
Nucleation phenomenon in nanoparticle self-assemblies

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Abstract: Dispersed nanoparticles self-assemble into complex structures when segregated from the solvent either by evaporation or precipitation. Thus, different micro- and macroscopic structures (opals, fractals, liquid crystals) formed by nanoparticles are observed as a result of the balance between electrostatic forces, surface tension, volume exclusion, substrate topography and affinity, and size, shape and concentration of the particles. The formation process is close to the hard-sphere case with two special features: nanoparticles are coated with surfactant molecules of roughly 1 nm in length, and nanoparticles are in the nanometric scale resulting in an increased mobility. Moreover, self-assembly does not take place in solution; hence, a minimum concentration is needed in order to start self-assembly. This process occurs in contact with the substrate, when the solvent cannot re-disperse the particles anymore.

Keywords: magnetic nanoparticles; self-assembly; solvent evaporation; two-dimensional.

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1 Introduction

Nanoparticle (NP) self-assembly (SA) phenomenon is commonly observed but only partially explained or understood. The remaining question being through which series of events the NP from a colloidal solution form the self-assembled structures upon evaporation of the solvent. Some appealing examples are extended 2D monolayers [1], bimodal arrays [2], 3D super-crystals of one [3] or different types of particles [4], structures formed by applying an external magnetic field [5], chains [6] and ring shapes [7], among others.

The genuine interest of understanding SA is the aim to make new molecular-based materials [8] from a bottom-up perspective, which should deliver more efficient systems in terms of the energy needed to produce them and implement Nature's

multi-functionality. Consequently, aggregation control is desirable; this can be achieved either by using biological molecules and their specific interactions [9,10], templates like porous matrix [11] or directing the SA. NP SA process is close to the large hard-sphere case with two special features:

- nanoparticles are coated with surfactant molecules of roughly 1 nm in length
- they are in the nanometric scale, which results in an increased mobility.

The transition between the hard spheres and the NP behaviour takes place when the thermal energy overcomes gravitational interaction (around 50 nm) [12,13]. In addition, such SAs do not take place in the dispersed colloid, indicating that a minimum value of the concentration is needed to start the process, in which case, the solvent cannot re-disperse the particles anymore. It has been proposed that, despite the difference in morphology, the formed structures could be explained with a long-range potential, which is attractive at long distances and repulsive at short ones [13,14]. The attractive force is expected to be van der Waals between highly polarisable metallic particles. The origin of the repulsion is not clear yet. Understanding the SA entails understanding of:

- the agglomeration process from a disperse solution
- the final dry arrangements of those agglomerates.

2 Experimental

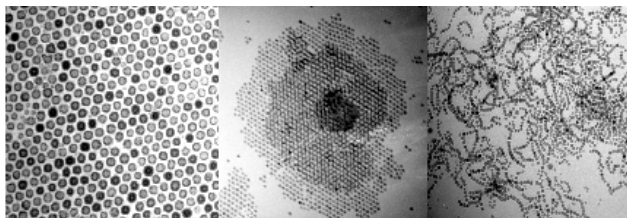
We used magnetic cobalt nanoparticles due to the ease of preparing large quantities of highly concentrated (10^{16} particles/ml) colloidal solutions of monodispersed NP [6,15] and their ability to agglomerate when their magnetic moment is large and stable. In such a way, by monitoring the magnetic dipole-dipole interaction, we may be able to explore more elusive forces acting on the NP assemblies.

Nanocrystal super-structures were investigated by transmission electron microscopy at 200 kV. A drop of the colloids (2% weight of particles) was put onto a carbon-coated TEM grid at room temperature and slowly evaporated (in a covered watch glass). The use of high boiling solvents (like *o*-dichlorobenzene) allows for slow evaporation at room temperature (RT), which permits the particles to diffuse towards their equilibrium structures during evaporation, producing well-defined super-structures. Depending on the picture capture system (negatives or digital camera), nanoparticles appear as white in a dark background or reverse.

3 Results

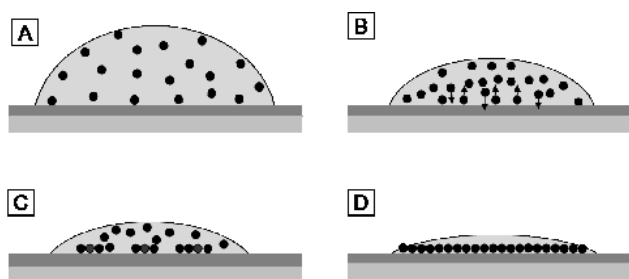
First, it is clear that SA does not occur either in the dispersed colloid, or in the colloid vessel walls (colloids are stable for months to years; it is well known that original Michael Faraday's colloids are still stable more than 150 years later). Besides, in addition to the well-known 2D SA, 3D structures that are repeated randomly on the substrate and chain-like arrangements crossing each other (Figure 1) suggest that the particles have mobility in the three directions of space while self-assembling. Thus, a minimal solvent amount has to be present even in the late stages of the self-assembling.

Figure 1 TEM images (left) 2D self-assembly of 9 nm Co NP, (centre) island of 7 nm NP (such islands were regularly present around the whole TEM grid) and (right) chains of 13 nm Co NP



These facts are difficult to explain just by the reduction in the size of the solvent droplet. In that case, the structure would be determined by the size and shape of the droplets when the solvent layer breaks [16,17]. It would be difficult to explain non-spherical drops or overlapping structures in such scenario. It seems clear that the size and concentration of the droplet and solvent dewetting will determine both the maximum size of the self-assembled structures and the number of particles in them. A minimum concentration is needed in order to start self-assembling, which lasts until there is no more solvent to allow particles to move and then, the structure freezes. It is likely that particles feel an effective attraction by the substrate (see Figures 2(a), (b)). Therefore, as a particle arrives at the substrate, it sticks to it for a while before going back to the solution. When the concentration is very high, the mobility of the particles out of the substrate surface is reduced and then SA starts (see Figure 2(c)), due to both a reduction in available positions for the NP and an increase in the self-assembled structure stability. At the same time, the structure itself becomes more ordered as more particles arrive at the growing structure (see Figure 2(d)). As experiments modifying evaporation temperature and time suggest, SA is a sort of collective behaviour rather than an analogue to an atom-by-atom aggregation process.

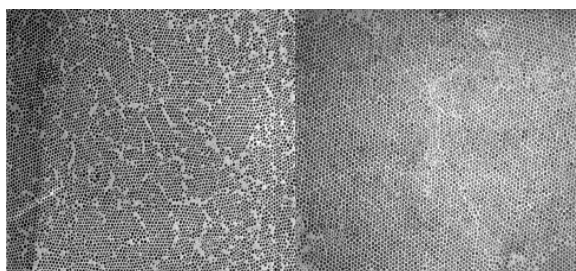
Figure 2 Schematic view of the NP mobility reduction as the solvent evaporation progresses



Then, once the concentration crossover regime is reached, the particles start self-assembling onto the substrate, since the concentration is always higher on its surface than in the solvent. This fact, together with a higher affinity of the particles to bond to the substrate than to other particles, favours 2D over 3D SAs. This balance between NP-NP and NP-substrate affinity may be modified by varying the hydrophobic/hydrophilic character of the substrate. In our case, both particles and substrate are highly hydrophobic, although the presence of the surfactant molecules results in a steric repulsion between particles and a lower NP-NP affinity.

In large 2D SA, well-defined boundaries between ordered domains are often observed (see Figure 3). This could be explained in two ways: the expulsion of defects to the border of the ordered area, or the occurrence of multiple nucleation events on the substrate, which induces the appearance of domain boundaries as a result of a defective percolation process. Both mechanisms support the idea that particles are able to move during structure formation, i.e., there is still solvent left in contact with the substrate, which is consistent with other observations [1].

Figure 3 TEM images of 8 nm Co NP, where domain boundaries between ordered regions are observed. In the left image, the density of defects is higher than that in the right one

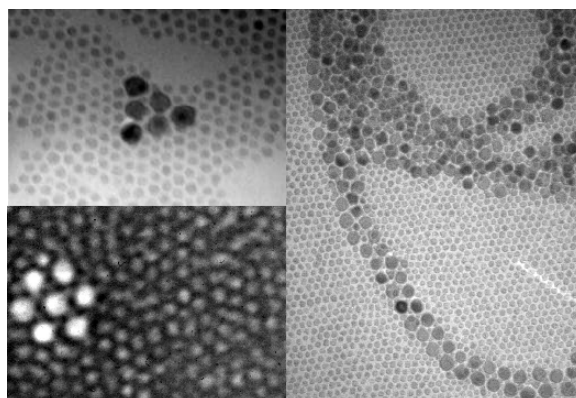


It could be assumed that the particles self-assemble in solution at very high concentrations (prior to deposition) when the majority of the solvent has been evaporated but still lose from the substrate, and then the structure is transferred to the substrate when the evaporation is completed. However, this simple scenario has been discarded by the work of Liangshi et al. [18], in which different structural patterns and dynamics were obtained with different substrates, indicating that, apart from concentration increase, substrate affinity also plays a crucial role [19]. This issue can be further corroborated by investigating the effect of NP mobility reduction by evaporating them onto substrates with different affinities. In Puntès et al. [20], a similar sample was evaporated onto a (111) single silicon crystal amine-functionalised substrate obtaining disordered Co monolayers. Amines are known to bind strongly to Co and, therefore, to reduce particle mobility onto such a substrate. These results suggest that certain mobility is needed once the nanoparticle reaches the substrate or the growing crystal, in order to form ordered structures.

Particle mobility is related to its size [21]; therefore, in the case of bimodal size distributions, particles self-assemble with similar ones and the smaller ones appear to be beneath the larger (Figure 4 left), as a result of the different mobility. Tilting experiments have been performed that confirm that the smaller particles are beneath. This is also observed when large magnetic particles make chain-like arrangements and small ones form triangular arrays (Figure 4 right). The fact that small particles are below can be easily checked by observing that their periodicity is not interrupted by the presence of the larger ones. The formation of these structures is surprising, since the solubility of the large particles and magnetic correlated assemblies are supposed to be smaller than that of the smaller ones. However, it is probable that the large mobility of the smallest particles and their strong affinity for the substrate are responsible for this phenomenon. Similar size segregation is obtained with different shapes as reported in Figure 2 of Puntès et al. [15]. This is not always the case for bimodal distributions. For instance, special geometric relationships between the particle diameters yield bimodal ordered

structures [2,4]. In these cases, a particular relationship between the particle ratios seems to favour more complex SAs without selective size segregation, in which the smallest particles are located in interstitial sites. In the case of polydisperse NP, the results observed are even more complex, the large particles being at the centre of the SA, acting as nucleation sites, with the smaller ones progressively surrounding them [22]. All these observations also suggest long-range collective effects in the SA process, which would be more important in the case of monodisperse NP.

Figure 4 Self-assembly of Co NP with two different sizes: (left) 6 and 8 nm and (right) 7 and 13 nm



In ferromagnetic materials, the dipolar magnetic interactions between particles add a new term in the energy balance, and they are not screened or affected by the surrounding materials (solvent, substrate, surfactants, etc.). In particular, as the mean dipolar energy increases with the particle volume, the thermal energy at RT becomes comparable to the dipolar energy of two sticking Co particles of about 12 nm. In particular, Co NP larger than about 16 nm tends to form chains and a variety of linear structures (see Figure 1 of Puentes et al. [6]).

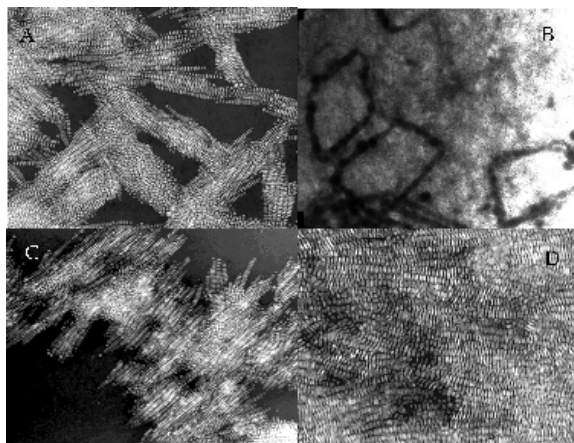
Other peculiar structure formation occurs with NP disks [15], which can be synthesised by the anisotropic growth of the crystal facets coated with different surfactants [23]. In this case, the disks tend to stack forming ribbons, which agglomerate in bundles (Figure 5(a)). Such agglomerates precipitate slowly from the colloid, being easily re-dispersible by mild agitation. These ribbons may appear as a result of three mechanisms:

- the different affinity of the disk crystal facets
- close packing
- magnetic dipolar interactions.

Taking into account that the ribbons constituted of magnetic disks show some peculiarities in their morphology with respect to the non-magnetic case [24], dipolar interactions should be partially responsible for the observed structures in Co. With increasing evaporation time, the observed structures (see Figure 5(a)) tend to anneal forming arrangements without open ends to satisfy flux closure, as those in Figure 5(b). A tendency of the magnetic disk assemblies to form parallel arrangements is usually

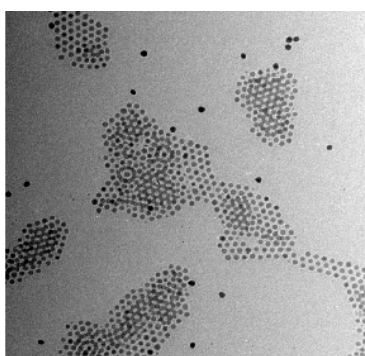
observed (Figure 5(c), (d)), this tendency being enhanced by applying an external magnetic field.

Figure 5 TEM images of Co nanodisks deposited under different conditions. Bars are 100 nm



Finally, in the case of droplet confinement as the main driving force for SA [16,17], contrary to the expected formation of close-packed structures, a consistent expansion of the first monolayers of the 2D structures is observed for a wide variety of NP. Such expansion could be related to particle mobility onto the substrate prior to total evaporation of the solvent. However, if the particles were just randomly moving and colliding until complete evaporation, ordered arrays would not be observed. This is a further evidence of the effect of long-range interactions on the formation of SA. This effect was first reported by Zanchet et al. [25] in Au NP, which dispose forming honey-comb expanded structures [26]. In the case of Co, particles maintain the triangular arrangement but not in a compact manner, leading to intricate structures (Figure 6).

Figure 6 TEM image of 8 nm Co NP self-assembly. Second layer does not properly sit in an HCP structure, due to the expansion of the first monolayer



In conclusion, the study of SA processes is relevant not only to built up super-structures for specific applications (such as compact monolayers for magnetic recording media) but also to elucidate the out-of-equilibrium behaviour of NPs in liquid media, aiming, for instance, at their integration in biological environments.

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References

- 1 Lin, X.M., Jaeger, H.M., Sorensen, C.M. and Klabunde, K.J. (2001) 'Formation of long range-ordered nanocrystal superlattices on silicon nitride substrates', *Journal of Physical Chemistry B*, Vol. 105, pp.3353–3357.
- 2 Kiely, C.J., Fink, J., Brust, M., Bethell, D. and Schiffrin, D.J. (1998) 'Spontaneous ordering of bimodal ensembles of nanoscopic gold clusters', *Nature*, London, Vol. 396, pp.444–446.
- 3 Murray, C.B., Kagan, C.R. and Bawendi, M.G. (2000) 'Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies', *Annual Review of Materials Science*, Vol. 30, pp.545–610.
- 4 Redl, F.X., Cho, K-S., Murray, C.B. and O'Brien, S. (2003) 'Three-dimensional binary superlattices of magnetic nanocrystals and semiconductor quantum dots', *Nature*, London, Vol. 423, pp.968–971.
- 5 Yin, J.S. and Wang, Z.L. (1999) 'Preparation of self-assembled cobalt nanocrystal arrays', *Nanostructured Materials*, Vol. 11, pp.845–852.
- 6 Puentes, V.F., Krishnan, K.M. and Alivisatos, A.P. (2001) 'Colloidal nanocrystal shape and size control: the case of cobalt', *Science*, Vol. 291, pp.2115–2117.
- 7 Maillard, M., Motte, L., Ngo, A.T. and Pileni, M.P. (2000) 'Rings and hexagons made of nanocrystals. a marangoni effect', *Journal of Physical Chemistry B*, Vol. 104, pp.11871–11877.
- 8 Alivisatos, A.P., Barbara, P.F., Castleman, A.W., Chang, J., Dixon, D.A., Klein, M.L., McLendon, G.L., Miller, J.S., Ratner, M.A., Rossky, P.J., Stupp, S.I. and Thompson, M.E. (1998) 'From molecules to materials: current trends and future directions', *Advanced Materials*, Vol. 10, pp.1297–1336.
- 9 Li, M., Schnablegger, H. and Mann, S. (1999) 'Coupled synthesis and self-assembly of nanoparticles to give structures with controlled organization', *Nature*, London, Vol. 402, pp.393–395.
- 10 Loweth, C.J., Caldwell, W.B., Peng, X., Alivisatos, A.P., and Schultz, P.G. (1999) 'DNA-based assembly of gold nanocrystals', *Angewandte Chemie*, Vol. 38, pp.1808–1812.
- 11 Kónya, Z., Puentes, V.F., Kiricsi, I., Zhu, J., Alivisatos, A.P. and Somorjai, G.A. (2002) 'Nanocrystal templating of silica mesopores with tunable pore sizes', *Nano Letters*, Vol. 2, pp.907–910.
- 12 Gravity force for a 10 nm Co nanoparticle is 0.04 fN, while the force associated to the [13] Brownian motion at 300 K is 4 fN.
- 13 Gelbart, W., Sear, R.P., Heath, J.R. and Chaney, S. (1999) 'Array formation in nano-colloids: theory and experiment in 2D', *Faraday Discussions*, Vol. 112, pp.299–307.
- 14 Sear, R.P., Chung, S.W., Markovich, G., Gelbart, W.M. and Heath, J.R. (1999) 'Spontaneous patterning of quantum dots at the air-water interface', *Phys Rev. E*, Vol. 59, pp.R6255–R6258.
- 15 Puentes, V.F., Zanchet, D., Erdonmez, C.K. and Alivisatos, A.P. (2002) 'Synthesis of HCPP. Co nanodisks', *Journal of the American Chemical Society*, Vol. 124, pp.12874–12780.
- 16 Pamela, C.O. and William, M.G. (1998) 'Interplay between hole instability and nanoparticle array formation in ultrathin liquid films', *Langmuir*, Vol. 14, pp.3418–3424.

- 17 Govor, L.V., Reiter, G., Bauer, G.H. and Parisi, J. (2004) 'Nanoparticle ring formation in evaporating micron-size droplets', *Applied Physics Letters*, Vol. 84, pp.4774–4776.
- 18 Liang-shi, L., Walda, J., Manna, L. and Alivisatos, A.P. (2002) 'Semiconductor Nanorod Liquid Crystals', *Nano Letters*, Vol. 2, pp.557–560.
- 19 Rabani, E., Reichman, D.R., Geissler, P.L. and Brus, L.E. (2003) 'Drying-mediated self-assembly of nanoparticles', *Nature*, London, Vol. 426, pp.271–274.
- 20 Puntès, V.F., Gorostiza, P., Aruguete D.M., Bastus N.G. and Alivisatos, A.P. (2004) 'Collective behaviour in two-dimensional cobalt nanoparticle assemblies observed by magnetic force microscopy', *Nature materials*, Vol. 3, pp. 263–268.
- 21 Root Mean Velocity (RMS): $V \text{ (RMS)} = (3RT/M)^{0.5}$ $R = 8.314 \text{ Joule/(Mole} \times \text{Kelvins)}$
T = Kelvin Temperature, M = molecular weight $\times 0.001$ (to give kilograms/mole).
- 22 Pamela C., Leff, D.V., Heath, J.R. and Gelbart, W.M. (1995) 'Crystallization of opals from polydisperse nanoparticles', *Physical Review Letters*, Vol. 75, pp. 3466–3469.
- 23 Peng, X., Manna, L., Yang, W., Wickham, J., Scher, E., Kadavanich, A. and Alivisatos A.P. (2000) 'Shape control of CdSe nanocrystals', *Nature*, London, Vol. 404, pp.59–61.
- 24 Jin, R., Cao, Y.C., Hao, E., Metraux, G.S., Schatz, G.C. and Mirkin, C.A. (2003) 'Controlling anisotropic nanoparticle growth through plasmon excitation', *Nature*, London, Vol. 425, pp.487–490.
- 25 Zanchet, D., Moreno, M.S. and Ugarte, D. (1999) 'Anomalous packing in thin nanoparticle supercrystals', *Physical Review Letters*, Vol. 82, pp.5277–5280.
- 26 Shevchenko, E.V., Talapin, D.V., Rogach, A.L., Kornowski, A., Haase, M. and Weller, H. (2002) 'Colloidal synthesis and self-assembly of CoPt(3) nanocrystals', *Journal of the American Chemical Society*, Vol. 124, pp.11480–11485.