PATTERN FORMATION AND SELECTION IN NANOTUBE ARRAYS

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Unul din provocările actuale în ştiinţa şi ingineria modernă a materialelor este de a elabora structuri controlabile la nivel de nano- sau micrometrii. O metodă convenientă şi relativ uşoară de a obţine astfel de structuri este prin auto-organizarea capilară a unor nanoparticule. În prezenta lucrare se studiează auto-organizarea capilară care apare în urma procesului de desicare a unui sistem de nanotuburi vertical orientate şi umezite. Datorită forţelor de adeziune şi a forţelor capilare care acţionează între nanotuburi, sistemul se auto-organizează în structuri celulare care prezintă interes pentru aplicaţii practice. În cadrul studiului nostru problema complexă tridimensională este modelată cu un sistem bidimensional de tip bloc-resort. Modelul rezultant este studiat prin simulări stohastice de tip automate-celulare.

Engineering practically interesting spatial patterns on nano- or micron scales is a top priority in modern material sciences. A convenient and relatively easy way to achieve this is through capillary self-organization. In the present work we study and model a nanotube array wetted by a liquid, which self-organizes during drying. As a result of the capillary and adhesion forces acting between the nanotubes puzzling cellular patterns appear, which can be useful for practical applications. Here, the originally three dimensional problem is mapped in a two-dimensional spring-block model. The resulting spring-block model is studied by stochastic cellular-automata like computer simulations.

Keywords: pattern formation, spring-block models, nanotubes

1. Introduction

Reproducible nanoscale patterns and structures are of wide interest nowadays for engineering components in modern small-scale electronic, optical and magnetic devices. The so-called bottom up approach for the fabrication of these nanostructures gains more and more popularity. Within this approach one uses the nanoparticles as elementary building blocks and searches for simple

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methods to organize them in the desired structures. An elegant possibility is to find some specific conditions under which the nanoparticles self-organize themselves [1]. A well-known and widely explored possibility [2,3] is to use the capillarity forces which appear during the drying of a liquid suspension of nanoparticles. Nowadays, regular and irregular two-dimensional polystyrene nanosphere arrays on silica substrates are generated by such methods [4,5]. These patterns are used as a convenient mask in the NanoSphere Litography (NSL) method. In the present paper we describe and model another capillarity driven self-organization phenomenon, where the elementary building blocks are vertically oriented nanotubes, grown on a crystalline surface. The method was first proposed by Chakrapani, et al. [6] and received a considerable interest in the scientific community [7, 8] due to the practically useful cellular structures that are obtained (Fig. 1).

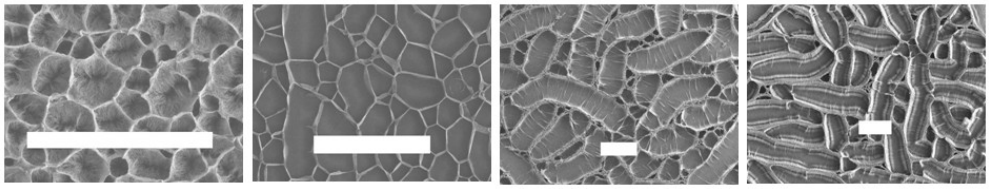

Fig.1 The nanotubes free ends self-organize in diverse cellular structures. The white line on the pictures indicates the scale of the structures. It's horizontal length corresponds to 100 μm. Experimental results are obtained at the Rensselaer Polytechnic Institute, Department of Material Science and Engineering, USA, group of Prof. P.M. Ajayan.

The model used here for describing the pattern selection phenomena is a mesoscopic one and it is based on the simple spring-block stick-slip model. This model family appeared in 1967, when R. Burridge and L. Knopoff [9] constructed a mechanical model for explaining the Guttenberg-Richter law for the earthquakes magnitude distribution. The basic elements of the model are blocks and springs that interconnect in a lattice-like topology. The blocks can slide with friction on a plane-like surface. The original system introduced by Burridge and Knopoff (BK) is a one-dimensional model. The BK model gained new perspectives with the strong development of the computers and computer simulation methods in the 1990's. Earthquake statistics have been simulated more realistically with the two-dimensional version elaborated by Olami, Feder and Christensen [10]. Variants of this model proved to be useful in describing complex phenomena where avalanche-like processes are present, pattern formation phenomena and mesoscopic processes in solid-state physics or material sciences. Recently the capillary self-organization of nanospheres was successfully modelled by using this model [4,5]. Motivated by the success of such models, in the present study we will map the capillarity driven nanotube array into a spring-block system, and investigate the pattern selection process through this model.

2. Experimental procedure

The experiments were realized by the group of Prof. P.M. Ajayan at the Rensselaer Polytechnic Institute in USA. As it is described in their article [6] the experimental procedure is quite simple. Multi-walled nanotube arrays are grown by chemical vapor deposition based on the decomposition of ferrocene and xylene. The obtained vertically aligned nanotube array is oxidized in oxygen plasma at room temperature and 133 Pa pressure for 10 minutes and immersed in a wetting fluid (water for example). After the water evaporates, characteristic cellular type patterns are formed, i.e. the ends of nanotubes self-organize in compact walls (Fig.1).

The cellular pattern formation mechanism was also revealed by the experiments. As the liquid evaporates the capillarity forces acting between the nanotubes will generate an increasing spatial disorder in the positions of the nanotubes free ends. Voids are nucleated in the nanotube forest and the stress field of the remaining capillarity forces will further increase these voids, propagating them in a crack-like manner. Finally, the tips of the nanotubes will self-organize in stable walls, leading to the cellular patterns illustrated in Figure 1.

3. The spring-block approach

The nanotube forest is mapped in a two-dimensional spring-block system. First, the nanotubes fixed, bottom ends are placed on a triangular lattice, while their top ends are free to move. Blocks will model the free ends of the nanotubes and springs that interconnect neighboring blocks model the resultant of the capillarity and adhesion forces acting between the neighboring tubes. Beside tensions in the spring there are also pinning forces (F_p) acting on the blocks on each lattice site, stabilizing the system. These pinning forces model the bending reluctance of the nanotubes. The free ends of the nanotubes (blocks) are not allowed to move continuously in space, they can only "jump" to the neighboring lattice sites. One site can be occupied by several blocks, assuming that their number is smaller than a fixed critical value n_c. Whenever two or more blocks will occupy the same lattice site, their bonds (springs) will become common, and the blocks will move together. In case the number of blocks on one lattice site exceeds n_c the incoming block is expulsed to a randomly chosen (and allowed) neighboring site. The length of the nanotubes determines the maximal possible distance L between the initial and actual position of a block. The main elements of this model are sketched in Fig. 2. The tensions in the springs are chosen realistically. Experimental studies proved that the lateral capillary force between micro and nanometer sized bars immersed in water is inversely proportional with the distance between the bars [11]. This result can be argued theoretically by considering three forces acting between the nanotubes partially immersed in water

(Fig.2c): the interfacial adhesion forces through the gas (F_{adh}^{g}) and through the liquid phase (F_{adh}^{l}) and the interfacial meniscus force (F_{men}) [12]. The proportionality factor is referred here as the spring constant, *k*. The values of the spring constants are randomly distributed (with a variance δ). This introduces a quenched disorder in the system, which is the main ingredient that launches the dynamics and governs the obtained patterns.

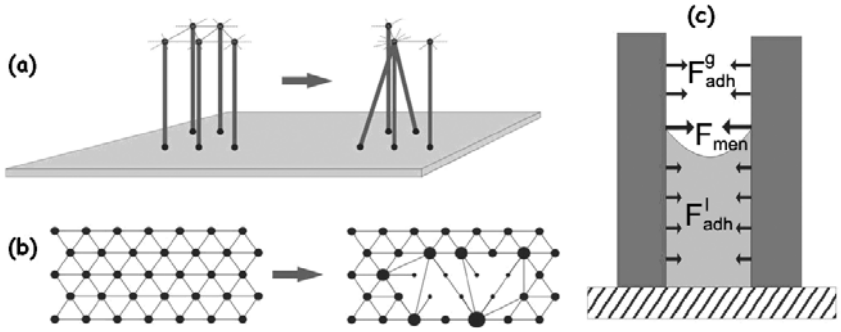

Fig. 2 Elements of the spring-block model. Figure (a) shows the nanotubes placed on a triangular lattice, and their bending due to capillarity and adhesion forces. Figure (b) illustrates the dynamics of the nanotubes top end (blocks), and Figure (c) shows the forces acting between two nanotubes.

During each simulation step the spring constants are increased by a small Δk value (typically $\Delta k = 0.1$) and the system relaxes to an equilibrium configuration where the total net force acting on each nanotube is lower in magnitude than the pinning force. The increase in the spring constant models the fact that the meniscus accounting for the capillarity forces gets more accentuated due to the continuously decreasing water level. Relaxation is realized through the following steps: (i) blocks are visited in a random order and for each of them the resultant spring force acting on it is calculated (ii) if the resultant force is greater then the pinning force the block jumps to the first neighbor in the direction closest to the direction of the force, (iii) in case the site is already occupied the necessary unifications are made and hereafter the united blocks will behave as one, (iv) in case the number of blocks on the new site exceeds the critical one, the block is repositioned on a randomly chosen and allowed neighboring site. Instead of a time-consuming molecular dynamics an over-damped cellular automata simulation is used.

4. Results and discussions

The model can be easily implemented on the computer, and in a reasonable computational time large scale simulations containing about $4x10^6$ nanotubes can be performed. The validation of the model is made by a visual

comparison of the resulting pattern with the experimentally obtained structures. In the left panel of Fig. 3 an experimental pattern is shown while on the right panel simulated structures are plotted. As one may observe, the cellular structures are nicely reproduced by the model.

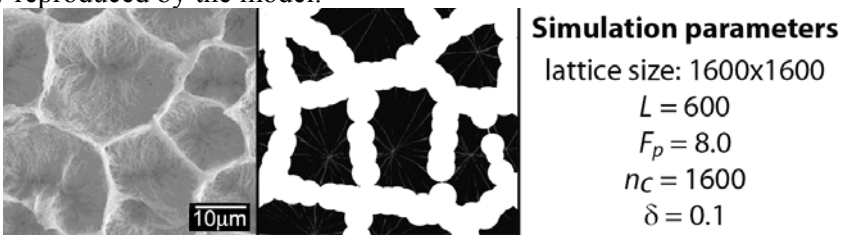

Fig. 3 A visual comparison between the experimental and simulated patterns.

The above described model takes into account the main mechanisms which lead to the cellular pattern formation in drying nanotube arrays. Accordingly, we believe that the dynamics offered by the time-evolution of the patterns in the model describes the reality. Figure 4 illustrates a typical time evolution obtained in the simulations.

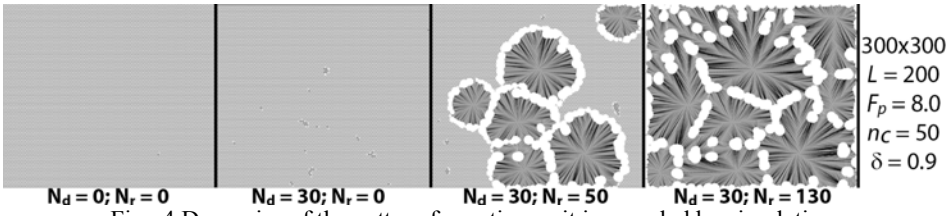

Fig. 4 Dynamics of the pattern formation as it is revealed by simulations

On Figure 4 snapshots are given at different drying and relaxation steps denoted by N_d and N_r, respectively. It can be observed that up to a certain relaxation step no structure is formed, and only a stress-field is built. Then, suddenly voids nucleate and are enlarged until the top of the nanotubes form a final and stable cellular structure.

Pattern selection is governed by the disorder in the system. This is quantified by the δ variance of the spring constant values. Figure 5 presents the effect of this disorder on the final pattern. As it is observable from the figure, this parameter controls the number of cells nucleated in the simulation field and therefore determines the typical cell size.

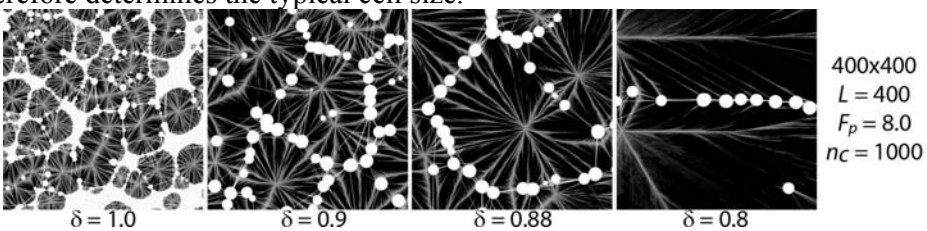

Fig. 5 Final and stable structures for different disorder level in the spring constants

5. Conclusions

A simple spring-block stick-slip model was built for reproducing cellular patterns obtained experimentally in drying nanotube arrays. The model reproduces nicely the polygonal-like patterns. The model in the present version fails however to generate elongated, swarm-like cells, which are also obtained during the experiments. The dynamics of the pattern formation phenomenon and the influence of the disorder in the spring constants of the resulting capillary forces on the final pattern selection are revealed.

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