Introduction

Experimental and theoretical studies of matter on a nanometer length scale are becoming increasingly important due to the development of modern technologies leading to significant reduction in the size of electronic and optical devices. Of particular importance is the ability to assemble nanoparticles into well-defined configurations in space. These spatial arrangements can be employed to build increasingly complex structures, thereby extending the variety of chemical materials that can be used for different purposes.

When a liquid containing nanoparticles evaporates, many qualitatively different transitory structures can form. This self-assembly is governed by a subtle interplay of forces, including interactions between nanoparticles as well as capillarity and wetting. While certain experimental results can be explained using thermodynamic arguments alone, drying-assisted aggregation of nanoparticles is, in principle, a nonequilibrium process. Understanding this evolution towards a new equilibrium state at a microscopic level is the first step in a systematic design of interesting and useful morphologies.

In this article, the dynamics of two-dimensional evaporation-mediated self-assembly process is analyzed using a simple coarse-grained lattice-gas model. Several structures formed by this model correspond closely to those found in experiments. But other structures, resembling crossed wires and dendrites, have not yet been observed. The results suggest ranges of experimental conditions appropriate for fabrication of these novel patterns.

Model

We propose a coarse-grained lattice-gas model of evaporation-mediated self-assembly in which fluctuations of the evaporating solvent are explicitly included. In detail, the density of the liquid and nanoparticles are described on a square lattice, where each lattice cell of the size of the correlation length of the solvent ($\xi = 1$ nm) is occupied by either liquid ($l_i = 1$) or nanoparticle ($n_i = 1$) or gas ($l_i = 0$ and $n_i = 0$). We use two sets of binary variable $l_i$ and $n_i$ that are roughly proportional to solvent and nanoparticle densities at lattice site $i$, respectively. Because the size of a nanoparticle, $d$, can exceed the range of correlated solvent fluctuations, we allow them to span several cells of the lattice.

In our model, adjacent liquid cells attract one another with a strength $\epsilon_{l_l}$ determined by the energy density of the fluid, and adjacent nanoparticle cells attract one another with strength $\epsilon_{n_n} > \epsilon_{l_l}$, so that they tend to aggregate in the absence of liquid. The coupling between the drying dynamics and the self-assembly is established by introducing attractions between neighboring liquid and nanoparticles (of strength $\epsilon_{nl}$). The system maybe described by the lattice-gas Hamiltonian given by

$$H = -\epsilon_{l_l} \sum_{\langle ij \rangle} l_i l_j - \mu \sum_i l_i - \epsilon_{n_n} \sum_{\langle ij \rangle} n_i n_j - \epsilon_{nl} \sum_{\langle ij \rangle} l_i n_j$$
where $\mu$ is the chemical potential used to control the average concentration of liquid and vapor cells at equilibrium, and the sums in the above equation run over nearest neighbors only. The geometry and relevant length scales of this lattice model are sketched in Fig. 1.

The dynamics of our model are stochastic, both for fluctuations in solvent density and for nanoparticle diffusion. In the former case, configurations evolve by Monte Carlo dynamics. We attempt to convert a randomly chosen lattice cell from liquid to vapor (or vice versa), with a Metropolis probability. Nanoparticles execute a random walk on the lattice, biased by their interactions with liquid cells and with each other. We attempt to displace a nanoparticle by single lattice spacing in a randomly chosen direction. Such a move is accepted also with the same Metropolis probability, but only if the region into which the nanoparticle moves is completely filled with liquid. This is done to mimic the low mobility of nanoparticles on a dry surface.

**Homogeneous Dynamics**

The self-assembled morphologies obtained in our model depend mainly on the evaporation dynamics. These can be controlled by changing the temperature or by changing the chemical potential (i.e., changing the solvent). In the right panels of Fig. 2 we show snapshots at intermediate times from representative nonequilibrium trajectories exhibiting homogeneous drying. The chosen trajectories differ from one another only in coverage (i.e., mean surface density) and mobility of nanoparticles. At low coverage (a) distinct, disk-like aggregates of nanoparticles dominate the self-assembly. At higher coverage (b, c and d) nanoparticle domains are anisotropic and nearly percolate through the lattice. In many cases, the growth of domain in the homogeneous drying limit is self-similar. The left panels of Fig. 2 are micrographs of nanoparticle self-assembly in the experiments of Brus and coworkers. In each cases, the nanoparticle coverage lies within two percent of the simulated system depicted in the adjacent panel. The strong visual correspondence between the experimental and theoretical results is evident.

Similarly, with a reasonable estimate of the physical time scale for computed trajectories the growth times of simulation and experiment also compare well. The agreement between the experimental and theoretical results in Fig. 2 demonstrates that our coarse-grained model successfully captures the

![Fig. 2: Self-assembled morphologies resulting from homogeneous evaporation. Right panels show results of model simulations for coverages of 5% (a), 30% (b), 40% (c), and 60% (d). Left panels show corresponding experimentally observed morphologies for CdSe nanocrystals at similar coverages.](image-url)
qualitative dynamics of nanoparticle assembly in the limit of spatially homogeneous evaporation. We have also made more quantitative comparison (not shown). We find that not only are coalescence and shape fluctuations similar to the eye, but the scaling of domain size with time is essentially identical. We conclude that when evaporation is spatially uniform, the coarsening of nanoparticle domains is essentially that of an appropriate one-component fluid. Solvent evaporation simply triggers the onset of coarsening, after which the mechanism and time scale of growth are determined by nanoparticle diffusion.

**Heterogeneous Dynamics**

When evaporation is instead strongly heterogeneous in space, the dynamics of self-assembly can be dramatically different. In this case evaporation occurs by nucleation and growth of vapor bubbles. At a given instant, the driving force for nanoparticle assembly therefore varies with position on the lattice. If nanoparticles are sufficiently mobile to track the fronts of growing vapor nuclei, their aggregate patterns will be shaped by the structural history of evaporation. This is a consequence of the coupling between two different phase transitions, one in solvent density (evaporation) and the other in nanoparticle density (self-assembly).

Fig. 3 shows two representative simulation trajectories under conditions of heterogeneous evaporation along with the corresponding experimental results. Panel (a) exemplify network formation when domain edges are effectively frozen following evaporation, so that aggregation essentially halts when vapor nuclei meet. Each cell of the network structures in panel (a) marks an independent nucleation event whose front pushed nanoparticles to the boundaries of adjacent cells. When domain edges remain mobile following heterogeneous evaporation, the network described above in panel (a) of Fig. 3 is not stable, long-lived structure. Nanoparticles continue to move in this case, strongly biased by the interfacial tension of cell boundaries. Cells break up as diffusion concentrates nanoparticle density at the nodes of the network, leaving distinct, worm-like domains. An example of such a pattern generated by our simulations compares well with worm-like morphologies observed in experiments (panel b in Fig. 3).

**Conclusions**

The theory presented here suggests two regimes of drying-mediated nanoparticle assembly. These regimes are distinguished by the spatial uniformity of solvent dynamics. When solvent evaporates homogeneously from the surface, disk-like or ribbon-like domains form at early times. If these aggregates remain mobile, they continue to evolve in a self-similar fashion, principally by diffusion and coalescence. If instead domain boundaries are frozen following evaporation, dynamical constraints arrest this growth at an early stage. When evaporation is inhomogeneous due to infrequent nucleation events, network structures are formed at early times as vapor nuclei meet. These cellular patterns are only stable if interfaces are frozen following evaporation. Otherwise, networks fragment to form distinct, worm-like, domains that asymptotically evolve as in homogeneous coarsening.
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References


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