Available online at www.sciencedirect.com
SCIENCE DIRECT®
Chemical Physics Letters 408 (2005) 241–246
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

Understanding self-assembled nanosphere patterns

Ferenc Járai-Szabó, Simion Aştilean, Zoltán Néda *

Babeş-Bolyai University, Department of Physics, str. Kogălniceanu 1, RO-400084 Cluj-Napoca, Cluj, Romania

Received 7 February 2005; in final form 5 April 2005
Available online 13 May 2005

Abstract

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 molecules or nanoparticles has become an increasingly popular topic in nanoscience and nanotechnology. Nowadays 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 [1,2]. The use of two-dimensional (2D) self-assembled array of nanometer-sized polystyrene spheres as deposition mask is known as nanosphere lithography (NSL) [3]. 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 [3–6]. 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 [7,8]. However, due to the rich physics and chemistry involved in the formation of nanoparticle arrays from colloidal suspensions, it is more and more clear that the likelihood of getting structures other than close-packed networks after solvent evaporation is very high [9,10]. 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 [11]. As a first step in such direction, a coarse-grained model defined on a square-lattice was recently studied by Rabani et. al [12]. This model proved to be successful in reproducing the complex boundaries of the nanosphere clusters. It does not account, however, for the observed triangular and square lattice crystallization phases of nanospheres, or the characteristic dislocation and fracture lines within structures. The present study proposes a model that can be easily studied through computer simulations and is able to qualitatively reproduce the wide variety of patterns, inclusive dislocation lines and crystallization

* Corresponding author. Fax: +40 264 591906.
E-mail address: zneda@phys.ubbcluj.ro (Z. Néda).

0009-2614/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2005.04.051

phases. We focus on an experimentally simple case, when 2D self-assembled arrays of nanometer-sized polystyrene spheres form from a colloidal suspension which is drying on a substrate. Some characteristic patterns obtained as a result of this phenomenon are presented in Fig. 1. The photos on the top line illustrate qualitatively different fracture-line topologies within the ordered nanosphere array. Beside the short and dense diffusive cracks, long and straight fractures-lines are also visible. On the bottom line of Fig. 1 samples with different nanosphere density are presented. The characteristic clusters that form at low densities are clearly 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 h. 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 h and sonicated in an ultrasonic bath for 1 h. 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 (4 wt%). The original suspension of polystyrene nanospheres was diluted by 10 and a volume of 100 μl diluted solution was evenly spread on the pretreated substrates. Finally, samples were dried in an oven at 65 °C for 45 min. As the water evaporates, the nanospheres self-assemble into close-packed monolayer arrays exhibiting many fracture lines, dislocations and other type of defects (Fig. 1). The microstructure of the samples were 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. The qualitatively different structures are a result of the uncontrollable and thus non-homogenous nanosphere density on the substrate.

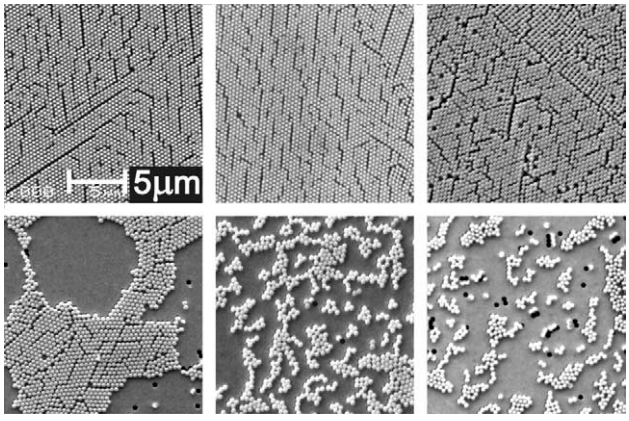

Fig. 1. Characteristic 2D patterns obtained from a colloidal suspension of 220-nm diameter nanospheres drying on a silica substrate.

Our model is rather similar with the spring-block stick-slip model, which was successfully used for describing fragmentation structures in drying granular materials in contact with a frictional substrate [13,14]. The new feature of the present model is that a predefined lattice is not considered anymore. 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 2D; its main elements are blocks which can move on a frictional substrate and springs connecting these blocks (Fig. 2d). Disks, all with the same radius R, model nanospheres, while elastic springs reproduce the capillarity effects of water between them. It worth mentioning that the coupling between nanospheres will behave as springs (i.e. the force will increase with the spacing) only in the case of a continuous film of liquid between them. In the present model, we use this assumption, however it would be also interesting to study the case when the film becomes discontinuous and clearly separated water-bridges form. In such case, the resulting coupling force decreases with the distance between the spheres, so the springs should behave non-classically. In our model, all springs have similar spring constants k, and their length is defined as the distance between the perimeters of connected disks. There is also a Lennard–Jones type interaction-force F_j, 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 interaction between nanospheres (Fig. 2b). The friction [15] between disks and surface equilibrates a net force less than F_f (Fig. 2a). Whenever the total

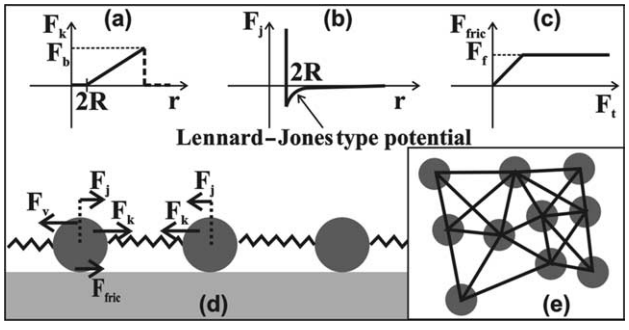

Fig. 2. Sketch of the spring-block stick-slip model. (a,b) The distance dependence of the tension F_k in the spring and the Van der Waals type force F_j between nanospheres, respectively. (c) The friction force (pinning) F_{fric} between nanospheres and substrate, as a function of total force F_t acting on the nanosphere. (d) The main elements of the model, and (e) example for a simplified spring-block monolayer system.

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 it has a breaking threshold F_b (Fig. 2a).

Initially disks are randomly distributed and connected by a network of springs (Fig. 2e). We put springs between those spheres, for which the centers 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 (d$t = 1$). (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 [13,14], we choose thus a simplified sequence of events, where the connection with real time is lost, but the relaxation remains realistic:

(1) For all springs, the tension $|\vec{F}_k^{ij}|$ is compared with F_b. If $|\vec{F}_k^{ij}| > F_b$, the spring is broken and taken away from the system.
(2) The total forces $\vec{F}_t^i = \sum_p (d_{ip}\vec{F}_k^{ip} + \vec{F}_j^{ip})$ 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 $|\vec{F}_t^i|$ acting on a disk is bigger than F_f, then the disk will slip with an over-damped motion governed by viscosity η, and its position will be changed by: $d\vec{r}^i = \vec{F}_t^i dt/\eta$. The repulsive part of the Lennard–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 in a random order 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 modeled.

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 step models the phenomenon that the water level of the continuous film decreases due to evaporation and the meniscus accounting for the capillarity forces gets more accentuated. 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 sequence of events can be easily implemented on computer and relatively big systems with over 10 000 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 conditions and initially positioning 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. The considered boundary condition will influence the

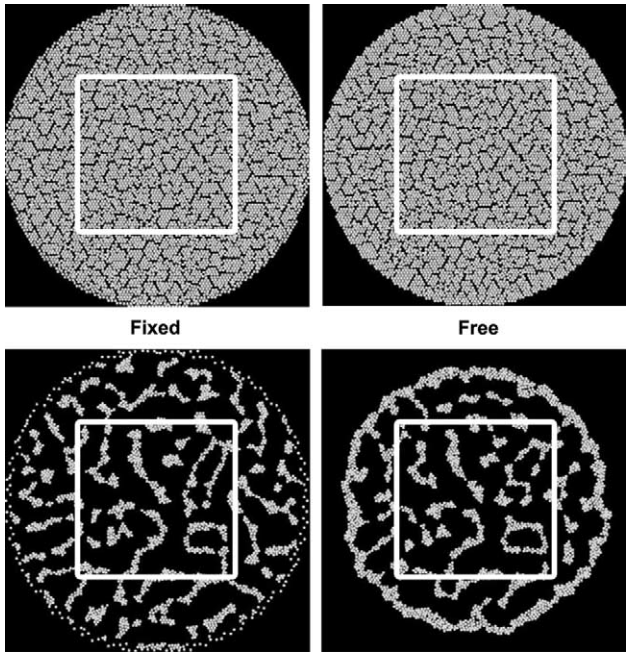

Fig. 3. Influence of the boundary conditions for the simulation results (two different sphere densities with fixed and free boundary conditions). The patterns inside the marked region are practically independent of the considered boundary condition.

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 (Fig. 3 illustrates this). Simulation results presented here are taken from a central rectangular part of the systems with $N > 10\,000$ disks, using fixed boundary conditions (Fig. 3).

The model, as described above, has several parameters: the static friction value F_f, the breaking threshold value F_b of springs, the initial value of spring constants k_{ini}, the spring constant increasing step dk, the viscosity η, the parameters of Lennard–Jones potential, the radius of disks R, and the initial nanosphere density $\rho = S/(N\pi R^2)$ (where S is the simulation area). By direct simulations, one can verify that if small enough dk is chosen, in case of 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 Lennard–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 ρ. The influence of these three parameters on the final structure was investigated and the obtained structures were visually compared with experimentally obtained ones. It worth mentioning here,

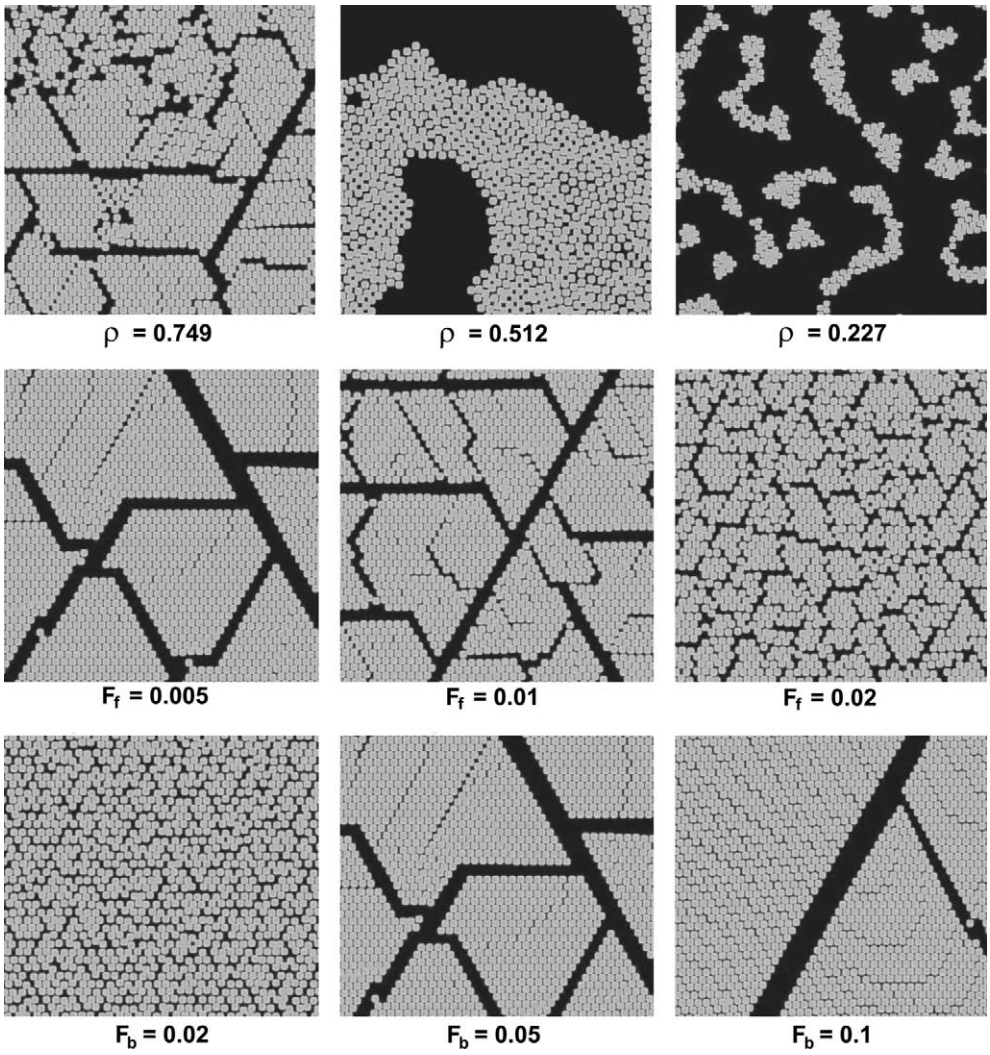

Fig. 4. Simulation results investigating the influence of parameters ρ, F_f and F_b on final patterns. On the top line ρ is changing ($F_f = 0.01$), in the middle line F_f is changing ($F_b = 0.05$, $\rho = 0.749$), on the bottom line the varied parameter is F_b ($F_f = 0.005$, $\rho = 0.749$). For all these simulations, the other parameters were chosen as: $k_{ini} = 0.1$, d$k = 0.002$, $\eta = 250$.

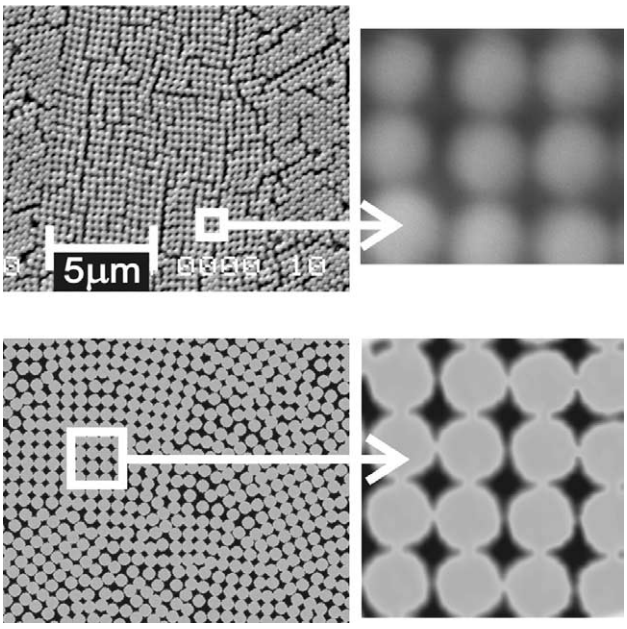

Fig. 5. Experimental (top) and simulation results (bottom) for the square lattice crystallization phase.

that for a successful simulation the values of ρ and F_b, has to be correlated. For small ρ 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.

On the top line of Fig. 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 and Néda [13], 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 (Fig. 4, middle line). Decreasing the value of F_b results in a similar effect (bottom line of Fig. 4). Experimentally, one could control F_f by changing the substrate and F_b by changing the evaporating liquid.

The sequence of events leading to the formation of final structures can be also 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 [16]. The formation of close packed (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 (Fig. 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 process 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 [17] 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 (Fig. 5 top line).

The success in reproducing this square-lattice crystallization phase and in general the qualitative agreement between simulation results (Fig. 4) and the experimentally observed structures (Fig. 1) encourages us to believe that the introduced model is reliable and the picture given for the underlying sequence of events 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.

Acknowledgment

The present study was supported by the CNCSIS Grant No. 183/2005.

References

[1] Y. Xia, B. Gates, Y. Yin, Y. Lu, Adv. Mater. 12 (2000) 693.
[2] D. Wang, H.J. Mohwald, Mater. Chem. 14 (2004) 459.
[3] Ch.L. Haynes, R.P. van Duyne, J. Phys. Chem. B 105 (2001) 5599.
[4] J. Rybczynski, U. Ebels, M. Giersig, Colloid. Surface. A 219 (2003) 1.
[5] K. Kempa et al., Nano Lett. 3 (2003) 13.
[6] W.A. Murray, S. Astilean, W.L. Barnes, Phys. Rev. B 69 (2004) 165407.
[7] A.A. Chabanov, Y. Jun, D.J. Norris, Appl. Phys. Lett. 84 (2004) 3573.
[8] J. Aizenberg, P.V. Braun, P. Wiltzius, Phys. Rev. Lett. 84 (2000) 2997.
[9] M.P. Pileni, J. Phys. Chem. B 105 (2001) 3358.
[10] G. Ge, L. Brus, J. Phys. Chem. B 104 (2000) 9573.
[11] E. Vasco, Appl. Phys. Lett. 85 (2004) 3714.
[12] E. Rabani, D.R. Reichman, P.L. Geissler, L.E. Brus, Nature 426 (2003) 271.

[13] K.-t. Leung, Z. Néda, Phys. Rev. Lett. 85 (2000) 662.
[14] Z. Néda, K.-t. Leung, L. Józsa, M. Ravasz, Phys. Rev. Lett. 88 (2002) 095502.
[15] Due to the characteristic nanoscale and due to the point-like contact between the nanospheres and surface the term 'pinning' is probably more relevant to categorize this force than 'friction'. The term 'friction' is used only for the sake of the simple mechanical analogy involved in our model.
[16] F. Járai-Szabó, Z. Néda, S. Aştilean, Available from: <http://www.phys.ubbcluj.ro/~jferenc/nanospheres>.
[17] E.W. Ong et al. Available from: <http://citeseer.ist.psu.edu/394899.html>.