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Spring-block type models for capillarity-driven self-organized nanostructures

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Self-organized nanostructures obtained through capillarity effects are modeled and studied by Monte-Carlo type computer simulations. We focus on two practically important systems, recently studied by experimentalist groups. The first system is a polysterene nanosphere suspension drying on a silica substrate. The second one is formed in a system of drying vertically aligned nanotube-array. For modeling these experimentally obtained and fascinating nano-patterns, spring-block type models are used. Stochastic simulations performed on these models reproduce qualitatively the experimentally obtained structures and gives thus a promising description for the pattern formation dynamics.

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1. Introduction

Nowadays it is widely realized that nanostructures represents the future for modern areas of electrical engineering, drug industry, optics, mechanical engineering or medical engineering. The urgent need for making devices as small as possible in order to use less material, to obtain better storage, bigger densities or easier access to tight and narrow spaces, makes the nanostructures an ideal candidate. Thanks to the efforts of nano-chemists nowadays various nanoparticles nearly monodisperse in terms of size, shape, internal structure, and surface chemistry, can be produced through reliable and standard manufacturing processes. These nanoparticles which can be nanospheres, nano-tubes or colloids can be used as building blocks for engineering more complex structures. Due to the strong adhesion and cohesion forces the word at nanolevel is very "sticky" and human assisted construction of nanostructures is complicated. At this point the self-assembled nanostructures become important. Self-assembling can be realized through Van der Waals type forces between constituents, geometrical constraints, magnetic interactions, thermal diffusion and capillary forces. In the present study we will investigate this latter possibility focusing on two interesting systems.

The first system in view is a polystyrene nanosphere suspension drying on a silica substrate - a system largely used in nano-sphere lithography [1-4]. The second system is a drying vertically aligned carbon nanotube array [5]. Both systems have been widely investigated by experimentalists, and presents major interest for generating self-assembled nanostructures. The nanosphere system can be useful for generating regular nano-dot patterns or nano-wires through nano-lithography, the nanotube system on the other hand can provide a technique to make shock-absorbers at nano-level or storage capabilities for biological cells. In the present paper we will show that the self-assembled patterns formed through capillarity effects in these systems can be successfully modeled by using Burridge-Knopoff type spring-block models [6, 7]. These models are appropriate for reproducing the wide variety of the experimentally obtained structures and to understand the influence of the experimentally controllable parameters.

2. Theoretical model

2.1 Modeling structures obtained in a drying suspension of polysterene nano-spheres

The use of two-dimensional (2D) self-assembled array of nanometer-sized polystyrene spheres as deposition mask is known as NanoSphere Lithography (NSL) [1-4]. NSL is now recognized as a powerful fabrication technique to inexpensively produce nanoparticle arrays with controlled shape, size and inter-particle spacing. The experimental method for getting nanosphere-structures appropriate for deposition (named the drop-coat method) is very simple. A monodisperse polystyrene nanosphere suspension is dried on a previously prepared silica substrate [1, 8]. During the drying process the capillarity and Lenard-Jones type forces, together with the pinning forces acting on the surface will self-organize the nanos-spheres. Apart of the ideal compact triangular lattice structure which is desirable for practical purposes many other structures can be formed. The final patterns usually present many dislocations, voids or clusters that can be again useful for nano-engineering purposes (see for example Fig. 2). The obtained structures can be influenced by changing the density of the nanospheres on the substrate, the used fluid, evaporation rate or substrate.

Here our goal is to understand and investigate the pattern-formation dynamics in this system by considering a Burridge-Knopoff type model.

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 [9, 10]. The new feature of the present model is that a predefined lattice is not considered anymore. The model is two-dimensional; its main elements are blocks which can move on a frictional substrate and springs connecting these blocks (Fig. 1d). Disks, all with the same radius R, model the nanospheres, while the elastic springs reproduce the capillarity effects of water between them. (It worth mentioning that the coupling between the 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 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 Lenard-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. 1b). The friction (pinning) between disks and surface equilibrates a net force less than F_f (Fig. 1a). 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 (Fig. 1a).

Initially disks are randomly distributed and connected by a network of springs (Fig. 1e). 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:

(1) For all springs the tension $\left|\vec{F}_k^{ij}\right|$ is compared with F_b. If $\left|\vec{F}_k^{ij}\right| > F_b$, the spring is broken and taken away from the system.

(2) The total forces $\vec{F}^i{}_t = \sum_p (d_{ip}\vec{F}_k^{ip} + \vec{F}_j^{ip})$ 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 $\left|\vec{F}_t^i\right|$ 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 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 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 effect 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. 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 lever 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.

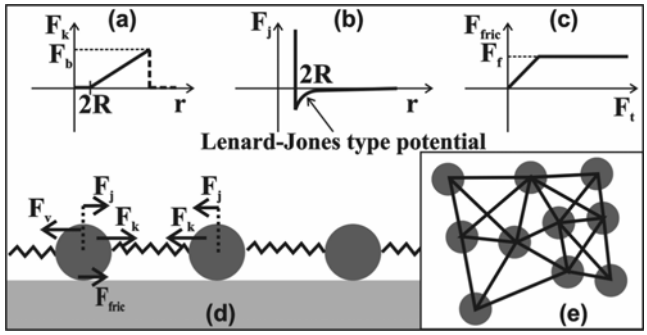

Fig. 1. Basic elements of the spring-block stick-slip model.

The above sequence of events can be easily implemented on computer and relatively big systems with over *10000* of disks can be simulated in reasonable computational time. The model, as described above, has several parameters: the value of the static friction F_f, the value of the breaking threshold F_b of springs, the initial value of spring constants k_{ini}, the spring constant increasing step dk, the value of viscosity η, 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). Varying these parameters several final stable structures can be generated, and almost all experimentally obtained ones can be successfully modeled.

As an illustration for this on Fig. 2 we present some experimentally obtained structures in comparison with the ones generated by our model. The similarity between the experimental and modeled structures is a hint that our model works fine, and can be used for predicting the effect of the relevant parameters on the final structure. We also believe that the dynamics of pattern formation offered by the time-evolution of our model describes well the reality. On Figs. 3 and 4 we illustrate the time evolution of the system for different nano-sphere densities.

2.2 Modeling capillarity-driven self-organization in a two-dimensional carbon nanotube array

Carbon nanotubes are considered again potentially useful building-blocks for engineering nanostructures. Recently, a clever method based on capillarity forces was proposed for obtaining self-organized structures from an array of vertically aligned nanotubes [5]. As described in [5], the method is relatively simple: A multiwall nanotube arrays is grown by chemical vapor deposition based on the decomposition of ferrocene and xylene. The vertically aligned nanotube array is oxidized in an oxygen plasma at room temperature and 133 Pa pressure for 10 minutes and immersed in a wetting fluid (water for example). After the water is evaporated characteristic cellular type patterns are formed, i.e the end of the nano-tubes self-organize in compact walls. Some characteristic patterns obtained with different fluids or nanotube lengths are visible on Fig. 5.

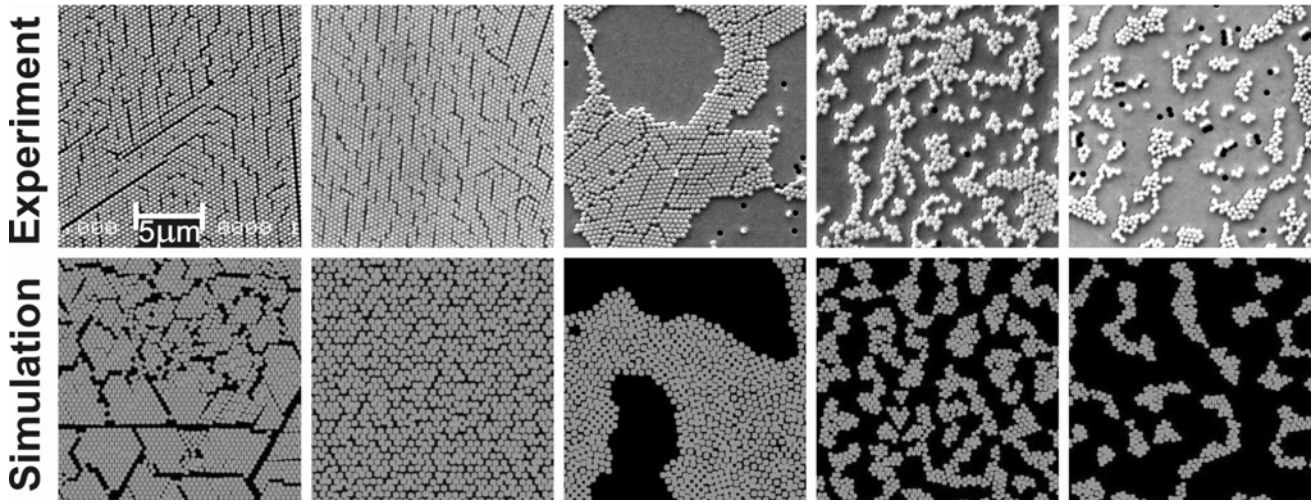

Fig. 2. Visual comparison of simulation and experiment.

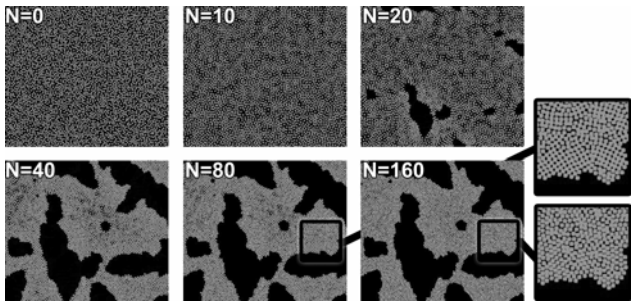

Fig. 3. Time evolution of a low density nanosphere system.(Ff=0.01, Fb=0.3, ρ=0.512).

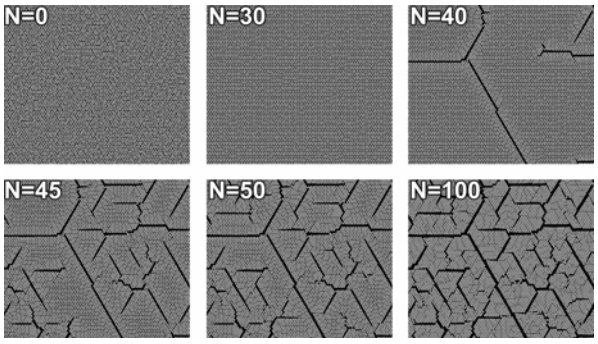

Fig. 4. Advancing fracture lines in a high density system.(Ff=0.01, Fb=0.05, ρ=0.749).

Similarly with the case of the previous problem, our goal is to elaborate a simple mechanical model that allows us to understand the pattern formation dynamics and to investigate the influence of the relevant parameters on the final structure. The model elaborated for this capillarity driven process is similar with the one elaborated for the nanosphere case. The problem can be mapped in a two-dimensional spring-block model (Fig. 6).

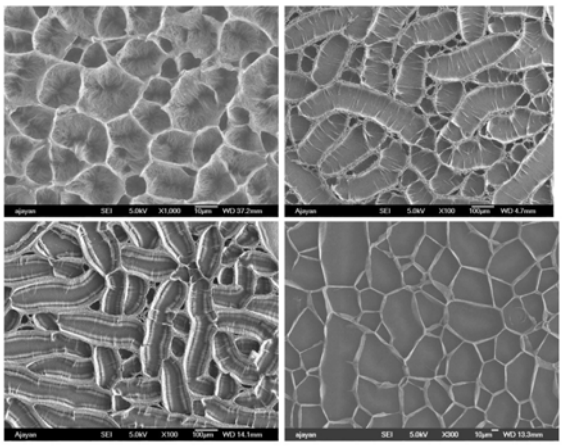

Fig. 5. Experimentally obtained structures after the evaporation of water in a system of vertically aligned nanotubes.

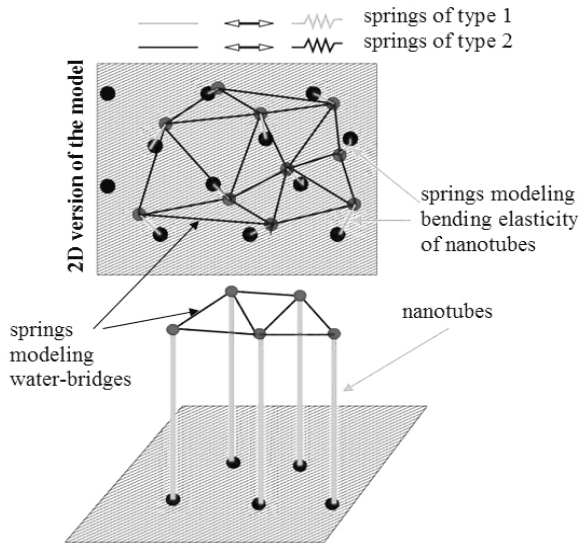

Fig. 6. Main elements of the two-dimensional spring-block model for the capillarity driven nanotube array.

There are two types of springs is the system. One type of springs (type 1) is modeling the bending elasticity of the nanotubes, and springs of type 2 is modeling the capillarity forces between the nanotubes. The bottom (basis) of the nanotubes is arranged on a predefined lattice and these are fixed centers where one end of the elastic springs of type 1 is anchored. The top of nanotubes are modeled by the blocks of the two-dimensional spring-block model. Each block is thus connected with an unbreakable spring of type 1 with the initially fixed position of the bottom. The blocks (top of nanotubes) are also connected with their nearest neighbors through springs of type 2. Similarly with the previous model the springs of type 2, have a breaking threshold F_b (if the tension is bigger than F_b the springs will break and are irreversibly taken out from the system). The blocks can slide now without friction on the surface. They are in equilibrium when there is no resultant force acting on them from springs of type 1 and type 2. There is also a viscosity tempering the free slide of the blocks and stabilizing unrealistic oscillations. The main difference relative to the model used for the nanosphere problem is that in this case there are no pinning forces between the substrate and nanotubes. Instead of this the stabilizing force is an extra elastic force that connects the top of the nanotubes to the projection of their bottom on the simulation plane. The dynamics of the system leading to pattern formation is than simple:

1. Blocks are placed on o lattice and the interconnecting spring-network is constructed. The spring constants for springs of type 1 and 2 are assigned. Spring constants for spring of type 1 are taken small, so that the tension in each spring is smaller than F_b.
2. A small number of links (springs of type 1) are removed, creating an initial randomness in the system.
3. The dynamics of blocks towards equilibrium is realized through an over-damped molecular dynamics simulation (parallel update) with a fixed time-step.
4. Whenever the tension in a spring of type 2 is greater than F_b the spring is irreversibly removed.
5. After all blocks reach equilibrium (the largest displacement per unit time is smaller than a fixed very small value) the spring constants for springs of type 2 are increased by a small *dk* amount. This process models the evaporation of liquid, and the fact that the meniscus in the water layer is getting stronger.
6. The dynamics is repeated from step nr. 3 and continued until a final, stable configuration of the blocks is reached.

Again, the model as described above can be easily implemented on the computer, and in a reasonable computational time many experimentally observed patterns can be qualitatively reproduced. Simulation results for different parameters of the model are plotted on Fig. 7.

Computer simulation suggests thus, that the model captures again the main ingredients necessary to understand pattern formation in the considered drying system. While much more work has to be done for clarifying the influence of the relevant parameters of the model or to investigate the obtained structures in a quantitative manner, the first results are promising. The preliminary simulations gave also a valuable image on the pattern formation dynamics. A characteristic time-sequence for this dynamics is plotted on Fig. 8.

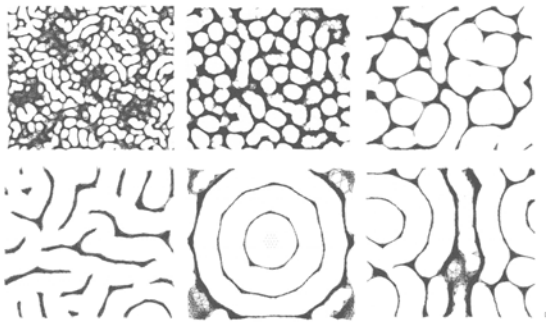

Fig. 7. Various structures simulated with the spring-block model defined in Fig. 5.

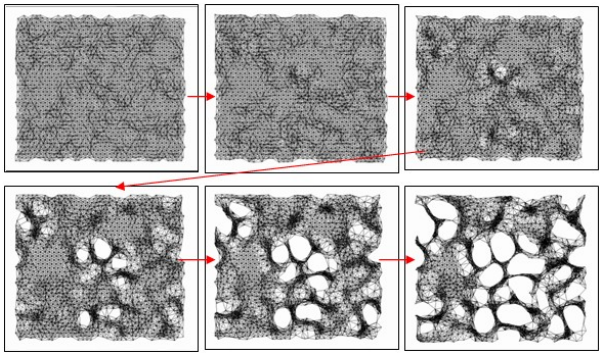

Fig. 8. Time evolution of the nanotube model.

As observable from the time-sequence in Fig. 8, the cellular pattern is formed after a void is nucleating in the breakable spring-network. This preliminary void is enlarged by the tensioned resort-network until the top of the nanotubes (blocks) will arrange in a final and stable cellular structure. The picture suggested by the simulation seems realistic, and it is in a complete agreement with the in-situ observations presented in [5].

3. Conclusions

Mechanical spring-block models with relaxational dynamics were used for modeling nano-pattern formation due to capillarity effects. Two practically important problems have been investigated. In the first problem the building-blocks were nanospheres while in the second one the building blocks were nano-tubes. In both cases a simple spring-block model could reproduce qualitatively well the self-assembled nanostructures and the dynamics leading to pattern formation. As a continuation thus of our previous studies concerning the applicability of the simple spring-block type models in materials science [9,10], we have proven again that such simple approaches could yield valuable and practically important results. The introduced models are appropriate for large-scale computer simulations and for investigating the influence of different experimentally controllable parameters. There is a possibility for predicting thus the effect of some key parameters on the final pattern or for designing a wide variety of self-assembled nanostructures on computer.

Acknowledgments

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