Gold Nanoparticles Under the Microscope

Gold Nanoparticles Under the Microscope. Patterned structures and surfaces are ubiquitous in nature: from the hide of a giraffe to the distribution of galaxies in the universe, similar repeating structural elements are seen on all length scales. These somewhat ordered structures can often be said to arise by a process of self-assembly or self-organisation. Self-assembly may prove to be an important tool for the future of nanotechnology; to design materials that build themselves rather than manually constructing devices from individual component parts is naturally compatible with mass-production. Atomic Force Microscopy (AFM) has shown that a wide range of quite complex structures can be produced simply by spin-casting a suspension of nanoparticles onto a substrate [1-3]. Morphological Image Analysis (MIA) techniques, in conjunction with Monte Carlo (MC) simulation, can lead us to a better understanding of the processes involved in this apparent self-organisation.

Far-from-Equilibrium Pattern Formation
Much research into self-assembly focuses on processes occurring close to equilibrium, such as the formation of self-assembled monolayers, or nanocrystal ‘superlattices’. In the latter case, solvent is evaporated very slowly, allowing each nanocrystal to find an equilibrium site. However, if we move to the extreme opposite end of the scale, driving the solvent off so rapidly that the system can be considered not only non-equilibrium, but far-from-equilibrium, then quite different results are obtained. Fig. 1a shows a schematic of the particles used in our experiments. Suspensions of these particles are generally stable for many months if not years, making them highly suitable for large-scale production and long-term study. When these suspensions are spincast onto native-oxide silicon substrates, a wide range of patterns is observed, with structures that vary depending on concentration, type of solvent, and surface chemistry of the substrate [1]. Fig. 1 shows two of these morphologies: panel b is an example of a bicontinuous structure, a morphology that is commonly associated with phase-separating systems that proceed by ‘spinodal’ mechanisms, and panel c, with a slightly higher particle concentration, shows what is commonly described as a cellular network.
This network looks much like the cracks that appear in drying mud, or the pattern on the hide of a giraffe. At higher concentration still, cellular structures begin to appear on two levels, with a larger network superimposed on a structure similar to Fig. 1c (not shown).

**Morphological Image Analysis**
The question of the origin of these structures can be investigated by the use of morphological image analysis (MIA) techniques. Perhaps the most commonly used of these is the **two-dimensional fast Fourier transform (2DFFT)**, which can pick out a directional or size preference of features in an image. However, in cases where the structure can be broken down into a series of points, such as the case of a cellular network, the Voronoi tessellation can provide complementary quantitative information. The **Voronoi tessellation** reduces a cellular network to a collection of tessellating polygons [4]. Two useful numbers that can be obtained from this construction are the variance of the probability of finding a cell with a given number of sides, and the entropy of the distribution of probabilities. Both of these quantities can be compared to the values expected for a random tessellation, and hence the degree of order of the structure can be established.

**Minkowski Functional Grain Growth**
Another technique for *analysing a distribution of points* is Minkowski functional grain growth [5]. In two dimensions, there are three Minkowski functionals. These are the total covered area, A, the perimeter, U, and the Euler characteristic, χ, of an image. The latter equals the number of regions of connected black pixels minus the number of enclosed regions of white pixels. If the points used for the Voronoi tessellation are used as germs for the growth of a two dimensional grain (e.g. a disc), then the values of A, U, and χ as a function of grain size can give us information about the distribution of the point set. Plots of these values can be compared to the known plots for a random distribution of points, and as with the Voronoi tessellation, the degree of order can be established.
Results from both techniques point strongly to a relatively high degree of order in Au cellular networks. This doesn’t directly resolve the question of the origin of these structures, but it does raise another question: what is the mechanism that drives these structures to order? Simulations have provided some interesting answers.

**Simulation**

The model used for our simulations is based on that of Rabani et al. [3], whereby the solvent is represented as a two-dimensional lattice gas, and fluctuations in solvent density and particle motion are controlled by the Metropolis algorithm. In brief, each cell of a square lattice may contain either liquid, vapour, or nanoparticle, and the particles are represented as 3 x 3 squares. Particles can only move into wet areas of the substrate, meaning once the vast majority of the solvent has evaporated, the structure becomes stable.

*Fig. 2* shows a series of images from a 4,008 x 4,008 simulation. The end result (2c) bears a striking resemblance to the network in *Fig. 1c*, and the radially-averaged 2DFFT (*panel 2d*) demonstrates there is a preferred cell size. In fact, comparison by Voronoi tessellation and **Minkowski functional analysis** reveals quantitatively indistinguishable morphology. So what is the mechanism in this case? This simulation represents behaviour best described as homogeneous thermal nucleation. Random thermal fluctuations lead to spatially uncorrelated nucleation of vapour bubbles, which grow until the vast majority of the solvent is gone. The conclusion we have reached in this case is that the apparent order arises from the limited time window available for nucleation, and the coalescence of adjacent cells [6]. The disorder of the original distribution of nucleation sites is hence replaced by a more ordered cellular array.

**Diverse Applications**

It has become apparent that the coarsegrained model used in these simulations can be applied to seemingly unrelated systems. *Fig. 3a* shows another simulation image, alongside 3b, an **AFM image** of dewetting organometallic clusters on silicon [7]. Once again, the qualitative similarity is striking, and Voronoi tessellation reveals no significant difference in morphology. Here, Minkowski functional analysis can prove its worth as a tool for comparison.

*Fig. 4* shows the **Minkowski grain growth plots** for both images. These plots not only demonstrate deviation from a random distribution, but also a near perfect agreement between simulation and experiment. This agreement is somewhat surprising, considering the systems are chemically and physically quite different. This suggests that the patterns in these two examples are controlled largely by the evaporation of the solvent: the final structures simply describe the history of evaporation. It seems probable that this model could be applied to other systems.
such as spin-cast polymer solutions [8], and in conjunction with MIA could shed light on formation mechanisms in a number of other areas.

**Outlook**

We have yet to form a complete understanding of pattern formation in nanoparticle systems. Recent results have indicated it may be possible to control the type of structures formed by local modification of the surface chemistry of the substrate [8]. This, in conjunction with the nonlinear electrical properties of gold nanoparticle arrays, could lead to the construction of novel devices in the future. In the meantime, morphological image analysis techniques such as Minkowski grain growth are likely to prove important in the understanding of pattern formation in many diverse systems.

**References :**


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