force arising from the creation of interphase boundary area.*
- In fact, the size of these clusters fluctuates continuously due to incorporation of additional constituents to, and disappearance of constituents from, the clusters. During such size fluctuations, some of the clusters eventually reach or exceed a critical size at which point the energy barrier for structural fluctuations of these critical-sized clusters becomes sufficiently high and such clusters start growing spontaneously. *The critical-sized species has a well-defined structure and is called critical nucleus (or critical cluster or seed). Once the irreversible seed forms, it acts as a convergence point for the growth units and may grow in dimension.*
- *The shapes of the nuclei as well as their subsequent growth stages play important roles in controlling the nanoparticle shape/morphology, because nuclei are the starting point from which particle growth commences. We shall discuss this later.*

## The nucleation depicted in the diagram above can be understood in 3 thermodynamic regimes:

- 1) nucleation from the free molecules or atoms (monomers) to form small particles (nucleus). As the particles grow,  $\Delta G(r)$  increases (mainly dominated by the rapid increase in surface energy), implying that the particle growth or the continuous nucleation in this regime is not thermodynamically favorable, i.e., most of the clusters smaller than  $r^*$  dissolve back to liquid phase to decrease the free energy. This is typically the case of homogeneous nucleation.
- 2) once some of the particles reach the size of  $r^*$  and pass the barrier of  $\Delta G(r^*)$ , further growth of particles will lead to decrease in  $\Delta G(r)$ , a tendency favorable for the continuous particle formation, although  $\Delta G(r)$  in this regime before reaching the size of  $r_0$  is still  $> 0$  (not thermodynamically favorable). *How many particles in this regime can pass over the barrier  $\Delta G(r^*)$  concerns the kinetics of nucleation* and will be addressed below.
- 3) after passing  $r_0$ ,  $\Delta G(r)$  will become more negative, and the growth of particle will be highly favored and eventually lead to formation of particles.

$$r^* = -\frac{2\gamma}{\Delta G_V} = \frac{2\gamma V_m}{RT \ln S} \quad (\text{Eq. 6.3})$$

- Equation (6.3) shows that the **critical nucleus size depends on the surface free energy and the degree of supersaturation**: *smaller critical nuclei ( $r_c$ ) will form when the surface free energy is smaller, and the degree of supersaturation is higher.*
- In other words, *if the degree of supersaturation is low, the critical size ( $r_c$ ) is large. In such case, only larger clusters are stable and will continue to grow, whereas smaller clusters are unstable and will dissolve.*
- *When the degree of supersaturation is high, the critical size ( $r_c$ ) is small. Therefore, small clusters are stable and tend to grow under these conditions.*
- ❖ **If one would like to prepare smaller sized nanoparticles,** *which supersaturation condition – high or low – would one create in the reaction medium?*



➤ Beyond  $r^*$ ,  $\Delta G(r)$  decreases with increasing  $r$ , but at  $r_0$ ,  $\Delta G(r) = 0$ .

$$4\pi r_0^2 \gamma + \frac{4}{3} \pi r_0^3 \Delta G_V = 0$$

➤ Then we have,

$$r_0 = -\frac{3\gamma}{\Delta G_V} \quad (\text{Eq. 6.6})$$

- ✓ When a particle size grows to  $r_0$ , the **nucleation barrier decreases to zero**.
- ✓ However,  $\Delta G(r_0)$  is not a minimum, the nucleation is presumed to continue as the  $\Delta G(r)$  will become  $< 0$  (*thermodynamically favorable*) after passing  $r_0$ .

- The nucleation reaction can be regarded as the phase transition of the monomer from solution to nanocrystal. There is an energetic barrier for the nucleation. We will now set out to estimate **the nucleation rate, i.e., the rate at which particles overcome the potential barrier.**
- Then, if  $\Delta G^*$  is the free energy of nucleation, the reaction **rate of nucleation** can be written in the Arrhenius form:

$$\frac{dN}{dt} = A \exp \left[ -\frac{\Delta G^*}{RT} \right] \quad (\text{Eq. 6.4})$$

where  $N$ ,  $A$ ,  $R$ , and  $T$  are the number of nuclei, the pre-exponential factor, the gas constant, and temperature, respectively.

- Inserting the relation in Equation (6.3) into Equation (6.1), we obtain the expression for  $\Delta G^*$ .

$$\Delta G^* = \frac{4\pi\gamma(r^*)^2}{3} = \frac{16\pi\gamma^3}{3(\Delta G_V)^2} = \frac{16\pi\gamma^3 V_m^2}{3(RT \ln S)^2} \quad (\text{Eq. 6.5})$$

Finally, by inserting Equation (6.5) into Equation (6.4), the ***nucleation rate equation is obtained***.

$$\frac{dN}{dt} = A \exp \left[ -\frac{16\pi\gamma^3 V_m^2}{3 (RT)^3 (\ln S)^2} \right] \quad (\text{Eq. 6.6})$$

- Equations (6.4 & 6.6) show that ***the rate of nucleation can be controlled by varying the surface free energy  $\gamma$ , temperature  $T$  of the solution, and the supersaturation ratio  $S$ .***
- ❖ The smaller the  $r^*$  or  $\Delta G^*$ , the easier to form the nuclei. *How can one achieve this?*
- ❖ ***A large  $\gamma$  is not favorable*** for the nucleation, ***additives like surfactants present in the reaction system can reduce the surface energy.***
- ❖ On the other hand, ***higher  $T$  and  $S$  accelerate the nucleation rate.***
- The nucleation period should be shorter and separated from the growth step in order to prepare uniform NPs. This concept is known as the “**nucleation burst**” mechanism, where the nucleation occurs abruptly and *then the solute concentration drops below the critical nucleation concentration*. If nucleation continues to occur when some other nuclei have grown to a significant extent, obviously polydispersed NPs will form.

*Q. What are the roles of the **stabilizing agents** or **capping agents** in the colloid chemical synthesis of nanocrystals?*

- ✓ *Often, we use specific molecules that act as terminating and **stabilizing agents** or **capping agents** that allowed for a higher control over the nucleation and growth rates of the particles and therefore also made smaller size regimes, down to the nanometer scale. **These molecules ensure controllable, i.e., slow growth rates, prevent interparticle agglomeration, and confer stability and further processability to the resulting nanoparticles.** Often, such molecules are chosen from the large class of surfactants, polymers, and ligands.*
  - *They provide means for controlling the growth rate and (avoid) coalescence of the particles.*
  - ✓ *Finally, provide an efficient way for collecting or isolating the final product.*
- (1) **To control of the size and shape of the nanocrystals;**
  - (2) **to prevent the aggregation of the nanocrystals;**
  - (3) **to provide their solubility in a wide range of solvents;**
  - (4) to be exchanged with another coating of organic molecules having different functional groups or polarity.
  - (5) **Surfactants reduce the surface energy of the particles and substrates, if any.**

# Heterogeneous Nucleation and Growth

- ❖ In many cases (some argue all cases!), nucleation occurs on a surface, interface, impurity, or other heterogeneities in the system.
- In the case of **heterogeneous nucleation**, the nucleation takes place by the formation of a condensed phase **on top of a preexisting condensed phase**.
- Nucleation occurs preferentially at special sites (e.g., grain boundaries, edges, and corners) on preexisting foreign bodies or solid structures.
- The two condensed phases can be of the same chemical nature or can be different from each other.
- ✓ If **there is partial affinity between the particle-forming solid and the foreign solid surface**, nucleation on the surface releases energy by the partial elimination of these preexisting interfaces. *This energy gain diminishes the free energy barrier and facilitates nucleation.*
- ✓ Therefore, *heterogeneous nucleation would be an easier process to occur than homogeneous nucleation and the heterogeneous nucleation occurs at lower supersaturation level and much more often compared to the homogeneous nucleation.*



**FIGURE....** Heterogeneous nucleus on a flat substrate/seed. The equilibrium condition at the interface (circle) between the three media, i.e., the vanishing of any force parallel to the surface of the substrate, determines the wetting (contact) angle  $\theta$ .

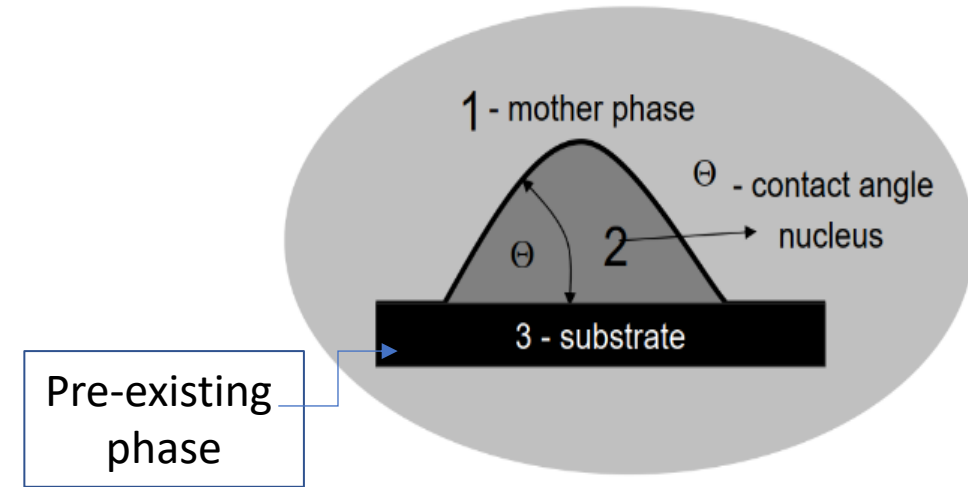
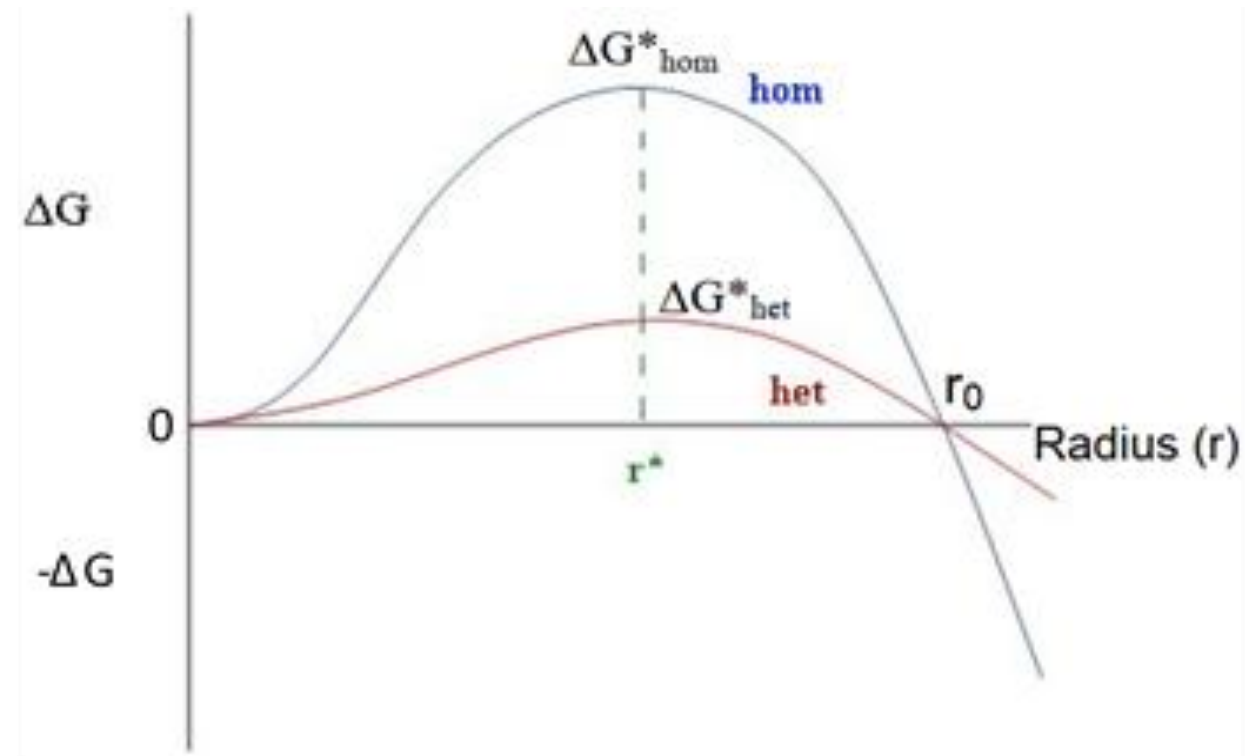


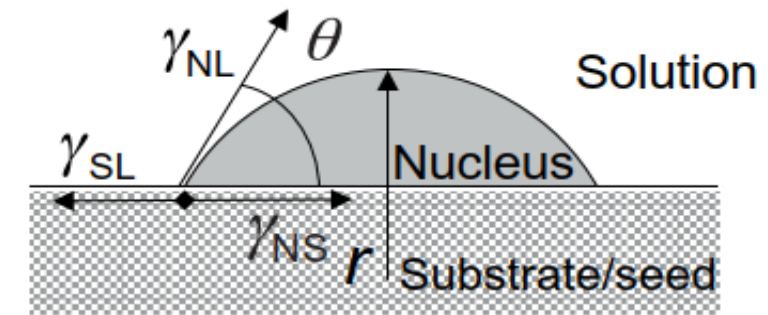
Fig. 5.6: **Comparison of free *energy barrier between homogeneous and heterogeneous nucleation highlighting*** that (i) the critical size is the same for the two processes and that (ii) the barrier for heterogeneous nucleation is smaller than that for homogeneous nucleation.

➤ *Note that the critical radius expression is the same only for the same material under the same supersaturation condition.*

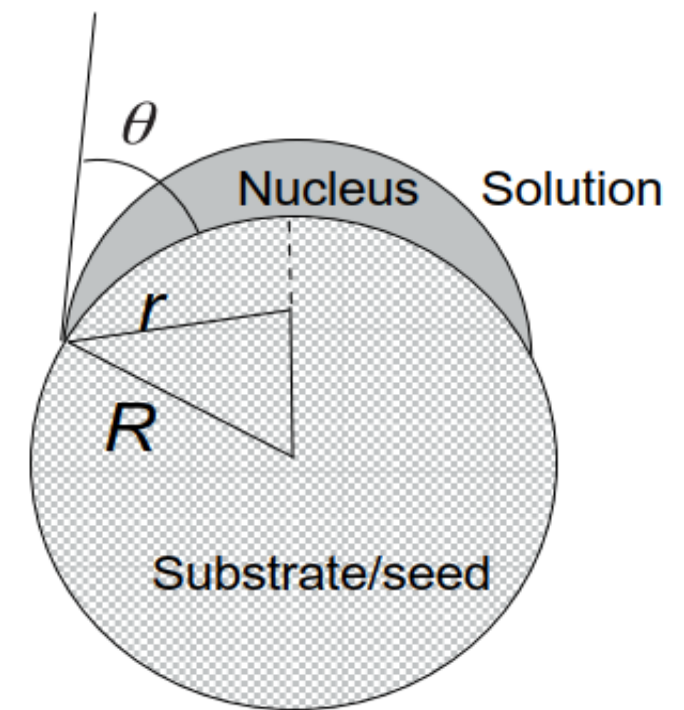


- The other extreme is the attempt of nucleating a material, which has **no affinity** to the preexisting phase.
- ✓ *In this case, the new material basically has to perform a homogeneous nucleation **as if** there was **no preexisting** phase.*
- ✓ However, in case of **complete nonaffinity** between the particle and the surface of the foreign body, the overall *free energy of heterogeneous nucleation is the same as that of the homogeneous nucleation.*
- On the other limit, in case of **complete affinity** (when nucleation occurs on a seed particle in a solution supersaturated with **the same solute**), the **free energy of nucleation is zero.**
- A real, i.e., a useful and successful, heterogeneous nucleation will be settled somewhere between these two extreme cases, and we can already guess that the nucleation barrier connected with the heterogeneous nucleation will be lower than in the case of homogeneous nucleation.
- In the following, we will show how to convert this guess into a more quantitative treatment of the problem.

- In the classical nucleation theory of heterogeneous nucleation, the two simple cases that are considered are those of a droplet (i.e., our “heterogeneous” nucleus) on a planar substrate and that of a droplet on a spherical substrate, as shown in Figure 3.5a and b.
- Here, we will discuss only the first case (flat substrate).
- An important parameter here is the contact angle  $\theta$  between the droplet (which forms a spherical section) and the substrate.



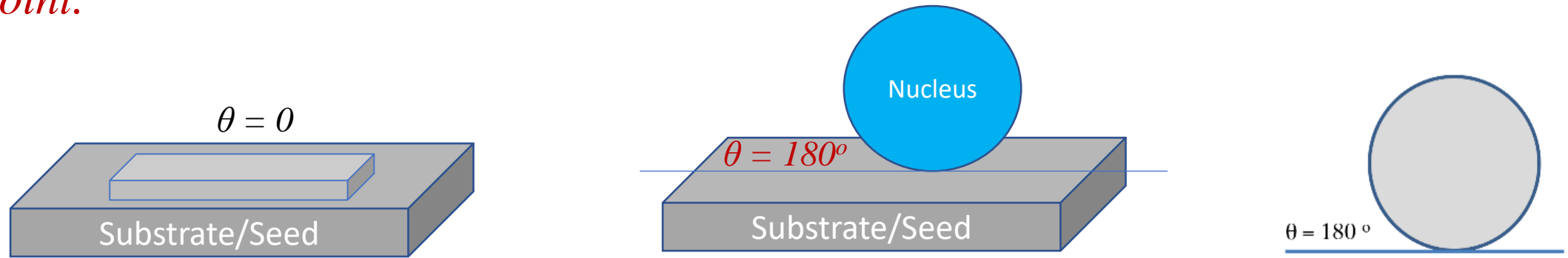
(a)



(b)

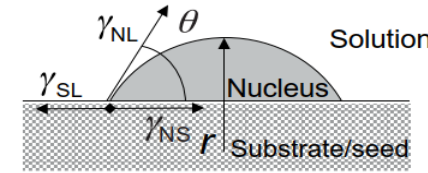
**FIGURE 3.5** Heterogeneous nucleus on a flat substrate/seed (a) and on a spherical substrate/seed (b) along with the relevant parameters as described by the classical theory on heterogeneous nucleation. Each of the three interfaces contributes with its own interfacial energy to the total free energy, as shown in (a). The equilibrium condition at the interface (circle) between the three media, i.e., the vanishing of any force parallel to the surface of the substrate, determines the wetting angle  $\theta$ .

- Depending on the wettability of the substrate with the “heterogeneous” nucleus, this **contact angle** ( $\theta$ ) can range from *zero, meaning complete wettability (complete affinity), i.e., the heterogeneous nucleus forms a continuous film on top of the substrate*, to  **$\pi$ , meaning complete non-wettability (non-affinity), i.e., the heterogeneous nucleus is now a perfect sphere (neglecting gravitational forces) that sits on top of the substrate and touches it only at one point**.



- Real situations clearly are found in between these two extremes.
- In any of the considered cases of heterogeneous nucleation (for instance, whether on a flat or on spherical substrate, see Figure 3.5a and b), we now have to consider three interfaces instead of a single one. Each of the interfaces contributes to the balance of free energy with its own interfacial energy.
- In the following, we briefly indicate a way to calculate the total free energy of the system.

- In the discussion on the homogeneous nucleation above, we only had to deal with one type of interfacial energy, the one between the nucleus and the solution,  $\gamma_{NL}$ .
- Here, *we have instead three types of interfaces, each with its associated interfacial energy: (i) nucleus-liquid solution ( $\gamma_{NL}$ ), (ii) nucleus-substrate ( $\gamma_{NS}$ ), and (iii) substrate-liquid solution ( $\gamma_{SL}$ ).*



- ✓ The interplay between the three interfacial energies determines the contact angle.
- ✓ If the droplet on the substrate is in equilibrium with its surrounding, its boundary will be free of any force. *The forces arise from the fact that the droplet will adopt a shape that minimizes the total interfacial energy.* They apply as sketched in Figure 3.5a.
- ✓ In the balance of forces, only those components that are parallel to the surface of the substrate need to be taken into consideration.
- ✓ If there would be a finite force parallel to that surface, it would result in a stretching or contraction of the droplet. The wetting angle is then determined by *Young's equation*:

$$\gamma_{NS} + \gamma_{NL}\cos\theta = \gamma_{SL}.$$

- Like in the case of the homogeneous nucleation, the interface between the nucleus and the solution will adopt a constant curvature, which is characterized by the radius  $r$ .

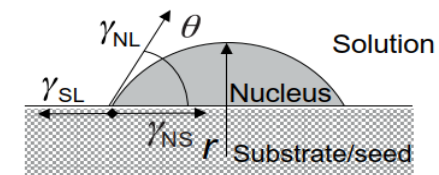


- The **energy required for nucleation is reduced by a factor related to the contact angle of the nucleus on the foreign surface**. One can demonstrate that the following relation holds between such barrier  $\Delta G_{het}$  and the barrier for homogeneous nucleation  $\Delta G_{hom}$

$$\Delta G_{het} = \Delta G_{hom} f(\theta) = \left\{ \frac{4}{3} \pi r^3 \Delta G_V + 4 \pi r^2 \gamma_{NL} \right\} f(\theta)$$

where  $f(\theta)$ , also known as the **contact parameter**, has the following dependence on  $\theta$ :

$$f(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} < 1$$



Critical  $r^*$  and  $\Delta G^*$ :  $r^* = -\frac{2\gamma_{NL}}{\Delta G_V}$ ; and  $\Delta G^* = \frac{16\pi\gamma_{NL}^3}{3\Delta G_V^2} f(\theta)$

- ✓ It is important to note that the critical radius  $r^*$  remains unchanged for heterogeneous nucleation and homogeneous nucleation.
- ✓ The **nucleation barrier can be significantly lower for heterogeneous nucleation due to wetting angle affecting the shape of the nucleus**.

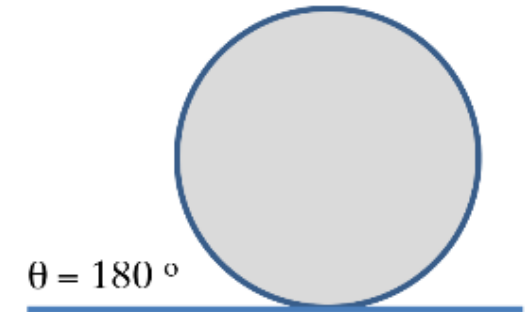
- As the **contact angle between two materials has usually a value in between 0 and  $\pi$** , the *contact parameter* will be **smaller than 1** and therefore the barrier for heterogeneous nucleation will be always lower than that of homogeneous nucleation.

$$0 \leq f(\theta) \leq 1.0$$

❖ *A smaller contact angle indicates a higher affinity of the heterogeneous nucleus for the substrate and a lower energetic barrier for heterogeneous nucleation.*

- A limiting case here would be represented by a ***complete affinity between the nucleus and the substrate (contact angle equal to zero)***. This can be clearly realized only if the substrate and the heterogeneous nucleus were made exactly of the same material. This is achieved, for example, by adding exogenous crystals in cryoscopy experiments to avoid supercooling or in crystallization to suppress supersaturation. Obviously, in this case, we would not be strictly speaking of heterogeneous nucleation, but simply of further growth of the initial substrate, and it is clear that *there should be no energetic barrier for such process to take place*.
- (i) For  $\theta = 0^\circ$ ,  $f(\theta) = 0 \rightarrow$  full wetting (complete affinity), ***fully catalyzed, no barrier for nucleation*** at surface.

- (ii) Another limiting case is the one in which the *contact angle between the heterogeneous nucleus and the substrate is  $\pi$* . In such case ( $\cos 180^\circ = -1$ ), *there is no wettability between them*, and indeed, one can consider this as the instance in which the *formation of the nucleus is not influenced* at all by the presence of the substrate. The contact parameter now is equal to 1, and indeed, the *barrier for heterogeneous nucleation is equal to that for homogeneous nucleation*. In practical cases, this would mean that heterogeneous nucleation does not take place at all, and separate nuclei are formed in solution, regardless of the presence of a substrate.
- For  $\theta = 180^\circ$ ,  $f(\theta) = 1 \rightarrow$  no wetting of the surface (*complete non-affinity*), and thus *no catalysis* by the surface  $\rightarrow$  falling into the case of *homogeneous nucleation*.



➤ For  $\theta = 90^\circ$  ...????

- A similar reasoning can be extended to the case of heterogeneous nucleation on the top of another type of substrate, i.e., a spherical seed (see Figure 3.5b). Now, the math gets a little bit more complicated, mainly in the definition of the contact parameter, which in this circumstance depends in a rather intricate way on the contact angle and additionally on the radius of the spherical seed, as indicated in Figure 3.5b. *Nevertheless, the final results are the same as before, that is, the critical radius remains the same, while the energetic barrier for nucleation is lowered with respect to the homogeneous case.*
- In the case of heterogeneous nucleation of a solid material on top of solid substrate, which often occurs in the synthesis of nanoparticles, a more elaborate *treatment of heterogeneous nucleation would need to take into account a misfit strain energy term.* This is required because the *substrate/seed and the heterogeneous nucleus have different lattice parameters and sometimes even different crystal structures.* Depending on all these factors, the second material *might be able to cover completely the first one and perhaps the interface between the two will be free of defects (the case of epitaxial growth).* *Alternatively, the second material might just grow in “patches,” or it might even nucleate selectively only on certain locations or facets of the starting seed.* This latter case is generally exploited for the fabrication of a wide variety of complex nanocrystal architectures. The discussion of these further issues is given later.

- ❑ In case of heterogeneous nucleation, the *particle growth occurs via epitaxial or nonepitaxial way*.
- *Epitaxy is the technique of growing a crystal (called deposit or overgrowth) layer by layer on another crystal (called substrate), as we have already discussed.*
- ✓ In the *epitaxial growth, the deposited metal takes on a lattice structure and orientation identical to those of the substrate.*
- ✓ Chemical compositions of the deposit and the substrate may be the same (when it is termed as *homoepitaxy*, for example, Au seed to Au nanorod growth) or different (in case of *heteroepitaxy* of the different metals).
- ✓ *The deposit and substrate may differ in the nature and strength of their chemical bonds as well as in their lattice structures.*
- ✓ *The **chemical bond** between the deposit and substrate **determines the degree of interaction** that can occur between the two, while *the lattice mismatch determines the spatial variation of the interaction.**
- ✓ *A **strong deposit–substrate interaction** and *a small lattice mismatch* aid the epitaxial growth.*



- According to the *Wulff–Kaischew theorem*, the *equilibrium shape* of a *supported* (macroscopic) crystal is *determined* not only *by the total surface energy* ( $\gamma$ ) of its facets but also *by its adhesion energy* ( $\hat{a}$ ) with the support.
- Depending on the magnitude of  $\gamma$  compared to  $\hat{a}$ , *various degrees of truncation* of epitaxially formed nuclei (compared to homogeneously formed nuclei) may result.
- The **presence of strain** at the interface due to a *mismatch (misfit)* between the lattice parameters of the support and the deposit crystal *may cause deviation from the equilibrium shape*.
- When *the crystal structures are the same*, the *mismatch between the two lattices is defined by*  $m = (a_d - a_s)/a_s$ , where  $a_d$  and  $a_s$  are the **lattice parameters** of the deposit and the substrate, respectively.
- ✓ For *zero mismatch* ( $m = 0$ ), *edges between the top facet parallel to the substrate*) and the lateral facets (*perpendicular to the substrate*) follow a straight line with crystal growth, meaning that the shape is self-similar (the Wulff–Kaischew case).

- ✓ However, *nonzero mismatch* ( $m \neq 0$ ) induces a *positive strain energy* ( $\gamma_{strain}$ ).
- ✓ The *larger the mismatch, the more positive the strain energy, and the strain energy increases rapidly with the increase in size of the nucleus.*
- ✓ Therefore, for *nonzero mismatch* ( $m \neq 0$ ), the *deposit crystal grows faster in height than in lateral direction* when the height-to-width aspect ratio is no longer constant and larger aspect ratios (i.e., *taller crystal*) are obtained with the larger mismatch.
- ✓ The *equilibrium shape then deviates from the Wulff–Kaischew case.*
- ✓ Qualitatively, as the depositing crystal layer is strained at the interface, it prefers to decrease the interface area and to grow at the top to relax more easily.
- ✓ However, the elastic energy increases with the size of the crystal and at a given size, the system will partially *relax the strain by the introduction of dislocation.*

□ In case of formation of an *epitaxial phase*, the mechanisms of nucleation and overgrowth have been observed to follow *three modes*, namely, the **Frank-van der Merwe (FM)**, **Stranski–Krastanov (SK)**, and **Volmer–Weber (VW)** modes (Figure 1.4).

- These modes have been deduced from the equilibrium considerations of *the energy balance between the surface energies and the interfacial energy for lattice-matched systems*.
- Briefly, the *overall excess free energy* is given according to Eq. (1.6):

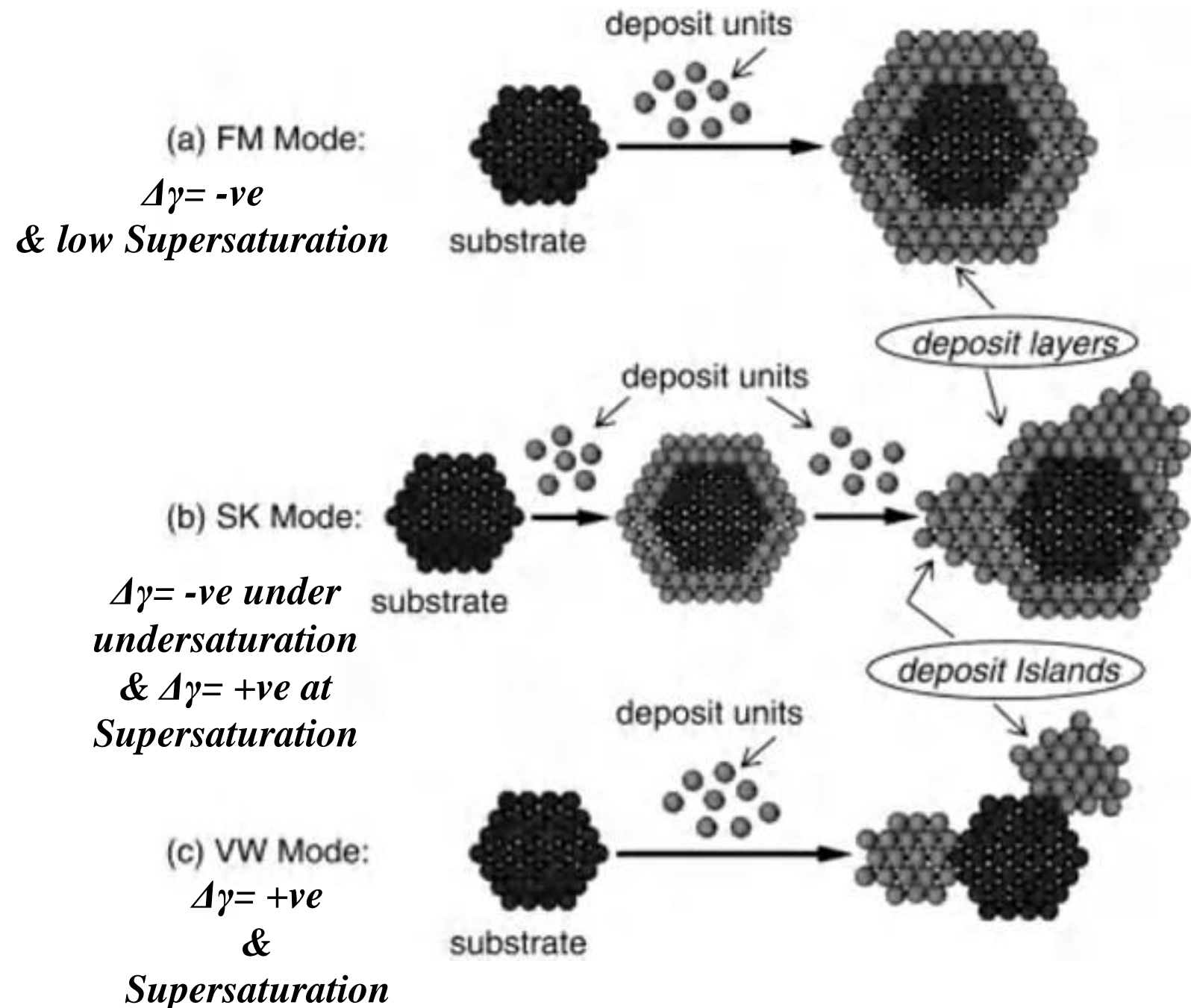
$$\Delta\gamma = \gamma_d + \gamma_{strain} + \gamma_i - \gamma_s \quad (\text{Eq. 1.6})$$

where  $\gamma_d$  and  $\gamma_s$  are *surface energies* of the *deposit* and the *substrate* materials, respectively,  $\gamma_{strain}$  is strain energy induced by lattice mismatch, and  $\gamma_i$  is the *interfacial energy* between the deposit and the substrate.

**Figure 1.4** Illustration of the formation of epitaxial phase. Three modes of nucleation and overgrowth observed are:

- (a) Frank-van der Merwe (FM)** mode or ***2D layer-by-layer*** growth of the deposit,
- (b) Stranski–Krastanov (SK)** mode or ***island on wetting layer growth mode***, and
- (c) Volmer–Weber (VW)** mode or ***island growth*** mode.

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- Under *lattice-matched (or slightly mismatched) conditions with high interfacial bond energies*,  $\Delta\gamma$  becomes *negative*. In such cases, *2D layer-by-layer growth of the deposit occurs under low supersaturation to suppress 3D nucleation*. This mode of growth is known as *Frank-van der Merwe mode*.
- If the *lattice mismatch is high and the surface energy term of the substrate cannot compensate for the sum of the surface energy of the deposit and the interfacial energy*,  $\Delta\gamma$  becomes *positive*. Under *these conditions, 3D nucleation occurs on high-energy sites of substrate under conditions of supersaturation*. The deposit forms 3D islands in order to minimize the strain energy, followed by the growth of 3D islands eventually leading to their coalescence. *The “island growth” mode is known as Volmer–Weber mode*.
- In the *intermediate regime*, when the lattice mismatch is not very large, one expects a *transition from a 2D layer growth to 3D layer growth*. If  $\Delta\gamma$  is negative at the initial growth stage, then the 2D layer-by-layer growth of the deposit occurs. However, *the strain energy increases with the number of layers of the deposit making  $\Delta\gamma$  positive after formation of a few layers of the deposit*. At this stage, the *growth changes from 2D layer growth to 3D island growth* on the wetting layers in order to release the strain energy. This kind of growth is known as *“island-on-wetting-layer growth” mode or Stranski–Krastanov mode*, where 2D layer of adsorbed atoms forms under conditions of undersaturation, which turns into 3D growth under conditions of supersaturation.

- The above three kinds of growth modes have been invoked to understand the mechanisms of solution-phase development of a range of complex particle morphologies such as core–shell, heterodimer, overgrowth, and so on.
- *Epitaxial/Core–Shell/Heterodimer/Overgrowth Particles*  
Complexity of nanomaterials can be further increased by the formation of multicomponent (e.g., core–shell and multi-segment) NPs. Development of these structures is motivated by the idea that the resulting particles will combine the properties of the various materials or give rise to novel collective properties. A variety of metallic multicomponent NPs have been reported (Figure 1.11).
- The **multicomponent NPs** take a variety of forms, such as core–shell, heterodimer, dumbbell, and so on. Such materials are mostly prepared via precipitation–deposition techniques. In this strategy, one of the components of the NP is first produced and then the reaction environment is changed so that a second component can grow on the first NP via heterogeneous nucleation. In the cases where heterogeneous nucleation is difficult, smaller particles have been first attached to the other component particle by using electrostatic or chemical interaction properties, followed by their growth.



**Figure 1.11** Examples of various kinds of multicomponent metallic NPs.

(a) Dielectric@metal core-shell.

(b) Metal@dielectric core-shell.

(c) Metal@metal core-shell.

(d) Metal@metal@metal core-shell.

(e) Metallic nanotriangle with overcoat of second metal.

(f) Heterodimer composed of dielectric and metal parts.

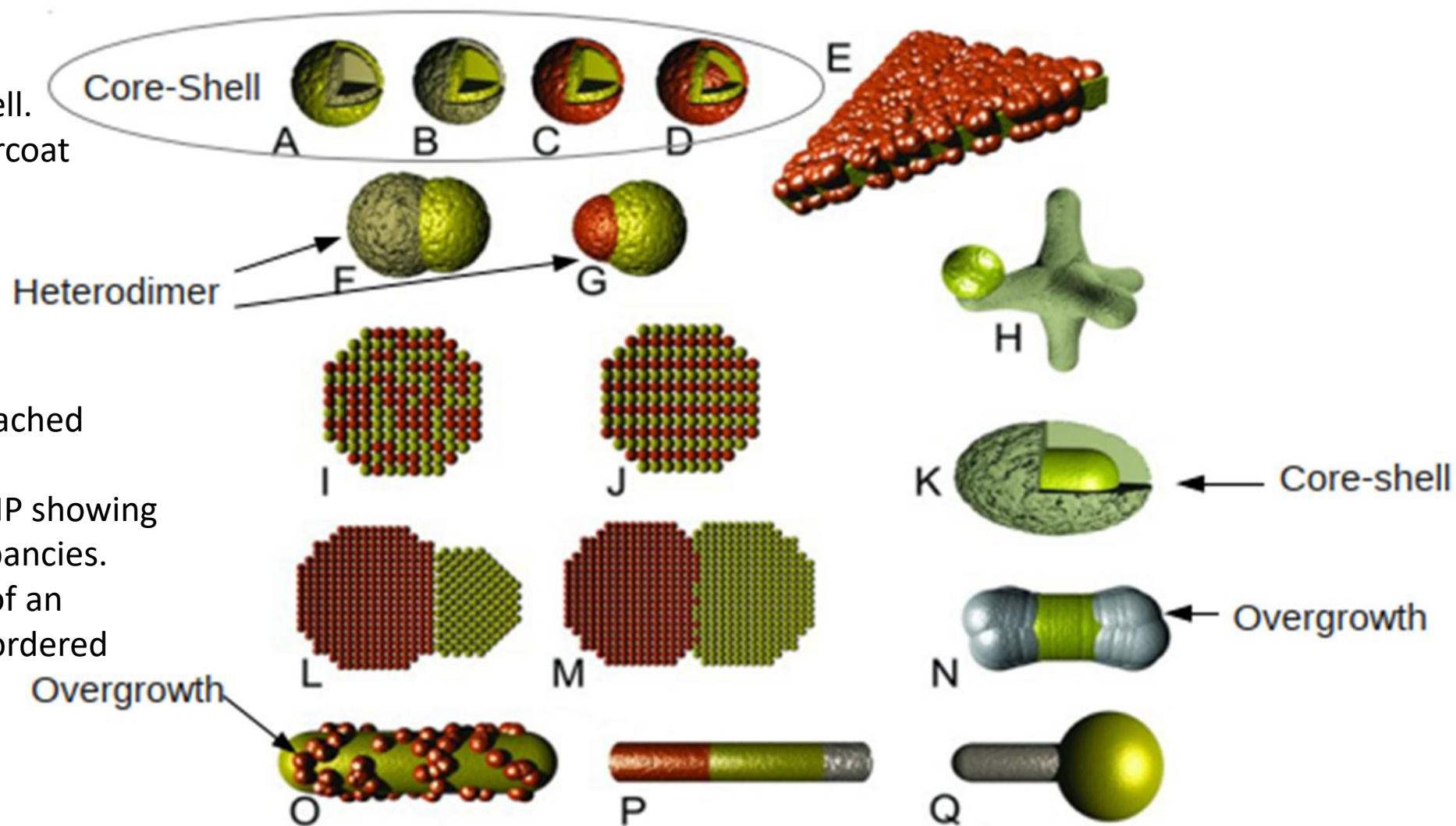
(g) Heterodimer composed of two different metal parts.

(h) Semiconductor crystal with attached metal nanosphere.

(i) Cross section of alloyed metal NP showing disordered nature of atomic occupancies.

(j) Cross section of NP composed of an Intermetallic compound showing ordered atomic occupancy.

(k) Metal nanorods coated in a thick shell of dielectric.



(l) Dimer with incoherent crystalline interface between the parts. (m) Dimer with coherent interface between the parts.

(n) Nanorods with overgrowth of another metal at the rod ends. (o) Nanorods with a sparse overgrowth of a second metal.

(p) Segmented nanowires or nanowire composed of two or more elements. (q) Nanotadpole.

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- Why is the energetic barrier for heterogeneous nucleation smaller than the homogeneous nucleation for a given material under a given supersaturation condition?

❑ Airplanes flying through clouds face small liquid water droplets. These liquid water droplets can be sustained as liquid below the freezing point. Everybody knows that 0 degree Celsius (32 degrees Fahrenheit) is where water freezes. It turns out that if the water is very pure—if it is condensed out of the atmosphere—and there is nothing for that water to freeze on, it can be sustained below the normal freezing point. What we find in the wintertime is clouds that are made up of small water droplets where the water temperature can be as low as **minus 40 degrees C**. Here comes this plane flying through the cloud, and the water droplets impact the airplane and then freeze because now they have a surface to freeze on. Now, chemists may have solved one enigma by showing **how cold water can get before it absolutely must freeze?: 48 degrees below zero Celsius (minus 48 degree Celsius or minus 55 Fahrenheit)**. While dust or impurities normally offer a nucleus, very pure water won't crystallize until the structure of liquid water molecules approaches that of solid ice.

Clouds are at ~6000 feet or above with temperature ~(-10) degree Celsius or below.

➤ AT HIGH ALTITUDE DOES WATER FREEZE AT A HIGHER OR LOWER TEMPERATURE THAN AT SEA LEVEL?

(I think that it freezes at a higher temperature at high altitude than at sea level due to the lower pressure on the water. Since the liquid water has less volume than the ice, lower pressure favors the ice. That should raise the freezing point.)

- ❑ The *shapes of the nuclei as well as their subsequent growth stages play important roles in controlling the NP morphology*, because *nuclei are the starting point from which particle growth commences*.
- Nuclei *shapes and their growth*, in turn, *depend on a number of **thermodynamic** and **kinetic parameters***.
- ✓ For example, *nuclei can acquire a variety of shapes depending on the surface energies (chemical potentials) of its different crystallographic faces*. On the other hand, *the surface energies (chemical potentials) of different crystallographic faces can be modulated by the manipulation of the parameters such as the reaction temperature and the solute concentration*.
- The *manipulation of the thermodynamic and kinetic growth conditions* allows generation of a *rich variety of particle morphologies*.
- However, the thermodynamic or equilibrium growth conditions require that the particle remain in equilibrium with its surroundings at all stages of the growth process at constant temperature and pressure. Therefore, the thermodynamic or equilibrium growth conditions are rarely attained in practice.
- We have seen earlier that the *particle formation takes place under supersaturation condition, that is, under a finite driving force*. Nonetheless, *the nuclei usually pick up the equilibrium shapes, because mainly the surface energy commands the energy and stability of the nuclei during their early stages of formation*.

❑ In case of *homogeneous nucleation*, if a seed crystal develops *under thermodynamic (equilibrium) conditions*, the *crystal will adopt its “equilibrium” shape*.

➤ The “*equilibrium*” shape is governed by the *surface free energy of the emerging crystal* and can be predicted by the *Gibbs–Wulff theorem*.

➤ According to this theorem, the *development of various faces occurs in such a way that the whole crystal has a minimum total surface free energy for a given volume*. That is,

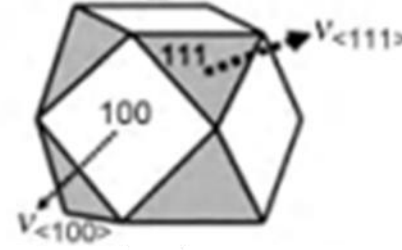
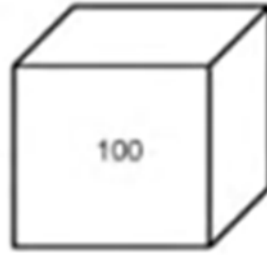
$$\sum_{i=1}^n a_i \gamma_i = \text{minimum},$$

where  $a_i$  is the area of the  $i$ -th face of a crystal bounded by  $n$  faces and  $\gamma_i$  is the surface free energy per unit area of the  $i$ -th face.

➤ In the cases of crystalline solids, the surface free energy is anisotropic and depends on the nature of the crystal facets. Therefore, the *surface energy-minimizing shape is obtained by enclosing the crystal with the facets of the lowest possible surface energy as well as truncating the facets in order to provide minimum possible surface area for a given volume, which results in a polyhedron shape*.



- ❑ The thermodynamic effects on equilibrium shapes have been extensively explored for face-centered cubic (fcc) noble metal particles.
- ✓ For a fcc crystal structure, the surface energies of the low-index crystallographic facets are given in the order  $\gamma\{111\} < \gamma\{100\} < \gamma\{110\}$ .
- ✓ It is recalled here that the coordination number (CN) of the respective crystallographic facets follows the reverse order:  $\text{CN}\{111\} > \text{CN}\{100\} > \text{CN}\{110\}$ .
- ✓ Based on the facet energy, *the **minimum surface energy requirement** predicts that the seed crystals of fcc metals should adopt **a tetrahedral** or **an octahedral** shape* enclosed by the  $\{111\}$  facets.
- ✓ At very small (nanometer) sizes, the equilibrium shape is an octahedron, corresponding to the disappearance of the  $\{100\}$  facets.
- ✓ **However, tetrahedron or octahedron shapes are **not the minimum area** shapes** for a given volume.
- ✓ Therefore, *the Gibbs–Wulff shape for fcc crystal is **truncated octahedron***, which is enclosed by eight hexagonal  $\{111\}$  facets and six square  $\{100\}$  facets.
- ✓ Note that *the truncation introduces a relatively high-energy  $\{100\}$  facet but generates nearly spherical shape, thereby decreasing the total surface area and the free energy.*



- ❑ The *regular polyhedron shapes can be obtained only at 0 K where the surface energy anisotropy is maximal.*
- ✓ The surface energy anisotropy decreases at high temperatures, and rounded parts appear in the equilibrium shape.
- ✓ In this context, *we remember that the surface energy is isotropic for a liquid or for an amorphous solid and, therefore, the equilibrium shape in such cases will be determined only by the minimum surface area criterion.*
- ✓ This yields *spherical shapes for a small liquid drop or for a small amorphous solid particle because the sphere has the minimum surface area for a given volume.*



□ According to Wulff, *crystal faces would grow at rates proportional to their respective surface energies*.

- ✓ Because a *surface with the highest coordination in the plane has the least number of unsatisfied (dangling) bonds per unit area* and hence *the lowest surface energy*, the surface energy as well as the *rate of growth of a face is inversely proportional to the reticular or lattice density of the respective lattice plane*.
- ✓ This suggests that the *high-index faces having low reticular densities grow faster* than the low-index ones and *may disappear eventually* under appropriate conditions.
- ✓ This *results in stable morphologies of particles*, which are *bounded by the low-index crystal planes* that exhibit closest atomic packing.
- ✓ It should be mentioned in this context that the noble metal nanocrystals are mostly composed of the low-index crystal planes. Surface energy calculations for Ag at zero temperature predict that any high-index Ag (hkl) crystal plane will spontaneously facet into linear combinations of the low-index {111}, {100}, and {110} planes. Theoretical calculations have also shown that the *high-index fcc crystal planes* in single-crystalline structures of Cu, Ni, Au, Pd, and Pt are not stable and *undergo reconstruction*. However, clean low-index surfaces have also been observed to undergo surface reconstructions or lattice rearrangement and NPs with high-index planes have also been synthesized.