

Basic Concepts in Self Assembly

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The tendency of a system to spontaneously reach a well-defined structure is often named "self-assembly" [1].² Originally used in biology to describe the process that brings to the self organization of proteins into complex structures (like virus capsides), the word self-assembly has progressively permeated physics, chemistry and material science, becoming almost a substitute (despite its equivalence) for the more precise thermodynamic term, the minimization of the system free energy on going from a collection of disordered particles to the final (possibly ordered) structure. Crystallization of a metastable fluid can be properly considered as a well known example of self-assembly.

While the search for a minimum free energy state is ubiquitous, the word self-assembly, especially in the context used in this school, is commonly limited to the case in which the final structure is composed by (often ordered) aggregates of finite size [2]: micelles, vesicles, filaments, ribbons, self-assembling spontaneously under the appropriate external conditions (density, temperature, salt concentration, pH and so on).

Given the generality of the concept, a lecture on self-assembly can take an enormous number of directions (some of which will be exploited in details by the school lecturers). Here I will limit myself to some general consideration on self-assembly of one-component systems into finite size aggregates, and more specifically on its thermodynamic basis. Specifically, I will focus on particles whose interaction energy scale is indicated by ϵ and whose interaction range is indicated by Δ . I will use the generic word "particle", which according to the context can refer to an atom, a molecule, a macromolecule, a colloidal particle.

To exploit self-assembly into finite size structures it is fundamental to understand:

- 1) the need of operating at low $k_B T$ (compared to ϵ)
- 2) the need of directional attractive interactions (or alternatively of highly non-monotonic interaction potentials)
- 3) the need to suppress collective phenomena (competition with crystallization and phase separation)
- 4) how to predict the structure of the aggregate from the knowledge of the interaction potential (direct) or how to design the interaction potential to spontaneously assemble a desired structure (inverse).
- 5) how to develop a thermodynamic description of the clustering process, highlighting the role of the bonding volume compared to the volume per particle and the bonding energy and the competition between the entropic driving force disfavoring self-assembly and the energetic (or enthalpic) driving force favoring the formation of low energy aggregates
- 6) How external fields can be exploited to modify the routes toward the assembly of ordered structures.

The next sections address some of these points in more detail, for one-component systems. Others will be discussed in the school lectures.

LOW T

Differently from bulk (infinite size) systems which can be stabilized also by repulsive interactions (as in the paradigmatic case of hard-sphere crystallization), the formation of a stable aggregate of finite size requires attraction between the participating particles. When the distance between two particles is within σ and $\sigma + \Delta$ (being σ the characteristic particle size), a "bond" of strength $\epsilon > 0$ sets in. The values of Δ and ϵ enter in the evaluation of the partition function of the system (and hence in the free energy) determining the

temperature T and density ρ conditions under which bonding becomes statistically relevant. Typically, Δ is a fraction of σ (larger Δ values do not allow for self-assembly of finite size clusters). As we will demonstrate later on, the probability of creating a bond between two particles reaches a value of the order 0.5 when $\rho\sigma^2\Delta \exp(\epsilon/k_B T) \approx 1$. Assuming typical values for $\Delta \approx 0.1\sigma$ and for the packing fraction $\phi \equiv \frac{\pi}{6}\sigma^3\rho \approx 0.1$ this condition already teach us that since $\rho\sigma^2\Delta \approx 0.01$, $k_B T$ must be smaller than ϵ if the probability that the bond is formed have to be not negligible (more precisely $k_b T/\epsilon \approx (\ln \rho\sigma^2\Delta)^{-1} \approx -(\ln 0.01)^{-1} \approx 0.2$),

It is also important to consider the lifetime of the bonds, i.e. their persistence. As a first approximation, the lifetime of this bond is proportional to $\exp(\epsilon/k_B T)$. This immediately clarifies that to form a stable aggregate, i.e. an aggregate in which the relative position of the constituent particles is persistent in time, one need to go to $k_B T \ll \epsilon$. It also clarifies that at the typical temperature when fifty per cent of the possible bonds are formed (i.e. $\exp(\epsilon/k_B T) \approx 100$) the bonds are generally still very intermittent and the aggregates are to be considered as transient clusters with significant exchange of particles between aggregates. To generate bonds that are persistent (e.g. long compared to the experimental observation time) already at the temperature where they form requires to find ways to significantly lower the term $\rho\sigma^2\Delta$, compared to the typical case. We will come back to this point later on.

A persistent bond typically requires $10^8 - 10^9$ attempts before breaking (this estimate of course depend on the attempt rate and the experimental observation time). This correspond to $k_B T/\epsilon \approx 0.045 - 0.05$. Hence, in summary, at the temperature where bonds start to form between spherically interacting particles, they are very transient.

THE NEED OF DIRECTIONAL ATTRACTIVE INTERACTIONS

In the previous section we have seen that the formation of stable bonds between the particles require T significantly smaller than $k_B T$. At these low T , if the interaction potential is isotropic, the particles will have a tendency to phase separate, forming coarsening liquid droplets in the interior of which each particle is surrounded by approximatively twelve neighbours. Indeed, particles interacting via isotropic potentials (and with short-ranged interactions) are known to phase separate when the normalised second virial coefficient B_2^* (normalized to the hard-sphere value B_2^{HS}) reaches the value $(B_2^*)_{T_c} \approx -1.2$ [3]. For the isotropic square-well potentials (our paradigmatic potential)

$$B_2^* \equiv \frac{B_2}{B_2^{HS}} = 1 - \frac{(\sigma + \Delta)^3 - \sigma^3}{\sigma^3} \left(e^{\epsilon/k_B T} - 1 \right) \quad (1)$$

which means that

$$\frac{k_B T_c}{\epsilon} = \left\{ \ln \left[1 + \frac{(1 - B_2^*)_{T_c} \sigma^3}{[(\sigma + \Delta)^3 - \sigma^3]} \right] \right\}^{-1} \quad (2)$$

For a typical range $\Delta \approx 0.1$, $k_B T_c/\epsilon \approx 0.5$ and hence it is impossible to bring the system to the T at which the bond lifetime would be sufficiently long to observe the presence of long-living well-defined aggregates, without phase separation.

In principle one could attempt to decrease Δ to lower T_c . Still, Eq. 2, in the limit of $\Delta/\sigma \rightarrow 0$, tends to

$$\frac{k_B T_c}{\epsilon} \approx \left\{ \ln \left[\frac{(1 - B_2^*)_{T_c} \sigma}{3\Delta} \right] \right\}^{-1} \approx (\ln \Delta/\sigma)^{-1} \quad (3)$$

which means that in the case of spherically interacting potentials only in the limit of very sticky (almost unphysical) interactions ($\Delta/\sigma \approx 10^{-9}$ or smaller) T_c is so small that the bond lifetime becomes longer than the experimental observation lifetime before the phase separation is encountered, at least for interactions potentials which can be modelled as short-range attraction. As a word of caution, we note that in soft matter, it may happen that bonding arises as a result of an effective interaction which may involve a large entropic component. One typical case is offered by electrostatic interactions when counter ions redistribute in space as a consequence of bonding or when significant conformational changes are associated to the bond-formation process (see DNA self-assembly). Under these conditions, it is possible to modulate the bond lifetime and generate persistent bonds even for $T > T_c$.

Isotropic attractive interactions are thus not suited for self-assembly. Can the picture change with directional interactions? The answer is certainly positive. Directional attractive interactions offers many advantages. For a conical bonding surface of semi-angle $\theta = 30^\circ$ the entropic reduction is of the order of 10^3 compared to the isotropic case. Indeed, the bonding volume changes from the value $4\pi\sigma^2\Delta$ typical of spherical potential to $4\pi\chi^2\sigma^2\Delta$, where $\chi = (1 - \cos(\theta))/2$, commonly indicates the fraction of solid angle accessible for bonding. This reduction in the entropy help making the temperature at which bonds form and the temperature at which bonds are stable for sufficiently long times closer. There is another very important consequence of directional interactions. The possible suppression of the gas-liquid phase separation [4, 5]. Indeed, already the reduction in the number of bonded neighbours has a dramatic effect on the gas-liquid phase diagram, progressively decreasing both the critical temperature and the density of the liquid coexisting with the gas. This opens a region of packing fractions (above the coexisting liquid density but still smaller than the density at which packing becomes relevant) where it is possible to cool the system down to very low T without encountering phase separation. The suppression of the gas-liquid phase separation is even more striking if the directional interactions favor the formation of aggregates that do not significantly attract each other. If bonding sites are completely saturated in each aggregate than these super-particles will feel each other essentially as hard-spheres suppressing any driving force toward phase separation. This important consideration clarifies why long range attractive interactions and isotropic potentials are not suited for self-assembly.

Fig. 1 shows schematic examples of one component system (Janus particles), interacting via hard-core (red) and square-well (green) potentials, which form aggregates similar to micelles and vesicles at low T for which the intra-aggregate attraction can be considered negligible [6, 7].

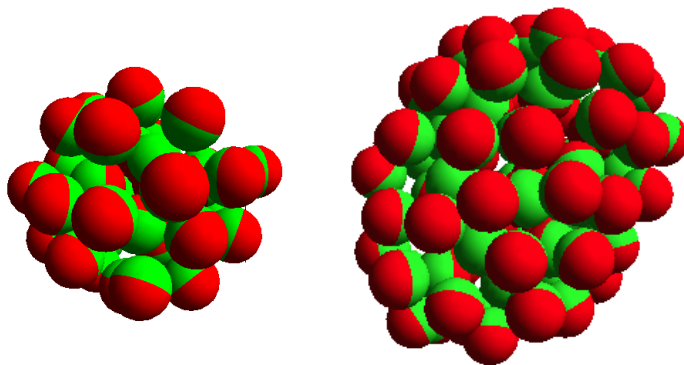


FIG. 1. example caption

In the case in which clusters do not significantly interact (e.g. in the case in which the dominant contribution is excluded volume and the system packing fraction is small, then clusters can be considered isolated) the thermodynamic of the system significantly simplify. The definition of a cluster as an entity requires first a definition of existence of a bond between particles and of the cluster as a set of particles connected by an uninterrupted sequence of bonds. In the case of strong bonds (the one commonly found in association) or in the case of square-well like interaction, the definition of "bond" is unambiguous.

The partition function of the system, in the NVT ensemble (where N is the total number of monomers) can be written as [8]

$$Q = \prod_{n=1}^{\infty} \frac{Q_n^{N_n}}{N_n!} \quad (4)$$

where Q_n is the partition function of the cluster composed of n monomers and N_n is the number of clusters of size n . For isotropic interactions

$$Q_n = \frac{1}{n!\lambda^{3n}} \int' d\vec{r}_1 \dots d\vec{r}_n \exp -\beta V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) \quad (5)$$

where the ' sign in the integration limits indicates that only points in phase space $d\vec{r}_1 \dots d\vec{r}_n$ for which the cluster does not break into disconnected smaller clusters should be considered.

For the monomer,

$$Q_1 = \frac{V}{\lambda^3}$$

For directional interactions, one need to integrate over all Euler angles of the particles Ω_j and the partition function becomes

$$Q_n = \frac{1}{n!\lambda^{3n}} \int' d\vec{r}_1 \dots d\vec{r}_n d\Omega_1 \dots d\Omega_n \exp -\beta V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n, \Omega_1, \dots, \Omega_n) \quad (6)$$

where now λ includes the rotational component of the integral over the kinetic energy. In these cases it is convenient to redefine $\Lambda^3 = \lambda^3 / \int d\Omega_1$ and define a spherically averaged partition function

$$Q_n = \frac{1}{n!\Lambda^{3n}} \frac{\int' d\vec{r}_1 \dots d\vec{r}_n d\Omega_1 \dots d\Omega_n \exp -\beta V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n, \Omega_1, \dots, \Omega_n)}{\int d\Omega_1 \dots d\Omega_n} \quad (7)$$

The Helmutz free energy F , is then given by

6

$$\beta F = -\ln Q = -\sum_{n=1}^{\infty} [N_n \ln Q_n - N_n \ln N_n + N_n] = \sum_{n=1}^{\infty} N_n [\ln Q_n - \ln N_n + 1] \quad (8)$$

and we have to minimize over all possible cluster sizes N_n to find the lowest free energy value. Still, we must satisfy the constraint $\sum_n nN_n = N$. Introducing a Lagrange multiplier α , we get

$$\frac{\partial(\beta F + \alpha \sum_k kN_k)}{\partial N_n} = 0 \quad (9)$$

$$\ln \frac{N_n}{Q_n} - n\alpha = 0 \quad (10)$$

or

$$N_n = Q_n (\exp \alpha)^n \quad (11)$$

Since $N_1 = Q_1 \exp \alpha$, the same expression can be written as

$$N_n = Q_n \frac{N_1^n}{Q_1^n} = Q_n (\rho_1 \Lambda^3)^n \quad (12)$$

This expression is particularly informative, since it shows that the probability of observing an aggregate of size n is proportional to the strenght of the partition function Q_n .

Often one find defined

$$Q_n = e^{-\beta f_n}$$

so that

$$\frac{N_n}{N} = Q_n \frac{N_1^n N^{n-1}}{N^n Q_1^n} = \left(\frac{N_1}{N} \right)^n e^{-\beta[(f_n + \ln N) - n(\beta f_1 + \ln N)]} \quad (13)$$

The resulting free energy is

$$\beta F = -\sum_{n=1}^{\infty} \left[N_n \ln Q_n - N_n \ln Q_n \frac{N_1^n}{Q_1^n} + N_n \right] = -\sum_{n=1}^{\infty} \left[nN_n \ln \frac{N_1}{Q_1} + N_n \right] = N \ln N_1/Q_1 - \#_c \quad (14)$$

where $\#_c$ is the total number of clusters in the system. The free energy, in the ideal gas of cluster approximation, can always be written as

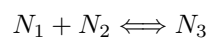
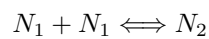
$$\boxed{\beta F = N\beta\mu - \#_c} \quad (15)$$

It is interesting to note that, being an ideal gas, the pressure is proportional to the number of clusters ($\#_c = \beta PV$) and that the monomer concentration (which fix the value of μ) and the total number of clusters are the only information requested to write down the system free energy.

ANALOGIES WITH CHEMICAL REACTIONS (USEFUL TO TALK TO CHEMISTS)

An equivalent way of looking at the problem of clustering can be derived in term of chemical reactions. Each cluster can be considered a different chemical species and the equilibration process that starts from a collection of monomers and ends into an equilibrium distribution of different clusters can be considered as the progression of the reactions toward equilibrium.

In this terminology, we could write



and so on and associate to each of these reactions a reaction constant K_n (with the dimension of an inverse concentration). We would thus write

$$\frac{[N_2]}{[N_1]^2} = K_2 \quad (16)$$

$$\frac{[N_3]}{[N_1][N_2]} = K_3$$

or substituting the precedent expression

$$\frac{[N_3]}{[N_1]^3} = K_2 K_3$$

and so on. In the case of an isolated chemical reaction (e.g. Eq. 16) the equilibrium constant indicates the volume per particle at which half of the particles are in monomeric state and half in dimeric. Indeed, due to particle conservation when $N_1 = N/2$, $N_2 = N/2$ and

$$K_2 = \frac{N/4V}{(N/2)^2} = \frac{V}{N} \Big|_{N_1 = \frac{N}{2}} \quad (17)$$

With the expression previously derived for the ideal gas of cluster (Eq. 13)

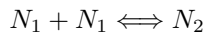
$$\frac{[N_2]}{[N_1]^2} = K_2 = \frac{Q_2}{Q_1^2 V}$$

$$\frac{[N_3]}{[N_1]^3} = K_2 K_3 = \frac{Q_3}{Q_1^3 V^2}$$

or

$$K_3 = \frac{Q_3}{Q_1 Q_2 V}$$

Chemical constant provide information on the change in free energy associated to the clustering process at fixed center of mass, e.g. independently from the system volume. For example, for the reaction



$$K_2 = \frac{N_2/V}{(N_1/V)^2} = V \frac{N_2}{N_1^2} = V \frac{Q_2 N_1^2 \Lambda^6}{N_1^2} = V \frac{V K_{bond}}{\Lambda^6} \Lambda^6 = K_{bond}$$

where

$$K_{bond} = \int' d\mathbf{r}_{12} e^{-\beta V(\mathbf{r}_{12})} \approx V_{bond} e^{\beta \epsilon}$$

THE SIMPLEST SELF-ASSEMBLY PROCESS. EQUILIBRIUM POLYMERIZATION

The simplest case of self-assembly refers to particles that can form two bonds each (e.g. particles with functionality $f = 2$) [9–12]. To evaluate the partition function we make a few approximations. First of all we consider that the surface of the particle is decorated with two patches on the poles, and that a bond is present between the two patches when the relative distance between the particles is within $\sigma + \Delta$ (like in a square well interaction) but also when the orientation of both patches involved in the bonds is within a cone of semiamplitude $\cos \theta$. This model is commonly named Kern-Frenkel [13]. For example, for a dimer we have

$$Q_2 = \frac{1}{2! \Lambda^6} \int' d\vec{r}_1 d\vec{r}_2 d\Omega_1 d\Omega_2 e^{-\beta V(\vec{r}_1, \vec{r}_2, \Omega_1, \Omega_2)} / \int d\Omega_1 d\Omega_2 \quad (18)$$

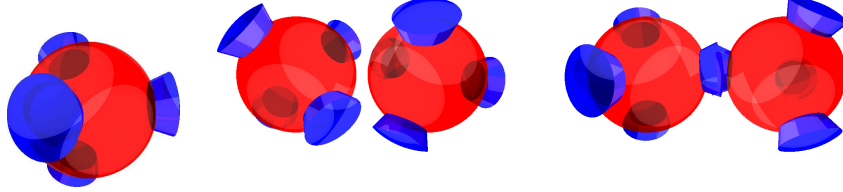
With the simple model selected, the Boltzmann factor $\exp(\beta \epsilon)$ is constant in all points in space where a bond is present. Changing variable to \vec{r}_1 and $\vec{r}_2 - \vec{r}_1$, the integration over \vec{r}_1 is immediate and gives a V term. The integration over $\vec{r}_2 - \vec{r}_1$ is limited for relative distances between σ and $\sigma + \Delta$ and so it gives $\frac{4}{3} \pi [(\sigma + \Delta)^3 - \sigma^3]$ while the integration over angles. Normalized by the $(4\pi)^2$ factor, gives a contribution $(\frac{1 - \cos \theta}{2})^2$. This last term correspond to the coverage χ (the fraction of the sphere surface associated to bonding) squared. The resulting partition function is

$$Q_2 = \frac{V}{2\Lambda^6} f^2 \frac{4}{3} \pi [(\sigma + \Delta)^3 - \sigma^3] \chi^2 \exp(\beta \epsilon)$$

where the term f^2 counts the four ways a bond can be formed between two particles with two patches each. Condensating in a term commonly named bonding volume $V_b \equiv \frac{4}{3} \pi [(\sigma + \Delta)^3 - \sigma^3] \chi^2$, one can write in a transparent way

$$Q_2 = 2 \frac{V V_b}{\Lambda^6} \exp(\beta\epsilon) = \frac{V}{\Lambda^3} Q_{bond} \quad Q_{bond} = 2 \frac{V_b}{\Lambda^3} \exp(\beta\epsilon) \quad (19)$$

where the term V/λ^3 indicates the contribution to the partition function associated to the exploration of the system volume of the cluster center of mass, while the remaining part is the bond partition function in which the term $2V_b/\lambda^3$ counts the number of microstates associated to the existence of the bond and $\exp(\beta\epsilon)$ is the Boltzmann term, which depends on the ratio between the bond energy and the thermal energy.



Pictorial representation of a $f = 4$ Kern-Frenkel particle (left), in a non-bonded dimer configuration (center) and in a bonded one (right)

Generalization to the case of a cluster of size n (neglecting self-avoiding contributions and under the assumption that there is no change in the bonding energy on clustering, the so-called isodesmic hypothesis, implicit in the simple classical potential we are using) the partition function can be written as

$$Q_n^{f=2} = \frac{\omega_n}{n! \lambda^{3n}} V [V_b^{11} \exp(\beta\epsilon)]^{\#_b} \quad (20)$$

with $\#_b = n - 1$ and

$$\frac{\omega_n}{n!} = 2^{n-1} \quad (21)$$

where ω_n counts the number of distinct bonded chains that can be formed by n distinguishable particles. To calculate ω_n one considers that the first particle can be selected in n ways and that it has two possible bonding configurations. The second one among the $n - 1$ remaining particles, always with two bonding possibilities. Hence

$$\omega_n = 2n \times 2(n-1) \times 2(n-2) \times \dots \times 2 = n! 2^{n-1}$$

and

$$Q_n^{f=2} = 2^{n-1} \frac{V}{\lambda^3} \left[\frac{V_b}{\lambda^3} \exp(\beta\epsilon) \right]^{n-1} = \frac{V}{\lambda^3} \left[2 \frac{V_b}{\lambda^3} \exp(\beta\epsilon) \right]^{n-1} = \frac{V}{\Lambda^3} Q_{bond}^{n-1} \quad (22)$$

which can be interpreted as the center of mass partition function (V/Λ^3) and the bonds $(n - 1)$ partition function Q_{bond}^{n-1} .

The cluster size distribution is then given by

$$N_n = \frac{N_1^n}{Q_1^n} Q_n = \left(\frac{N_1 \lambda^3}{V} \right)^n \frac{V}{\lambda^3} Q_{bond}^{n-1} = \rho_1 V (\rho_1 \lambda^3 Q_{bond})^{n-1} = N_1 (\rho_1 \lambda^3 Q_{bond})^{n-1} = N_1 e^{(n-1) \ln(\rho_1 \lambda^3 Q_{bond})}$$

e.g. an exponential distribution of polymer lengths, with characteristic decay $\bar{n} = -[\ln(\rho_1 \lambda^3 Q_{bond})]^{-1}$.

In chemical language, the case of equilibrium polymerization correspond to assuming that the equilibrium constant K_n are all identical and equal to K_2 . Under this hypothesis,

$$\frac{[N_n]}{[N_1]^n} = K_2 K_3 \dots K_n = \prod_2^n K_n = K_2^{n-1}$$

and

$$N_n = N_1^n (K_2/V)^{n-1} = N_1 (K_2 \rho_1)^{n-1}$$

and remembering that $K_2 = \frac{Q_2}{Q_1^2 V}$ we recover the same expression we derived thermodynamically in the previous section

$$N_n = N_1 (Q_b \rho_1 \lambda^3)^{n-1}$$

COOPERATIVE POLYMERIZATION: SLAVED EQUILIBRIUM POLYMERIZATION

A relevant case of self-assembly is provided by the "explosive" formation of very long one dimensional aggregates (fibers, fibrils and so on) [14?]. In this cases, a very small change in the external control parameters determines the formation of extremely long chains. Behind this important case is the presence of two mechanisms. A very slow preliminary aggregation process, with a very small reaction constant and a following aggregation process with a large reaction constant. A typical example is provided by the coil to helix transition, where first four monomers need to arrange in an proto-helix configuration and then the helix polymerization is rather fast.

This time let's formulate the problem in chemical language first and then look at the thermodynamic analog. Let's start with the usual expressions

$$\frac{[N_2]}{[N_1]^2} = K_2$$

$$\frac{[N_3]}{[N_1][N_2]} = K_3$$

but this time we assume that K_3 and K_4 are unrelated, while all successive terms are equal to K_3 . In other words, we assume that first one need to nucleate a dimer and then the dimer can grow with an isodesmic process. In this case

$$\frac{[N_n]}{[N_{n-1}][N_1]} = K_3, \quad n \geq 3$$

In terms of concentrations

$$\frac{[N_2]}{[N_1]^2} = K_2$$

and

$$\frac{[N_n]}{[N_1]^n} = K_2 K_3^{n-2}, \quad n \geq 3$$

The total monomer concentration can thus be written as

$$\rho = \sum_1^{\infty} n[N_n] = [N_1] + 2K_2[N_1]^2 + \sum_3^{\infty} nK_2K_3^{n-2}[N_1]^n = [N_1] + \sum_2^{\infty} nK_2K_3^{n-2}[N_1]^n$$

and using

$$\sum_2^{\infty} nx^n = \frac{(2-x)x^2}{(1-x)^2}$$

$$\rho = [N_1] + \frac{K_2}{K_3} \frac{(2 - K_3[N_1])K_3[N_1]^2}{(1 - K_3[N_1])^2}$$

By multiplying for K_3 and defining $\Sigma \equiv \frac{K_2}{K_3}$ one obtains a a-dimensional expression

$$K_3\rho = K_3[N_1] + \Sigma \frac{(2 - K_3[N_1])K_3^2[N_1]^2}{(1 - K_3[N_1])^2}$$

Fig. 2 shows that for small Σ the total density coincides with the monomer density till $\rho = K_3^{-1}$ and then it abruptly decay to zero.

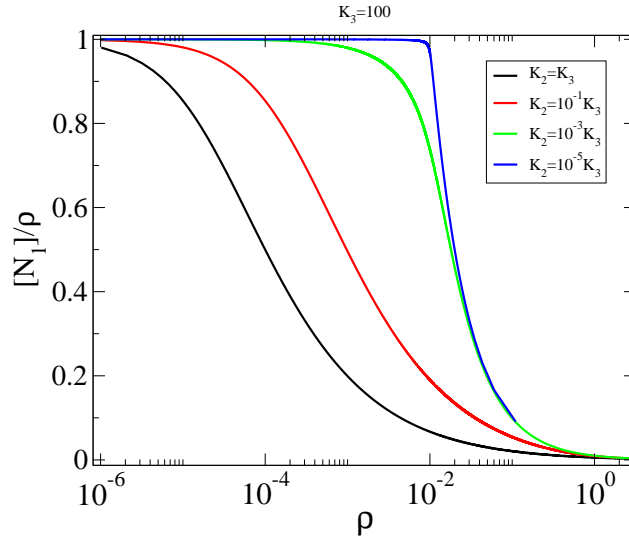


FIG. 2. Plot of the fraction of particles in monomeric state $[N_1]/\rho$ as a function of the total density ρ for different values of the ratio K_2/K_3 . Note the abrupt onset of polymerisation when K_2/K_3 is small.

Recently, a simple model for patchy particles interacting with pair-wise additive interactions has been shown to undergoes cooperative polymerisation [15], forming abruptly extremely long tuber, as shown in Fig. 3

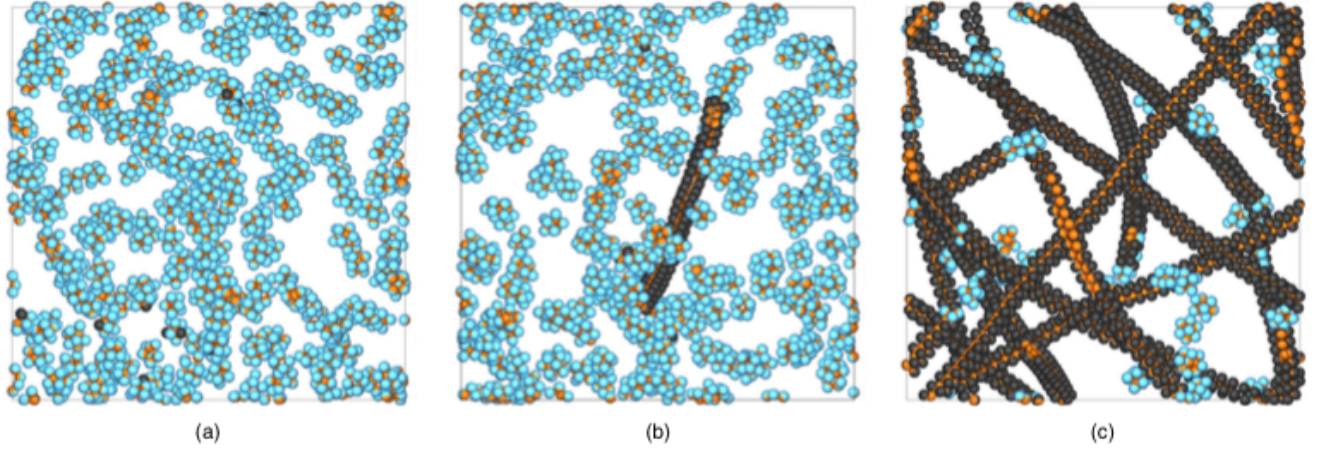


FIG. 3.

MICELLES

In this section I present a minimal model for micelle aggregation [16?]. For the sake of simplicity I assume that particles can only exist in monomeric state or in a cluster of $M \gg 1$ particles (the micelle)

As we have demonstrated previously, in the case of an ideal gas of non-interacting clusters

$$N_M = Q_M \frac{N_1^M}{Q_1^M}$$

Then, indicating with N the original number of particles in the system

$$N = N_1 + MN_M = N_1 + MQ_M \frac{N_1^M}{Q_1^M}$$

or

$$\frac{N_1}{N} = 1 - MQ_M \frac{N_1^M}{NQ_1^M}$$

Now we can write, assuming that a micelle has a well defined energy E_M in all of its configurations, the partition function of the micelle as

$$Q_M = \frac{V}{\lambda^3} \left(\frac{V_b}{\lambda^3} \right)^{M-1} \exp(-\beta E_M)$$

to emphasize the entropic and energetic (or enthalpic) contributions and the partition function of the monomer as $Q_1 = \frac{V}{\lambda^3}$. Then

$$\frac{N_1}{N} = 1 - M \frac{V}{\lambda^3} \left(\frac{V_b}{\lambda^3} \right)^{M-1} \exp(-\beta E_M) \frac{N_1^M}{N \left(\frac{V}{\lambda^3} \right)^M}$$

and after some algebra

$$\frac{N_1}{N} = 1 - M \left(\frac{N_1}{N} \right)^M \left(\frac{NV_b}{V} \right)^{M-1} \exp(-\beta E_M) \quad (23)$$

which can be written symbolically $x = 1 - x^M A$, with $A = M \left(\frac{NV_b}{V} \right)^{M-1} \exp(-\beta E_M)$. Fixing the properties of the micelle (M and the model parameters V_b and E_M) it is possible to solve Eq. 23 for all densities and temperatures. The solution for N_1/N depends on the value of A . For values of A smaller than one, $N_1/N \approx 1$ and the system is a monomeric state. For A greater than N , $\rho_1 \equiv N_1/V$ reaches a constant value, as shown in Fig. . Note also that both the entropic and the energetic contributions scale with M . Hence, the cross-over from values smaller than 1 to values larger than 1 is extremely fast. The concentration for which $A = 1$ is commonly indicated critical micelle concentration (cmc). Fig. 5 in Ref. ?? shows the analog of Fig. for the case of Janus colloidal particles aggregating in micelles and vesicles.

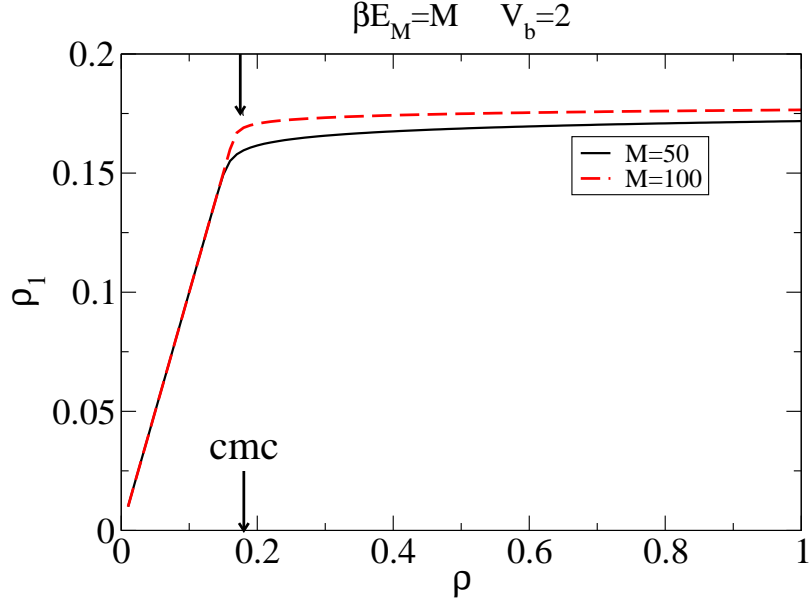


FIG. 4. Monomer density as a function of the total density for a system forming micelles composed each of $M = 100$ particles. The critical micelle concentration (cmc) marks the cross-over from the monomeric state to the aggregated micellar state. Beyond the cmc, increasing the density results in an increase of the number of micelles. No significant changes of the monomer density takes place.

The partition function Q_n for a cluster with a given size n , can be evaluated numerically [17–19]. An efficient numerical method is outlined in Refs. [19, 20], in which the relations between the various Q_n is obtained directly from a grand-canonical Monte Carlo (GCMC) simulation, i.e. a simulation at fixed T , V and chemical potential μ . The simulation starts with a single cluster and rejects all moves (insertion, deletion, translation or rotation) in which the system breaks into more than one cluster. By imposing the constraint of simulating only a single cluster, in the grand-canonical ensemble, the probability $\mathcal{P}(n)$ of observing a cluster of size n is

$$\mathcal{P}(n) = \frac{e^{n\beta\mu} Q_n}{\sum_n e^{n\beta\mu} Q_n}$$

so that

$$\frac{\mathcal{P}(n)}{\mathcal{P}(1)} = \frac{Q_n}{Q_1} e^{\beta\mu(n-1)}. \quad (24)$$

Hence, the ratio Q_n/Q_1 can be directly obtained for all n from a GCMC simulation. Note that Q_n/Q_1 is independent of μ , and therefore one can set $\mu = 0$ in the grand-canonical simulation without loss of generality. With this choice,

$$Q_n = \frac{\mathcal{P}(n)}{\mathcal{P}(1)} Q_1 = \frac{V}{\Lambda^3} \frac{\mathcal{P}(n)}{\mathcal{P}(1)}. \quad (25)$$

The procedure can be numerically optimised in several ways, as described in Refs. [19, 20]. Fig. 5 shows a comparison between the cluster size distribution calculated with the described methodology and the cluster size observed in standard Monte Carlo simulations for a Janus colloid model.

CONCLUSIONS

In this short lecture, I have presented some basic self-assembly introductory concepts. Building on these concepts, I hope it will be possible to better grasp the contents of the following lectures, and the sophisticated level of understanding and exploitation of self-assembly which is nowadays possible in colloidal science. Specifically, I like to recall two important aspects: (i) how to predict the structure of the aggregate from the knowledge of the interaction potential (direct) or how to design the interaction potential to spontaneously assemble a desired structure (inverse); (ii) how to exploit external fields to modify the pathways leading to self-assembly.

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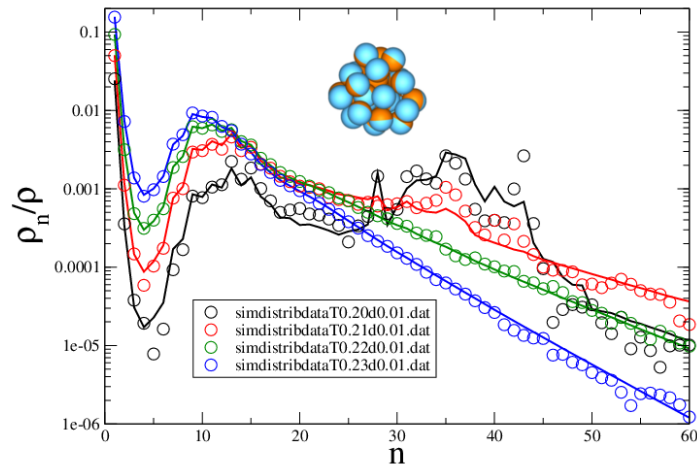


FIG. 5. Cluster size distributions at a density $\rho\sigma^3 = 0.01$ as a function of cluster size n for four different temperatures $k_B T / \epsilon = 0.20$, $k_B T / \epsilon = 0.21$, $k_B T / \epsilon = 0.22$, and $k_B T / \epsilon = 0.23$. The lines indicate the results from the single-cluster simulations, and the points are directly obtained from NVT-simulations. In the inset, a cluster consisting of 28 Janus particles is shown. Reproduced from Ref. [20]

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