Understanding self-assembled nanosphere patterns

Ferenc Járai-Szabó, Simion Aștilean, and Zoltán Nédé
Babeș-Bolyai University, Dept. of Physics, str. Kogălniceanu 1, RO – 400084, Cluj-Napoca, Romania
(Dated: November 17, 2018)

Patterns generated by a colloidal suspension of nanospheres drying on a frictional substrate are studied by experiments and computer simulations. The obtained two-dimensional self-assembled structures are commonly used for nanosphere lithography. A spring-block stick-slip model is introduced for simulating the phenomenon and the influence of several controllable parameters on the final structure is investigated. The model successfully reproduces the experimentally observed patterns and the dynamics leading to pattern formation is revealed.

The so-called bottom-up approach for the fabrication of nanostructures starting from stable building blocks such as molecules or nanoparticles has become an increasingly popular topic in nanoscience and nanotechnology. Thanks to the efforts of nanochemists, during the past decades various nanoparticles of polystyrene, silica, noble-metal and semiconductor, nearly monodisperse in terms of size, shape, internal structure, and surface chemistry, can be produced through a reliable, standard manufacturing process. Using these nanoparticles as building blocks, the synthesis of long-range-ordered monolayers and films of colloidal nanocrystals has been in particular focus. The revolutionary development of photonic crystals triggered efforts to get innovative methods for crystallizing polystyrene colloids and creating new crystal structures. The use of two-dimensional (2D) self-assembled array of nanometer-sized polystyrene spheres as deposition mask is known as NanoSphere Lithography (NSL). The homogeneous arrays of nanoparticles produced using NSL are potentially useful in studies of size-dependent optical, magnetic, catalytic and electrical transport properties of materials. NSL is now recognized as a powerful fabrication technique to inexpensively produce nanoparticle arrays with controlled shape, size and interparticle spacing. A fundamental goal for further progress in NSL is the development of experimental protocols to control the interactions, and thereby the ordering of nanoparticles on solid substrates. However, it is more and more clear that due to the rich physics and chemistry underlying the formation of nanoparticle arrays from colloidal suspensions, the likelihood of structures other than close-packed networks forming during solvent evaporation is very high. Therefore a major motivation for theoretical research in this field remains the challenge to understand how ordered or complex structures form spontaneously by self-assembly, and how such processes can be controlled in order to prepare structures with a pre-determined geometry. The present study intends to contribute in this sense by proposing a model that can be easily studied through computer simulations and it is able to qualitatively reproduce the wide variety of observed patterns. We focus on an experimentally simple case, when 2D self-assembled arrays of nanometer-sized polystyrene spheres will form from a colloidal suspension which is drying on a substrate. Some characteristic patterns obtained as a result of this phenomenon are present in Figure 1.

The model is rather similar with the spring-block stick-slip model successfully used for describing fragmentation structures obtained in drying granular materials in contact with a frictional substrate. The new feature of the present model is that a predefined lattice is not considered anymore. Proceeding in such manner the final lattice structure appears as a result of the underlying interactions governing the dynamics of the system and the existing geometrical constraints.

The model is two-dimensional; its main elements are blocks which can move on a frictional substrate and springs connecting these blocks (Figure 2). Disks, all with the same radius, model nanospheres, while springs which are characterized by their variable length and similar spring constants, represents water bridges between them. The length of a spring is defined as the distance between perimeters of connected disks. There is also a Lenard-Jones type interaction-force, between each pair of disk. This is characterized by a strong, almost hard-core type repulsion which forbids disks to interpenetrate each other and by a weak attractive type force, accounting for the electric Van der Waals type in-
interaction between nanospheres (Figure 2a). The friction between disks and surface equilibrates a net force less than $F_f$ (Figure 2a). Whenever the total force acting on a disk exceeds $F_f$, the disk slips with an over-damped motion. The tension in each spring is proportional with the length of the spring ($F_k = k \cdot l$), and has a breaking threshold $F_b$ (Figure 2a).

Initially disks are randomly distributed and connected by a network of springs (Figure 2b). We put springs between those spheres, for which their center can be connected without intersecting another sphere (this condition will be referred later as the geometric condition). An initially pre-stressed spring-block network is thus constructed. During each simulation step the spring constant is fixed and the system relaxes to an equilibrium configuration where the tension in each existing spring is lower than the breaking threshold $F_b$, and the total net force acting on each disk is lower in magnitude than the slipping threshold $F_f$. This relaxation is realized through several relaxation steps. The time length $dt$ for each relaxation step is taken as unity ($dt = 1$). (Since we are interested mostly in the final, stable structure, connection with real time is not crucial for us, and we can define time units in an arbitrary manner.) Considering a classical molecular dynamics simulation for relaxation would be very time-consuming. Following the method used for simulating drying processes in granular media, we choose thus a simplified dynamics, where the connection with real time is lost, but the relaxation remains realistic:

1. For all springs the tension $|F_{ij}^k|$ is compared with $F_b$. If $|F_{ij}^k| > F_b$, the spring is broken and taken away from the system.

2. The total forces $\vec{F}_i = \sum_p \left( d_{ip} \vec{F}_{kp}^i + \vec{F}_{jp}^i \right)$ acting on disks are calculated (the sum is over all the other disks $p$, $d_{ip}$ is 1 if the disks are connected by a spring and 0 otherwise, the subscripts $k$ and $j$ denotes elastic forces from springs and Van der Waals type forces between disks, respectively).

3. Each disk is analyzed. If the magnitude of the total force $|\vec{F}_i|$ acting on a disk is bigger than $F_f$, then the disk will slip with an over-damped motion governed by viscosity $\eta$, and its position will be changed by: $\vec{r}_i^t = \vec{r}_i^{t-1} + \frac{\vec{F}_i}{\eta} dt$. The repulsive part of the Lenard-Jones potential forbids the spheres to slide on each other and the presence of viscosity eliminates unrealistic oscillations.

4. During the motion of a disk it can happen that another spring is intersected. This intersected spring will brake and it will be taken away from the system.

5. After all disks have been visited and their possible motions done, the springs that fulfill the considered geometrical condition and for which the tension is lower than the breaking threshold are redone. By this the rearrangement of water between nanospheres is modelled.

This concludes one relaxation step. The relaxation is continued until a relaxation step is finished without having any spring breaking or disk slipping event. Since in our algorithm it takes a very long time to achieve a perfect relaxation, we introduce a tolerance, and assume the relaxation completed when the maximal slip is smaller than this tolerance. After the relaxation is done, we proceed to the next simulation step and increase all spring constants by an amount $dk$. This models that water bridges are getting thinner and the capillary forces increase the tension in them as the water evaporates. The system is relaxed for the new spring-constant value, and the spring constant is increased again, until all springs are broken or a stable limiting configuration is reached.

The above dynamics can be easily implemented on computer and relatively big systems with over 10000 of disks can be simulated in reasonable computational time. Several types of boundary conditions can be considered. One possibility is the use of free boundary condition which can be realized in a simple manner by positioning initially the disks inside a circle to minimize the effect of edges. Another possibility is to consider fixed boundary conditions. This can be realized for example by positioning again the disks inside a circle and considering a chain of fixed disks on the chosen circle. These fixed disks are then connected with geometrically allowed springs to other disks. One can also consider periodic boundary condition and position initially the disks inside a rectangle. It is quite easy to check that the considered boundary condition will influence the final stable structure only in the vicinity of boundaries. In the bulk, far from the boundaries, the obtained structures are rather independent of the imposed boundary conditions. Simulation results presented here are taken from a small central part of systems with $N > 10000$ disks using fixed boundary conditions.
conditions.

The model, as described above, has several parameters: the value of the static friction $F_f$, the spring breaking threshold value $F_b$, the initial value of spring constants $k_{ini}$, the spring constant increasing step $dk$, the viscosity $\eta$, the parameters of the Lenard-Jones potential, the radius of disks $R$, and the initial density of nanospheres $\rho = S/(N\pi R^2)$ (where $S$ is the simulation area). By direct simulations one can verify that if small enough $dk$ is chosen, in the quasi-static limit the final structures are not sensitively influenced by this parameter. The model will only work for viscosity values chosen between reasonable limits, and for these viscosity values the final patterns are rather similar. (Choosing a too small viscosity will result in unrealistic oscillations of disks, while a too high value will make the disk slip too small and increase considerably the simulation time). It is desirable to choose the value of $k_{ini}$ small, to simulate the whole stress building process in the system. The Lenard-Jones potential is fixed, so that the repulsive part gives a strong hard-core repulsion for distances smaller than $2R$, and a small attractive contribution to the net force between pairs of disks for distances bigger than $2R$. The radius of disks were considered as unity ($R = 1$), defining the unit length in the system. We remain thus with three main parameters governing the generated patterns: $F_b$, $F_f$ and $\rho$. The influence of these three parameters on the final structure was investigated and the obtained structures were visually compared with experimentally obtained ones. It is worth mentioning here, that for a successful simulation the values of $\rho$ and $F_b$, have to be correlated. For small $\rho$ values the value of $F_b$ has to be chosen high enough, otherwise the majority of springs would break in the very first simulation step, and no clusterization would be observable.

The experimental samples were prepared using the drop-coat method [3, 6]. Of critical importance for nanosphere ordering is the chemical treatment of the glass substrate to render the surface hydrophilic and improve its wettability. This was achieved by etching the substrate in a solution of sulphuric acid/hydrogen peroxide (3:1) for a period of 3 hours. The substrates were then washed in a copious amount of deionized water, immersed in a solution of ultra pure water/ammonium hydroxide/hydrogen peroxide (5:1:1) for 2 hours and sonicated in an ultrasonic bath for 1 hour. Finally, the substrates were thoroughly rinsed in ultra pure water and stored under ultra pure water. Polystyrene nanospheres of 220 nm diameter, exhibiting negatively charged carboxyl-terminated surface with a strongly hydrophobic nature, were supplied as monodispersed suspensions in deionised water (wt 4%). The original suspension of polystyrene nanospheres was diluted by 10 and a volume of 100 l diluted solution was evenly spread on the pre-treated substrates. Finally, samples were dried in an oven at 65 °C for 45 minutes. As the water evaporates the nanospheres

FIG. 3: Characteristic simulation results for the influence of nanosphere density on final patterns.

self-assemble into close-packed monolayer arrays exhibiting many fracture lines, dislocations and other type of defects (Figure 4). The microstructure of the sample was studied by scanning electron microscopy (SEM) using a JEOL JSM 5600 LV electronic microscope. By surveying the substrate, surface regions with different morphologies were found even within the same sample. These qualitatively different structures will arise mainly due to the non-homogenous nanosphere concentration in different parts of the sample.

On Figure 4 we show computer simulation results for the influence of nanosphere density on the final structure. For high densities, in agreement with experimental results, we obtain close-packed domains (triangular lattice structure), separated by realistic fracture lines and defects. As the nanosphere density decreases we reproduce the experimentally observed isolated and elongated islands.

Similarly with the results obtained by Leung et al. [12] we observed that the topology of the final structure is strongly affected by the values of $F_f$ and $F_b$. Increasing the value of $F_f$ will result in denser and thinner fracture line structure with smaller close-packed domains (top line of Figure 4). Decreasing the value of $F_b$ results in a similar effect (bottom line of Figure 4). Experimentally one could control $F_f$ by changing the substrate and $F_b$ by changing the evaporating liquid.

The dynamics leading to formation of final structures can be also easily revealed through simulations (to do that experimentally is quite a difficult task). Some movies in this sense are presented on the home-page dedicated to this study [12]. The formation of close packed
FIG. 4: Simulation results investigating the influence of parameters $F_f$ and $F_b$ on the final patterns. On the top line $F_f$ is changing ($F_b = 0.05$), while on the bottom line the varied parameter is $F_b$ ($F_f = 0.005$). For all these simulations the other parameters were chosen as: $k_{ini} = 0.1$, $dk = 0.002$, $\rho = 0.749$, $\eta = 250$.

FIG. 5: Experimental (top) and simulation results (bottom) for the square lattice crystallization phase. (triangular lattice) domains separated by characteristic fracture lines is realized through a series of stick-slip avalanches, as the value of the spring constant is increased. The initial nanosphere configuration is quickly lost, and due to long-range elastic forces an intermediate square lattice multi-domain structure is formed (Figure 5, bottom line). This intermediate (metastable) structure is lost as $k$ increases further (long springs are broken) and slowly the triangular symmetry is selected.

During the relaxation of stress and non-homogeneity in the system, fracture lines are nucleated and propagated. This process will lead to the final characteristic pattern.

The intermediate square lattice structure can be also revealed by experiments, either by analyzing samples that are not completely dried, or by considering a quick, non quasi-static drying procedure. It is believed that in case of non quasi-static drying the nanosphere system is blocked in this intermediate, metastable phase. Experimentally, we have also obtained samples that show this intermediate square-lattice crystallization phase (Figure 5, top line). The success in reproducing this square-lattice crystallization phase and in general the qualitative agreement between simulation results (Figure 2-3) and the experimentally observed structures (Figure 1) encourages us to believe that the introduced model is a good one and the picture we got for the underlying dynamics is correct.

We have introduced thus a successful model for describing monolayer patterns that are formed on a surface after quasi-static drying of a colloidal nanosphere suspension. By using this model one can get a first picture on the underlying nano-scale dynamics and can analyze the influence of the experimentally adjustable parameters on these practically important structures.

*zneda@phys.ubbcluj.ro*

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