
PART I

SELF-ASSEMBLY

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UNIFIED APPROACH TO SELF-ASSEMBLY

Traditionally, *self-assembly* has been defined as *spontaneous* association of molecules into defined three-dimensional geometry under a defined condition. It thus refers to a thermodynamics process, and the molecules and the self-assembled aggregates are in equilibrium. Formation of surfactant micelles might be one of the most widely studied systems that fits into this scheme of self-assembly. For this system, thermodynamic description starts from the equilibrium between surfactant molecules (monomer) and surfactant micelles (self-assembled aggregates). An alternative way is to treat the surfactant molecules in bulk (usually aqueous solution) and the surfactant micelles as a different phase (*pseudo*-phase separation) in equilibrium. These two major approaches for the surfactant self-assembly have been well formulated since the 1970s (Clint, 1992), and successfully been applied to a similar type of self-assembly for amphiphilic polymers, such as block copolymers, later in the 1990s (Alexandridis and Lindman, 2000). They are a useful tool to follow the thermodynamics of these self-assembly processes and give a reasonable prediction for the major parameters such as *critical micellar concentration* (*cmc*), aggregation number, counterion binding, micelle size, and micelle size distribution.

The phenomena associated with this scheme of *spontaneous* association are abundant in nature, and its building unit (or association unit) is not limited to

the surfactant molecules. Association of much bigger colloidal-size objects without involving strong chemical bonds has been known since the 1940s (Verwey and Overbeek, 1948; Overbeek, 1952). Formation of metal and semiconductor nanoparticles through the self-assembly of atoms in bulk has also been well established since the late 1990s (Fendler and Dékány, 1996). The self-assembly of dendritic polymers is also now well documented (Emrick and Fréchet, 1999). Thus, the term *self-assembly* actually embraces a wider range of building units. And based on the size/nature of the building units (primary building unit, defined in Section 1.2), they can be viewed mainly as atomic, molecular, and colloidal self-assemblies. Polymeric self-assembly can be classified as molecular self-assembly as the sense of the building unit is polymer molecules.

Spontaneous association phenomena have also been found in biological systems. They are not necessarily limited to the bulk solution, and can also occur at two-dimensional systems such as surfaces and interfaces. The biological system has long been known as a treasure house of intriguing self-assembly processes. Most of the cases are the processes of spontaneous association of biological building units such as lipids and amino acids. There are few covalent bonds involved except for the cases of peptides and thiol bonds. For two-dimensional systems, spontaneous association of metal or semiconductor atoms on a solid surface is now being observed *in situ*. A variety of self-assembly processes at different interfaces have been documented, too. Therefore, in addition to the above classification, self-assembly can be classified as biological or interfacial with the view where the self-assembly occurs. Figure 1.1 shows the schematics. Self-assembly can be classified:

1. By the size/nature of building unit: atomic, molecular, and colloidal
2. By the system where it occurs: biological and interfacial

The classification of self-assembly can be further expanded by the nature of its process: thermodynamic or kinetic. The former includes atomic, molecular, bio-

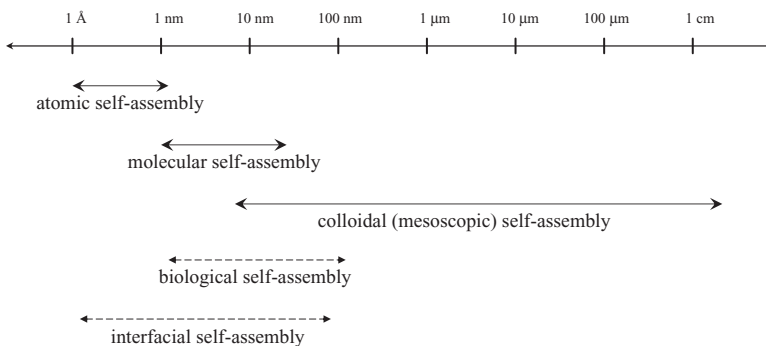


Figure 1.1. Classification of self-assemblies based on the size/nature (atomic, molecular, and colloidal) of building units and on the system where the self-assembly occurs (biological and interfacial); the length scale is also of building units.

logical, and interfacial self-assemblies, while the latter has colloidal and some interfacial self-assemblies. Some of the self-assembly processes are random, while others are directional to some degree. Molecular, colloidal, interfacial self-assemblies are random cases, and some atomic and biological self-assemblies are directional. Self-assembly that is associated with large building units, that is, colloidal self-assembly, can be sensitive to the external stimuli such as electric field, magnetic field, gravity, flow, and so forth.

Thus, the view of spontaneous association covers a broad range-of-length scale from Angström to centimeter, different dimensions, and different sources of origins. The main purpose of this chapter is to propose some unifying approach to this broad range of self-assembly. The very common aspect of these self-assemblies, that is, the interplay of intermolecular and colloidal forces, will be the starting point. It will be discussed for each case of self-assembly process, and then will be followed by the view of the force balance for the formation of self-assembled aggregates. The general scheme of self-assembly and the subsequent formulation will be presented, too. The rest of the chapters in Part I are based on the concept and scheme presented in this chapter. It will be also directly expanded to the implication of the self-assembly for nanotechnology later in Part II.

1.1. SELF-ASSEMBLY THROUGH FORCE BALANCE

Surfactant self-assembly is often called *micellization*: the process for the formation of micelles. With the view of the forces acting on this process, it is actually a process toward the delicate balance between the attractive and repulsive intermolecular forces. Attractive forces directly act on surfactant molecules to bring them close together, while repulsive forces act against the molecules. Hence, the former can be defined as the *driving force* for the micellization, and the latter as the *opposition force*. No strong chemical bond such as a covalent bond is involved during this process. More specifically, the driving force for this process is usually the hydrophobic attraction and the opposition force is the electrostatic repulsion and/or solvation force. First, the long-range hydrophobic force acts as a main force to bring the surfactant molecules together. As the process continues, the opposition forces such as electric double-layer repulsion or hydration forces start to impose. These forces originate from the charge-bearing or hydrated head groups, and are relatively short-range forces compared with the hydrophobic interaction. As will be discussed in Chapter 2, these two types of forces are variable as a function of intermolecular distance, but in opposite ways. Consequently, the attractive and repulsive forces should be balanced at a certain point of the process. Micelles are formed at this point, and the further growth of micelles is prevented. But, since there are no chemical bonds involved, the surfactant monomers in the micelles are free to be exchanged with the monomers in the bulk solution, depending on their molecular dynamic properties. The concentration of this monomer is the concentration that is necessary to form the first

micelle (critical micellar concentration). Any additional amounts of surfactant molecules in the bulk solution will follow the same force balance scheme, thereby forming the additional amounts of micelles while keeping the size of the micelles constant. The concentration of surfactant monomer in solution is also kept constant.

Surfactant micelles are not the only system that fits into this picture of self-assembly. Long-studied colloidal suspensions, emulsions, and microemulsions are also systems where the interaction between the similar intermolecular/colloidal attractive and repulsive forces determines the formation of these self-assembled aggregates.

For colloidal suspension, no coagulation will occur while the repulsive forces are dominant between colloidal objects. However, when the attractive forces are dominant, it is coagulated. Now, let us look at this concept of colloidal stability with the notion of the self-assembly discussed above. The van der Waals force is now the self-assembly driving attractive force, whereas the electric double-layer interaction is the self-assembly opposition repulsive force. Then, the situation of the formulation of the DLVO theory (Derjaguin-Landau-Verwey-Overbeek; Chapter 2) can become a useful tool to describe the self-assembly processes of colloidal objects. Self-assembly of nanoparticles with charged surfaces can be one good example. When the potential barrier between nanoparticles is overcome, the coagulation begins as a result of van der Waals attraction. But, since the electric double-layer repulsion is already there along with the van der Waals force (both as a function of the distance between the nanoparticles), any changes that can change the potential curve can change the whole coagulation process. As long as there is a constant supply of nanoparticles that overcome this energy barrier either by change of the electrolyte concentration or by change of pH, the coagulation will continue until it is compensated by the thermal or gravitational force. With the sense of spontaneous association by the interplay of intermolecular/colloidal forces, this coagulation process can be considered as the self-assembly that now occurs with colloidal-size objects. The opposite change of condition that can make the electric double-layer repulsion dominant will reverse the whole process.

Microemulsion is formed based on the surfactant micelle. But the process is somewhat more complex than surfactant micellization. The attractive driving force is hydrophobic interaction between the surfactant molecules. As for the micellization, the surfactant molecules are brought together by this force. Then, the electric double-layer repulsion and/or hydration force is being balanced with the hydrophobic force. The difference is that there is a significant amount of water or oil in the systems, and they are part of the micelle. This situation is usually recognized as the formation of nanometer-sized water droplets in reverse micelles or as swelled normal micelles. They are thermodynamically stable systems and the process is reversible.

Emulsion (or macroemulsion) is formed when two immiscible liquids (usually water and oil phases) are mixed and stabilized by the self-assembled surfactant, polymer, or colloidal particle at the water–oil interface. Since the interfacial

tension at this interface can never reach zero, this is a thermodynamically unstable system. The long-term stability is acquired by its extremely slow phase separation kinetics. Besides this difference, the self-assembly process itself for emulsion formation is quite similar to the formation of microemulsion. For the surfactants and polymers, the attractive driving force for the self-assembly is again hydrophobic force, and the opposition repulsive force is electric double-layer and/or hydration force. For the colloidal particles, the DLVO-force mentioned above for the self-assembly of colloidal particles becomes the main mechanism. Table 1.1 represents the typical attractive and repulsive forces that can be found in self-assembly processes.

Biological systems are full of self-assembly processes in this sense. Biological membranes, DNA, RNA, enzymes, and proteins are formed by the delicate force balance between the attractive and repulsive forces. However, the uniqueness of these systems compared with the micelles and colloids is that the biological self-assembled systems, in many cases, are formed with some degree of directionality. And this directionality seems to be closely related with the unique functionality of each self-assembled system and the biological systems in general.

Biological systems are not the only ones that show directionality during self-assembly processes. Many bio-mimetic systems, such as systems with synthetic amino acids, carboxylic acids, and dendric polymers, and even nonbiological graphitic supermolecules, show a unique directionality during the self-assembly processes. This directionality is closely related with a unique functionality such as transport, conductivity, and catalytic activity. Helical structure is among the

TABLE 1.1. Representative intermolecular/colloidal attractive and repulsive forces for self-assembly.

Attractive Force	Repulsive Force
Van der waals ^a	Electric double-layer ^b
Solvation	Solvation
Depletion	Hydration
Bridging	Steric
Hydrophobic	
π - π stacking	
Hydrogen bond	
Coordination bond ^c	

^a Some cases of interaction between dissimilar colloidal objects can be repulsive (Figure 2.2).

^b This force sometimes can be attractive when (1) interaction occurs between molecules or colloids with different charges, (2) with the same charge but at very small separation, and (3) between zwitterionic molecules and colloids.

^c Coordination bond is a strong chemical bond compared with the rest of the forces, but serves as a unique attractive force for some of the supramolecular self-assembly systems.

common self-assembled structures, but others such as tube, rod, and ring structures are also being found.

For these directional self-assembly processes, the attractive driving forces and repulsive opposition forces always function as those in the nondirectional self-assembly ones. But there is another class of forces in these directional self-assembly systems that is directly responsible for the directionality. These forces act uniquely as a *functional force*. Hydrogen bond and coordination bond are among the most commonly found functional forces. But much weaker forces, like steric repulsion, are also commonly found functional forces. These forces can be a part of a driving or opposition force during the self-assembly process, but sometimes act almost exclusively as directional force.

1.2. GENERAL SCHEME FOR THE FORMATION OF SELF-ASSEMBLED AGGREGATES

Based on the above discussion, the general scheme for the self-assembly process that can encompass the length scale from atomic to colloidal can be drawn. Figure 1.2 shows the schematics. Self-assembly is the force balance process between three classes of forces: attractive driving, repulsive opposition, and directional force. Directional force can be considered functional force in the sense that it is also responsible for the functionality. When only the first two classes of forces are in action, the self-assembly process is a random and usually one-step process. The self-assembled aggregates show nonhierarchical structure. Most of the molecular self-assembly processes such as micellization and most of the colloidal systems belong to this category of self-assembly. When the third class of force is involved with the first two classes of force, the self-assembly processes are now directional, and in many cases, they occur as multi-stepwise processes. The self-assembled aggregates usually show hierarchical structure. Most of the biological and bio-mimetic systems belong to this category of self-assembly.

This picture also can be applied to more complex two-dimensional self-assembly systems. Spontaneous association of metal or semiconductor atoms on solid substrates forms a unique self-assembled aggregate, such as quantum dots.

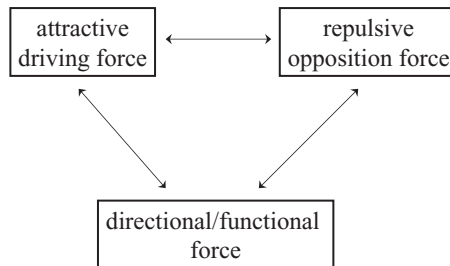


Figure 1.2. Self-assembly *in general* can be defined as the cooperative interaction and balance between three classes of distinctive forces.

Their size can range 1–10 nm and the shapes can be spherical or pyramidal. This is the result of the force balance mainly between the attractive van der Waals force and repulsive electrostatic force. The unique atom–substrate interaction for this system can be considered as directional force, because this force is responsible for the two-dimensionality of this self-assembly. Epitaxial film growth is a good example. The atom–substrate interaction and the epitaxy of the substrate strongly determine the direction of the patterning of quantum dots. This self-assembly process is directional and one-step, and the self-assembled aggregates have nonhierarchical structure.

The same principle can be deduced from interfacial self-assembly processes. Three liquid phase–based solid–liquid, liquid–gas, and liquid–liquid interfaces can be a *confined* substrate for two-dimensional interfacial self-assembly. Surfactant, polymer, and colloidal particles can be self-assembled in this two-dimensional space. The picture for the attractive and repulsive forces is similar to the self-assembly process in macroemulsion systems. The characteristics of the interfaces such as interfacial energy, mechanical force, or interaction of building units with interfaces now act as functional force. Thus, this self-assembly process is also directional and one-step, and the self-assembled aggregates have mostly nonhierarchical structure. Table 1.2 summarizes these aspects. It also shows the

TABLE 1.2. Five classes of self-assemblies, typical building units, examples of self-assembled systems, and characteristics of assembly process.

Classification	Building Units	Self-assembled Systems	Characteristics
Atomic	Metal atom	Epitaxial film, quantum dot	Directional, one-step, nonhierarchical
Molecular	Surfactant, polymer	Micelle, bilayer microemulsion, emulsion	Random, one-step, nonhierarchical
Colloidal	Nanoparticle, nanotube, fullerene colloidal object	Suspension, dispersion, sol, colloidal crystal	Random, one-step, nonhierarchical
Biological	Amino acid, lipid biopolymer	DNA, RNA, protein enzyme, membrane	Directional, stepwise, hierarchical,
Interfacial	Surfactant, polymer, lipid	Surface micelle, Langmuir monolayer, Langmuir-Blodgett film, self-assembled monolayer	Directional, one-step, nonhierarchical

five classes of self-assemblies defined in the first section, the typical building units of each system, and examples of self-assembled aggregates.

As the scheme of Figure 1.2 can predict, if the system is in the right condition, that is, when the attractive and repulsive forces are balanced, even the colloidal systems that usually show kinetic self-assembly process can experience the thermodynamical self-assembly phenomena. These thermodynamically stable self-assembled colloidal aggregates were recently discovered experimentally (Buitenhuis et al., 1994) and confirmed theoretically (van der Schoot, 1992; Groenewold and Kegel, 2001; Likos, 2001; Muratov, 2002; Sciortino et al., 2004). Sterically stabilized or partially charged colloidal objects can be in a condition of delicate balance between the attractive force (van der Waals or depletion) and the repulsive force (electrostatic) at a certain volume fraction. Much like the micellization of surfactant molecules, a certain number of colloidal objects in this condition can self-assemble into the colloidal aggregates with ~ 20 – $\sim 1,000$ of finite aggregation number. The individual colloidal particles (monomer) are in equilibrium with the self-assembled aggregate, and the whole process is dependent on physicochemical parameters such as temperature and solvent. There is also the exchange of free monomer with self-assembled aggregates. And the change in the shape of the self-assembled aggregates can be induced from spherical, to disk, and to rod as the force balance changes. This force balance change can be induced by the change in the shape/size of colloidal object (monomer), surface charge density of colloid, and dielectric constant of solvent. By rough analogy, for the case of surfactant micellization, the main factors for the change of force balance between attractive and repulsive forces are the shape/length of surfactant molecule (monomer), charge density (for ionic surfactant) or degree of hydration (for nonionic surfactant) on the micelle surface, and the solvent properties such as dielectric constant or pH. While the concept of DLVO describes the irreversible kinetical self-assembly of colloidal objects, again this case represents the reversible equilibrium self-assembly of colloidal objects.

1.3. GENERAL SCHEME FOR SELF-ASSEMBLY PROCESS

In the previous section, the balance between the distinctive but cooperative three classes of forces has been proposed for the formation of self-assembled aggregates. This general scheme can encompass a variety of self-assembly building units with the length scale ranging from atomic to colloidal. Since the self-assembly process can occur in such a wide range of length scale (10^7 difference of order from Angström to centimeter) and the same types of forces are governing the process, the self-assembled aggregates formed by the initial self-assembly step can in many cases become another building unit for the subsequent self-assembly processes at given conditions. That is, self-assembly in fact is not always a single-step process; it can occur in a double-, triple-, and multi-stepwise pattern.

A typical example can be found in the formation of surfactant micelle and its subsequent transition to mesophase structures (Clint, 1992). First, the most common spherical micelles are formed by the typical self-assembly of surfactant molecules. As the solution condition is changed into the subsequent favorable self-assembly, such as increased surfactant concentration, change of pH, or increased concentration of counterion, these micelles begin to interact with each other and can self-assemble together. This process is governed by the intermicellar colloidal forces. Thus, the surfactant molecule can be defined as the *primary building unit* in this sense and the micelle as the *secondary building unit*. And the micelle can be viewed as the *primary self-aggregate* and mesophase (the self-assembled micelle) as the *secondary self-aggregate*. Amphiphilic polymers such as a block copolymer can in many cases follow a similar scheme and form similar polymer mesophases (Alexandridis and Lindman, 2000).

Another example can be found in the consecutive self-assembly of atoms to colloidal-size objects. Certain numbers of metal or semiconductor atoms (<1 nm diameter) (known as the *magic number of aggregation*) can self-assemble into quantum dots or nanoparticles in bulk (2–5 nm diameter) (primary self-aggregates), and the subsequent self-assembly (again associated with the magic number of aggregation) brings those quantum dots or nanoparticles into giant quantum dots or giant nanoparticles of 20–50 nm diameter (secondary self-aggregates) (Rao et al., 2000; Rao, 2001). Van der Waals attraction is the primary driving force for both processes, while some degree of structural constraints seems to be the opposition force. The second process is different from the self-assembly of surfactant- or alkyl chain-modified nanoparticles at the surface or in bulk that occurs by van der Waals and electric double-layer forces. A similar process can occur during the epitaxial film growth of metal or semiconductor at solid surfaces, which can be considered as interfacial self-assembly with a multi-stepwise process from atomics to colloidal-length scale.

Formation of large-scale aggregates of colloidal particles with a centimeter-length scale such as fractals (secondary self-aggregate) occurs in many cases through the assembly of clusters that are formed by the self-assembly of individual colloidal objects (primary self-aggregate).

For biological self-assembly processes, a typical example can be found in the formation of proteins. First, DNA is formed by the self-assembly of amino acids. Thus, the amino acids are the primary building units for this initial self-assembly, and the DNA is the primary self-aggregate. DNA is then self-assembled into a primary structure of protein via the secondary self-assembly process. DNA is now the secondary building unit and the protein is the secondary self-aggregate. Further self-assembly (tertiary, quaternary, etc.) is abundant in biological systems and often is involved with the hetero-building units such as membrane and bioinorganics. Tertiary and quaternary structures

Along with the intermolecular forces, peptide bond formation is greatly involved. This issue will be discussed in detail in Chapter 7.

of proteins are the result of the intra-self-assembly of the secondary self-aggregates.

The general scheme for the self-assembly process that can occur as a single-to multiple-step and hierarchical-wise pattern can be proposed as shown in Figure 1.3. Any of the atoms, molecules, polymers, colloidal objects, or biological molecules can be a primary building unit for the initial step of the self-assembly. This primary self-assembly is governed by the balance between the intermolecular/colloidal forces as shown in Figure 1.2. The self-assembled aggregate formed is the primary self-aggregate, and can be the building unit (secondary building unit) of the subsequent self-assembly (secondary self-assembly). This process forms the secondary self-aggregate, which can be the building unit of the next self-assembly process. As long as the major forces for this process are the intermolecular/colloidal forces, further assembly is possible as tertiary and quaternary self-assemblies. And the general scheme in Figure 1.2 governs each of the processes.

We now consider the general formulation of this scheme that includes Figures 1.2 and 1.3. Figure 1.4 represents the schematics of some of the intermolecular/colloidal forces that will be discussed in Chapter 2. As a function of the distances between either molecules or colloidal objects, it shows quite complex features both in magnitudes and the ranges of length scale. For example, the curve that represents the case when the van der Waals attractive force has relatively comparable magnitude to the electric double-layer repulsive force shows both the attractive and repulsive nature of the total force as the distances between the two colloidal objects are changed. This is a typical situation for *kinetically* stable colloidal suspension. As long as the maximum energy barrier is high enough and the energy minimum after that (at longer distance; secondary minimum) is deep enough, the colloidal objects keep the constant distance in average. But, this energy barrier is not ultimate, so there are colloidal subjects that can overcome this barrier at any time. By the terms of self-assembly we discussed above, this situation means that the explicit formulation such as for the micellization of surfactant is not quite possible for the kinetical self-assembly of colloidal objects. Also, the range in which each of the forces is exerted is different. While the van

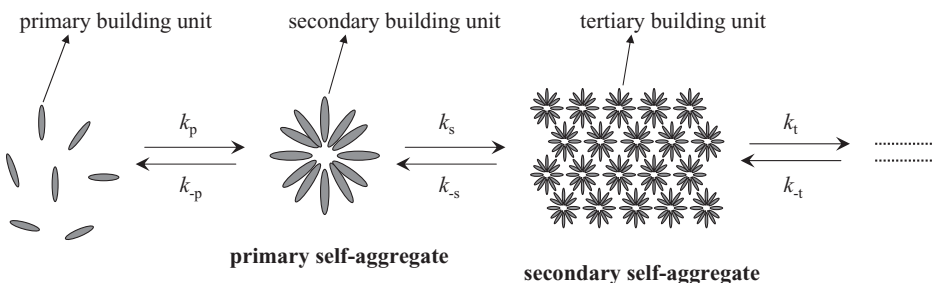


Figure 1.3. General scheme for self-assembly.

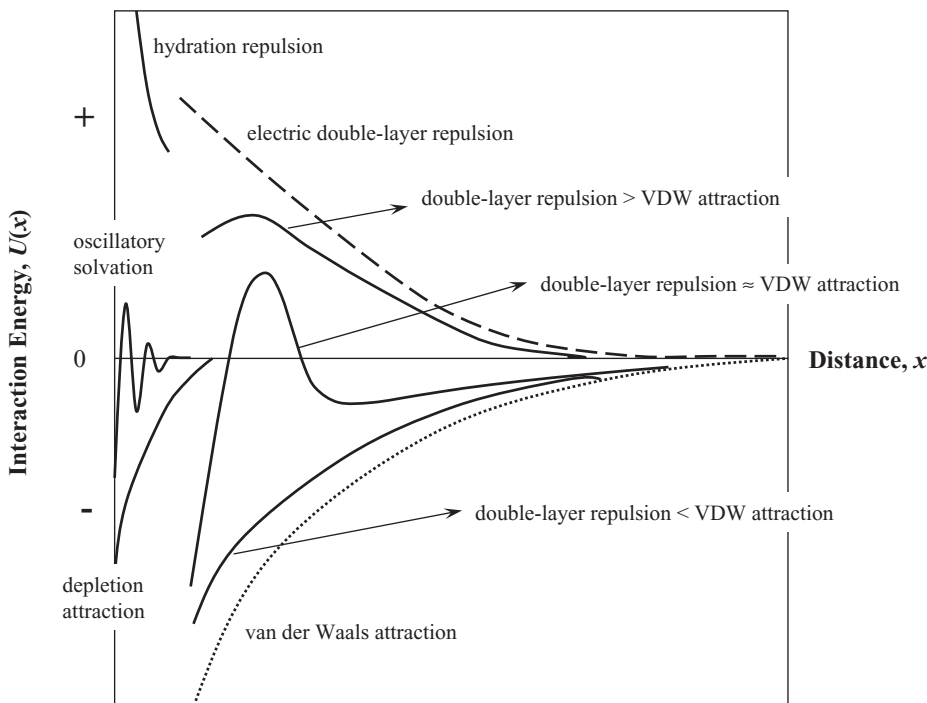


Figure 1.4. Schematic representation of the intermolecular and colloidal potential energies as a function of the distance between two objects (molecule or colloid). Range and magnitude are relative scales.

der Waals and electric double-layer forces are exerted at long and wide ranges, the hydration, solvation, and depletion forces have short- and narrow-range characters. This creates the notion that a *unique* expression that can cover the entire general scheme of the self-assembly might not be possible.

The following formulation is an expression with which we can overview the general self-assembly scheme. Suppose that the total net potential of the entire self-assembly processes with a given building unit is $U_{total}(x)$. Then, the $U_{total}(x)$ can be described as the net total of all of the attractive and repulsive potentials involved in each step of the self-assembly as follows:

$$U_{total}(x) = f_P \cdot [U_{A,P}(x) + U_{R,P}(x)] + f_S \cdot [U_{A,S}(x) + U_{R,S}(x)] + f_T \cdot [U_{A,T}(x) + U_{R,T}(x)] + \dots + U_{ext}(x) \tag{1.1}$$

with

$$\sum f_P + f_S + f_T + \dots = 1 \tag{1.2}$$

$U_{A,P}(x)$ and $U_{R,P}(x)$ represent the attractive and repulsive potentials for the self-assembly of primary building units, respectively. $U_{A,S}(x)$ and $U_{R,S}(x)$, and $U_{A,T}(x)$ and $U_{R,T}(x)$ are for the self-assembly of secondary and tertiary building units, respectively. f_P , f_S , and f_T are the fraction coefficients of the contribution of the net potential of each self-assembly step to the total net potential. $U_{ext}(x)$ is the potential contribution by the external forces when they are applied. The external forces become comparable to the self-assembly especially with the van der Waals and electric double-layer forces whenever the size of the building units is in the range of colloidal size. The details of this general form follow.

Type I. When the self-assembly occurs through only the primary self-assembly step, only the first term of the right-hand side of equation (1.1) is valid, with $f_P = 1$. The rest of the terms are not necessarily zero, but should be much smaller than the first term, so can be negligible. Thus, equation (1.1) becomes

$$U_{total}(x) = U_{A,P}(x) + U_{R,P}(x) \quad (1.3)$$

Typical examples are the micelle formation of surfactants or amphiphilic polymers at low concentration, formation of vesicle or microemulsion, and stable colloidal suspension. The interplay between the attractive and repulsive forces between the primary building units solely determines the self-assembly process.

For the case of colloidal suspension, equation (1.3) becomes the DLVO force with $U_{A,P}(x)$ and $U_{R,P}(x)$ as van der Waals force and electric double-layer force, respectively. The primary building unit is the colloidal objects.

For the cases of surfactant or polymer micelles, the primary building units are the surfactant or polymer molecules. Intermolecular hydrophobic force is now the major component of $U_{A,P}(x)$, and intermolecular steric, hydration (or solvation), and electric double-layer forces are of $U_{R,P}(x)$. The exact solution for equation (1.3) for this case is not known. But the semiempirical dimensionless thermodynamic solution of the packing parameter (or g -factor) (Chapter 17 of Israelachvili, 1992) provides an excellent tool for the formation and structural transition of the surfactant and polymer micelles. As long as the monomer concentration is kept low enough to minimize the intermicellar interaction (colloidal interactions between self-aggregates), this relation is also valid for the formation of vesicle, bilayer, and microemulsion.

Type II. The cases of self-assembly with both primary and secondary processes can be found in the formation of surfactant and polymer mesophases such as liquid crystals and the formation of secondary structures, such as tube and ring, of certain bio-mimetic systems (Chapter 7). Equation (1.1) now becomes

$$U_{total}(x) = f_P \cdot [U_{A,P}(x) + U_{R,P}(x)] + f_S \cdot [U_{A,S}(x) + U_{R,S}(x)] \quad (1.4)$$

As in the type I cases, surfactant, polymer, and bio-mimetic molecules are the primary building units in this scenario. But the secondary self-assembly is being induced either by interaggregates or by specific functional forces. For the formation of mesophases that can be induced above a certain concentration of surfactant or polymer, the micelles that have been formed via the primary self-assembly now face strong intermicellar colloidal interactions due to the increased concentration of the micelles. This interaction can be either attractive or repulsive. When it is mainly attractive, the micelles are directly assembled together. Thus, the micelles are the secondary building unit for this secondary self-assembly. The formed mesophases are the secondary self-aggregates. Due to the fact that these building units are the self-aggregates of molecules where the molecular rearrangement is obeyed by the energetics of each case, the mesophase can be in different forms. This includes typical liquid crystal structures such as hexagonal, cubic, and lamellar. When the interaction is mainly repulsive, the primary self-aggregates experience the structural transition that is involved with mainly additional monomer in the micelle (increased aggregation number) rather than the direct assembly between the micelles. This results in the formation of ellipsoidal, rodlike, or wormlike micelles.

For bio-mimetic molecules, the functional force, like hydrogen bond, induces the specific assembly of the primary self-aggregates. Thus, the secondary self-aggregates show characteristic directionality.

The fraction coefficients f_P and f_S in equation (1.4) should be correlated at some degree, and $f_P + f_S$ is unity. When $f_P > f_S$, the primary self-assembly should be dominant with the fraction of the secondary self-assembly. When $f_P \cong f_S$, the primary and secondary self-aggregates should be coexisting and thermodynamically favorable. The case of $f_P < f_S$ represents the favorable proceeding to the secondary self-assembly, and the dominance of the secondary self-aggregates. The exact solutions for any of these cases will require the exact knowledge of each form of the potentials as a function of the distances between each of the building units. This is a formidable task. Thus, this equation is not going to be able to provide preknowledge on the self-assembly processes. However, by acknowledging the individual forces functioning on the self-assembly processes along with their functioning range, this concept can provide the qualitative route to predict the entire self-assembly process with quite reasonable accuracy.

Type III. The third type of self-assembly is the self-assembly with the higher order of primary, secondary, tertiary, and above. Many of the self-assembly processes from biological systems show these types of characteristics. The abovementioned case of the formation of proteins that started from the self-assembly of amino acids is a typical example. Formation of a typical extracellular protein such as collagen that is being formed via multilevel hierarchical self-assembly is an excellent example of the self-assembly that occurs well beyond the tertiary self-assembly. The abovementioned formation of giant nanoparticles via magic number of aggregation is an example of the self-assembly up to the tertiary step. Equation (1.1) becomes

$$U_{total}(x) = f_P \cdot [U_{A,P}(x) + U_{R,P}(x)] + f_S \cdot [U_{A,S}(x) + U_{R,S}(x)] + f_T \cdot [U_{A,T}(x) + U_{R,T}(x)] + \dots \quad (1.5)$$

The summation of all fraction coefficients should be $\sum f_P + f_S + f_T + \dots = 1$. As with type II above, the exact solution of equation (1.5) can be obtained only by identifying the forces involved in each of the self-assembly steps and with the exact forms of the potentials. But the relation between the fraction coefficients can provide some qualitative picture of this type of self-assembly. For example, when any one of the coefficients is dominant over the rest of them, the self-aggregate represented by that coefficient is dominant with the coexistence of the rest of the two types of self-aggregates with minor amounts. When $f_P > (f_S, f_T)$, the primary self-aggregates are the major forms of the system, while $(f_P, f_S) < f_T$ represents the case of the dominance of the tertiary self-aggregates such as proteins. $f_S > (f_P, f_T)$ may be the case of the high concentration of nanoparticle assembly with magic number. Part of the giant nanoparticles can form clusters such as fractals that can be considered as the tertiary self-aggregates. When $f_P \cong f_S \cong f_T$, all three types of self-aggregates coexist.

Type IV. Since self-assembly is a process of force balancing between building units without the intervening of strong chemical bonds, it can be affected by the external forces that can have an influence on the intermolecular/colloidal forces during the process. Thus, for cases with the influence of external forces, equation (1.1) generally represents the entire self-assembly. The summation of fraction coefficients should be fitted with equation (1.2). For example, when this is the case with the primary self-assembly only, equation (1.1) becomes

$$U_{total}(x) = f_P \cdot [U_{A,P}(x) + U_{R,P}(x)] + U_{ext}(x) \quad (1.6)$$

When the secondary self-assembly process is also involved, it becomes

$$U_{total}(x) = f_P \cdot [U_{A,P}(x) + U_{R,P}(x)] + f_S \cdot [U_{A,S}(x) + U_{R,S}(x)] + U_{ext}(x) \quad (1.7)$$

Typical examples of the external forces include magnetic force, electric force, flow stress, capillary force, gravity, and interaction with substrate in a confined space. These forces actually can be present at all times in a real situation of the self-assembly process. But, regardless of the magnitude difference between the fraction coefficients, whenever the external potential begins to be dominant (or can compete) over the summation of intrinsic intermolecular/colloidal forces, the whole self-assembly process is affected.

For example, when the sterically modified polymer colloidal spheres that are given as a glass state under gravity (on Earth) are placed under microgravity (in space), they are rapidly crystallized. On Earth, gravity is comparative (or dominant) to the particle diffusion and intercolloidal interaction at this given condition, and thus acts on them to settle on the bottom of the container as a glass

state. This intervening gravity effect is minimized in space; the self-assembly of this colloidal system now is solely controlled by the intercolloidal forces. Colloidal spheres that can have enough diffusion time to be balanced by the attractive and repulsive forces are crystallized into the regular lattice. The first experimental observation of this phenomenon was made on the Space Shuttle (Zhu et al., 1997) and was proved by theoretical calculation later (Simeonova and Kegel, 2004).

Another example that has become an interesting issue is the self-assembly of surfactant molecules or colloidal objects in a confined space. As the space between the self-assembly building units and the substrate is decreased below a certain range, the interaction of the building units with the surface of the substrate becomes comparable to the intermolecular/colloidal forces. Thus, this situation can considerably affect the whole self-assembly process. This interaction can be considered as the external force of this type of system. Recent examples include the self-assembly of mixed ionic micelles in a confined space of two parallel charged spaces (Yuet, 2004) and the dramatic effect of a geometrical confinement on the shear-induced self-assembly of colloidal polymer spheres (Cohen et al., 2004).

The general picture can be summarized as follows:

1. When $U_{total}(x)$ is equal to or close to zero with zero of $U_{ext}(x)$, the self-assembly is thermodynamically driven. The building units of each of the self-assembly steps are in equilibrium with the self-aggregates. The self-aggregates have finite sizes and defined shapes. Examples of this category include surfactant or polymer micelles, vesicles, proteins, and microemulsions.
2. When $U_{total}(x)$ is negative with zero of $U_{ext}(x)$, the self-assembly is kinetically driven. The self-assembly, in most cases, occurs until most of the building units are exhausted. The self-aggregates have indefinite sizes and less-defined shapes. Examples are coagulated colloidal or nanoparticle precipitates, bilayers, gels, some types of liquid crystals, and macroemulsions.
3. When $U_{total}(x)$ is positive with zero of $U_{ext}(x)$, the self-assembly is not possible in most cases. If this condition is exerted on self-assembled systems or during the self-assembly process, disassembly will be the most likely scenario.

1.4. CONCLUDING REMARKS

It would be fair to say that the schemes proposed in this chapter are nowhere near perfection, nor can they bring the exact solution for the exact prediction of a variety of self-assembly processes. But it would also be fair to say that by accepting the concept of force balance for self-assembly and the general concept of multistep self-assembly processes, we can benefit in the following ways:

1. A variety of processes in nature that are mainly governed by the intermolecular and/or colloidal forces can be integrated into the picture of the self-assembly, which includes a variety of building units with different-length scales and different origins.
2. A variety of self-assembly processes we acknowledged earlier in the chapter can be understood as one unified concept.
3. Each of those self-assembly processes and the physical properties of the self-assembled aggregates can be qualitatively explained with reasonable accuracy.

These issues will be examined throughout the rest of Part I with detailed explanations and examples. Also, it will be shown that they can be directly correlated with the self-assemblies in nanotechnology and provide useful tools to address a variety of nanotechnology issues. The general outline for this will be presented in Chapter 8 followed by the details in the rest of Part II.

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