

Coded nanoscale self-assembly

PRATHYUSH SAMINENI and DEBABRATA GOSWAMI*

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

*Corresponding author. E-mail: dgoswami@iitk.ac.in

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Abstract. We demonstrate coded self-assembly in nanostructures using the code seeded at the component level through computer simulations. Defects or cavities occur in all natural assembly processes including crystallization and our simulations capture this essential aspect under surface minimization constraints for self-assembly. Our bottom-up approach to nanostructures would provide a new dimension towards nanofabrication and better understanding of defects and crystallization process.

Keywords. Nano self-assembly; void; defects; crystallization.

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1. Introduction

Nanomaterials exhibit many unique and often tunable physical, chemical, and tribological properties that are nonexistent in their bulk counterparts, which has led to research in the generation of materials with controlled microstructural characteristics. In an effort to sustain and further such innovative developments, it is necessary to investigate the organization and growth of nanomaterials. In general, any rational approach towards designing materials are essentially of two kinds: In one method a big structure is cut down in size until the desired shape is achieved and this is called the ‘top-down’ approach, which is similar to carving a piece of marble into a sculpture. The other method is called the ‘bottom-up’ approach, where a big structure is built from smaller pieces. This is the preferred method for macroscopic objects; common examples being our roads and buildings that are built by putting together bricks and mortar in some specific pattern. But this gets difficult if the objects to be placed into a pattern are molecule-sized, in the realm of nanoscale. Still, if the constituting objects would themselves arrange into patterns then it again becomes a feasible approach through ‘self-assembly’. The technique of self-assembly is one of the few practical strategies available to arrive at ensembles of nanostructures based on this bottom-up strategy unlike the top-down approach of traditional lithography. The design of systems of components with nanodimensions

for self-assembly can be aided enormously by considering analogies with molecular systems [1].

Molecular self-assembly is the spontaneous organization of molecules (or parts of molecules) under thermodynamic equilibrium conditions into structurally well-defined stable arrangements through a number of noncovalent interactions [2–4] without any human intervention. The formation of molecular crystals [5], colloids [6], lipid bilayers [7], phase-separated polymers [8], and self-assembled monolayers [9] are all examples of molecular self-assembly. Although self-assembly originated in the study of molecules, it is a strategy that is, in principle, applicable at all size scales. The self-assembly process thus, in general, can be defined as the autonomous organization of components into structurally well-defined aggregates.

In this paper, we investigate nanoscale self-assembly by computer simulation to better understand the bottom-up approach to fabrication and use this understanding towards a better design strategy. In fact, we show that such an approach enables us to evolve coded bottom-up approach to fabrication through self-assembly. We also extend the ideas of our model on self-assembly to the process of crystallization and illustrate the experimentally observed aspects of cavities or crystal defects.

2. Formalism

Our model is based on individual sub-Angstrom size squares which were considered as the replicating building blocks, which could represent molecules. The molecules can either be same or different in reality but, for simplicity, we have considered the case of similar molecules. N squares were placed randomly with respect to position and angle on a square canvas of size twice the number $N \times (\text{side})$, where side is the length of each square as shown in figure 1. The self-assembly process is initiated with a seed square which we have chosen as the central one for convenience and the process is started. The idea of using square shape as the simplest building block also explores the issue of voids or ‘empty space’ in the self-assembly process. Though spheres form a more realistic model for molecules, squares can really generate a completely space-filled model and as such appearance of voids under such a model is more easy to follow.

Self-assembly occurs when molecules interact with one another through a balance of attractive and repulsive interactions. These interactions are generally weak (that is, comparable to thermal energies) and noncovalent (van der Waals and Coulomb interactions, hydrophobic interactions, and hydrogen bonds) but relatively weak covalent bonds (coordination bonds) are recognized increasingly as appropriate for self-assembly [10,11]. Complementarities in shapes among the self-assembling components are also crucial. We have used capillary interactions that are forces resulting from minimizing the contribution of interfaces to free energies by minimizing interfacial areas.

We have used Lennard–Jones potential to describe interaction between squares in this simulation. It has the form, $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where r is the distance between the centres of two squares in the simulation. The constants ϵ (epsilon) and σ (sigma) are important to determine the strength and shape of the interaction. The force between two squares is of course, just the negative

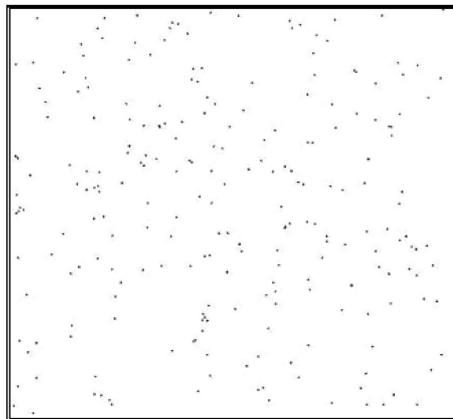


Figure 1. Starting point of a simulation where N squares were placed randomly with respect to position and angle on a square canvas of size twice the number $N \times (\text{side})$. The centre square in the canvas is taken as the seed square. See text for details.

of the gradient of the potential. The $(1/r)^{12}$ term describes the repulsive force and the $(1/r)^6$ term describes the attractive force. The force exerted by the seed on each square is calculated as described above and using that the acceleration, velocity and distance to be moved are calculated using the Newtonian equations and an arbitrarily defined step size. Force exerted on each square is considered to be applied by the centroid of the seed. Thus, all the squares move towards the centroid of the seed at any instant.

As squares get attached, the size of seed increases as seen in figure 2 and also the net force it exerts on individual squares as the force exerted by the seed on each individual square is directly proportional to the number of squares the seed is presently made up of. Each time a square is attached the new centroid is calculated and all the squares move towards this centroid then onwards. All the cases of contact are considered as shown in figure 3 and squares are allowed to adjust. For self-assembly to generate ordered structures the association either must be reversible or these must be sufficient flexibility so that the components can adjust their positions within an aggregate once it has formed. The strength of the bonds between the components, therefore, must be comparable to the forces tending to disrupt them. Processes in which collision between molecules leads to irreversible sticking generate glasses, not crystals. The environment can strongly influence the process and its result by interacting with the components but here we are not considering any effects of the environment on the system consisting of the group of molecules.

The minimum perimeter condition is always used for placing the square when it comes in contact with the seed square, which corresponds to minimizing surface energy of the system at every point.

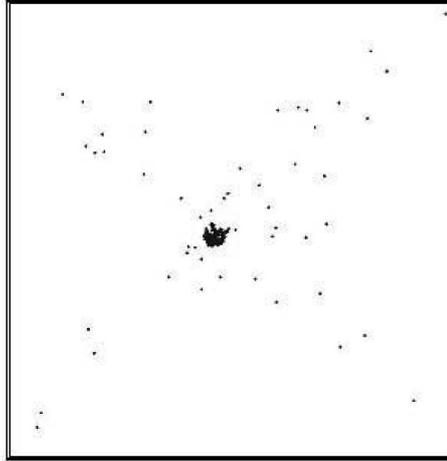


Figure 2. An intermediate point in simulation where the seed has grown and essentially speeds up the process.

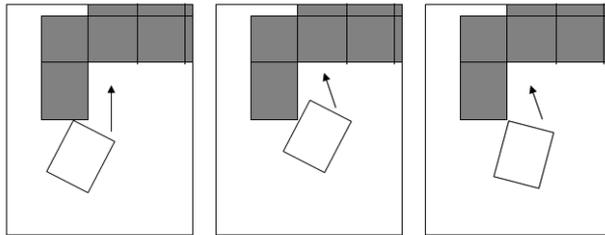


Figure 3. All the three cases of contact are shown here. The grey squares are part of the seed and the white square is the new square which comes into contact with the seed. As shown, always the position which results in minimum perimeter is selected.

3. Results and discussion

A typical number of iterations for completing a simulation for such a model without any preconditions could be very large to converge. However, the density of the squares turns out to be an important parameter that could be fine-tuned to make the process faster, though it is very important to ensure that this does not create complications such that the collisions start happening before the reorganization of the squares as shown in figure 3 are not completed. In general, the initial seed square would freeze with another square or two in about 10 iterations to the equilibrium position. As the size of the seed structure increases, the process begins to get accelerated although computationally the process of recalculating the centre of mass of the ever changing seed counters this speed advantage. Thus, it is a tricky and computationally very long exercise to approach the statistical limit in this model. Physically, however, one can argue that this speed-up of the process leads to lesser ideal equilibration and is responsible for the void formation.

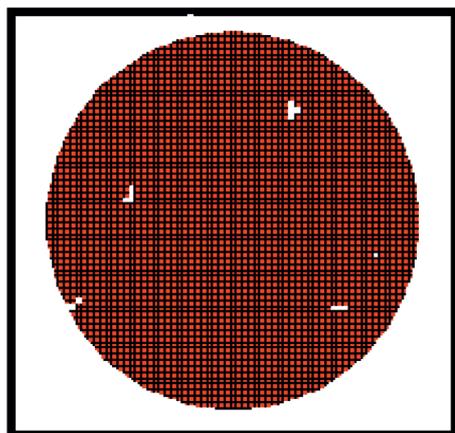


Figure 4. If we let the self-assembly process continues through the allowed reorganization and surface minimization, an expected shape of a circle is achieved for a large enough number of particles N .

Since circle has minimum perimeter per given surface area, as the number of squares becomes very large, i.e., when N tends to infinity or reaches the statistical limit, the final shape of the structure will be circular with voids or cavities as shown in figure 4. For any other point of calculation where the statistical limit has not been reached, any arbitrary shape as shown in figure 5 can result. The presence of voids shows the proximity of the self-assembly as a process for nanoscale materials processing or for that matter any natural assembly process. In fact, the natural evolution shown here through this simple model can easily capture the dynamics of the crystallization process with the same aspects of seed-molecule being the starting point for crystallization. The self-assembly method can efficiently overcome the size limitation of the present-day technology while offering the benefits of a bottom-up strategy for nanoscale material fabrication.

Self-assembly has information coded in itself as shape, surface properties, charge, polarizability, magnetic dipole, etc. These characteristics determine the interactions among molecules. The design of components that organize themselves into desired patterns is the key to applications of self-assembly. We can manually modify the conditions to produce desired patterns. This is coded self-assembly wherein by putting some restrictions on the binding conditions or by selecting the interactions and including interactions such as gravitational attraction, external electromagnetic fields, magnetic, and entropic interactions, which do not have considerable effect in the case of molecules, we can have control on the results. On using a binding condition like only negative-negative can bind and positive side does not involve in binding we were able to obtain straight chains. This is like considering the cells polar with one direction positive and negative in the other perpendicular direction. The result always leads to a linear code as shown in figure 6, and this is our demonstration of coded self-assembly. As far as we know, this is the first simulation effort to explicitly demonstrate this bottom-up approach. We have allowed for multiple seeds in this particular simulation, which further shows that with coding

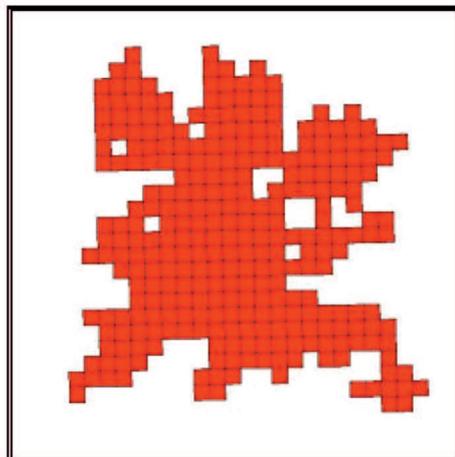


Figure 5. A typical simulation result which shows how the uncoded self-assembly assumes arbitrary shapes depending on the simulation length and the number of starting particles.

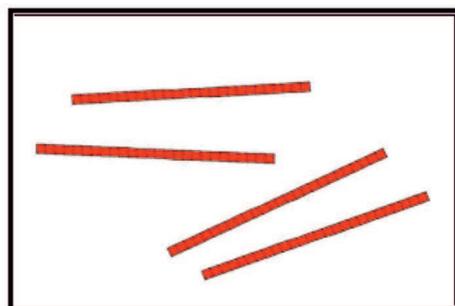


Figure 6. Coded self-assembly results in specific shapes. When the constituent particles are coded to only combine in a certain defined rules, it always manages to generate the same shape. The simplest case of linear coding with multiseed option is presented here.

in place the resultant shape is always achieved irrespective of multiple starting points.

4. Conclusion

Coded self-assembly as demonstrated in this paper can have far reaching effects. Design considerations in this bottom-up approach enables molecular level coding to be propagated to macroscopic designs for the first time making it highly generalized and robust. It can also be perceived as a major step towards nanosynthetic manufacturing route wherein the nature of the nanoparticle properties could be the driving force towards the coded design as they self-assemble towards a macro or a mesostructure.

The void areas as uncovered in this modelling process brings out the reality of the model to the actual physical processes involved. It turns out that a simple surface minimization constraint along with the acceleration gained in the progress of the self-assembly or crystallization process is the key towards the deviation from ideality of most optimal equilibrium positions. This results in the generation of void area in these processes. An immediate correlation of the rapidly frozen solids with high void areas and low density completely conforms to the validity of this simple yet elegant model presented here.

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