Out-of-Equilibrium Self-Assembly of Binary Mixtures of Nanoparticles

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The self-assembly of nanoparticles is one of the most promising techniques currently used to develop advanced materials.[1,2] The distinct properties of the nanoparticles can be integrated into assemblies of nanometer-scale building blocks, which leads to novel superstructures with unique collective properties. Most recent studies have focused on assemblies of single-component systems, such as semiconducting[3-11] magnetic,[12-16] and metal nanocrystals.[17-25] The study of multicomponent materials, i.e., assemblies of mixtures of nanoparticles, has received very little attention despite their role in the development of metamaterials[26] materials with properties arising from the controlled interactions between different nanoparticles in an assembly.

Previous studies of assemblies of multicomponent nanocrystals have usually resulted in amorphous materials.[27-30] This is because of the lack of directional forces or low diffusivity of the nanoparticles during the assembly process itself.[20] An exception is the work reported by Redl et al. where mixtures of PbSe semiconducting quantum dots and Fe3O4 magnetic nanocrystals were assembled into ordered three-dimensional arrays.[26] This was achieved by carefully controlling the solvent vapor pressure, thereby adjusting the rate of evaporation during the drying process. Redl et al. showed how the final superlattice crystal structure can be tuned by the size ratio of the two nanoparticle components.

In the present study, an attempt is made to model and understand the physical mechanisms of the assembly of binary mixtures of nanoparticles. For this, the model presented by Rabani and co-workers[31,32] is adopted and extended to describe the drying-mediated self-assembly of binary mixtures of nanoparticles. This out-of-equilibrium problem requires the dynamic treatment of three coupled phase transformations: the evaporation of the solvent (drying), the formation of domains (coarsening), and ordering within the domains (formation of superlattices). In the language of statistical mechanics the present paper treats the dynamics of the three coupled phase transformations, two are described by a conserved order parameter and one by a non-conserved order parameter.[33]

Three cases of the self-assembly of binary mixtures of nanoparticles under homogeneous and heterogeneous evaporation conditions are studied. The cases differ only in the interactions between the different nanoparticle species. For the case where the interactions between all the nanoparticles are equal, the dynamics of the model presented here and the resulting self-assembled morphologies are well described by the simplified single-component model.[31,32] However, in the other two cases studied, where the cross interactions are smaller/larger than the interactions between identical particles, it is found that the coarsening of the nanoparticle domains is strongly coupled to the superlattice formation within each domain. Furthermore, when evaporation is heterogeneous in space, the system shows a complex behavior that in some ways is similar to the arrested phase separation of glassy materials.[34-37]

The model presented here describes an experimental realization of a thin film that completely wets the substrate and contains two species of nanoparticles. It is assumed that under these conditions the self-assembly process can be described by a two-dimensional (2D) model.[32] The present coarse-grained lattice-gas model for a two-component system is similar to the model developed by Rabani et al.[31] for a single component system. The solvent and the two types of nanoparticles in the model here are represented as a 2D lattice gas.[30] Each cell of a square lattice can be occupied by either vapor, liquid, nanoparticle of type A, or nanoparticle of type B. The size of each cell in the lattice equals the typical solvent correlation length, $\xi \sim 1$ nm. Because the size of a nanoparticle can exceed the range of correlated solvent fluctuations, they are allowed to span several cells of the lattice. In all results reported below the nanoparticles span 16 cells. The lattice-gas Hamiltonian can be expressed in terms of three binary variables, $l_i$, $a_i$, and $b_i$:

$$
H = -\eta_l \sum_{\langle ij \rangle} l_i l_j - \eta_a \sum_{\langle ij \rangle} a_i a_j - \eta_b \sum_{\langle ij \rangle} b_i b_j - \eta_{al} \sum_{\langle ij \rangle} a_i l_j - \eta_{bl} \sum_{\langle ij \rangle} b_i l_j - \mu \sum_{\langle i \rangle} l_i \sum_{\langle ij \rangle} a_i b_j - \mu \sum_{\langle i \rangle} a_i b_i - \mu \sum_{\langle i \rangle} b_i a_i
$$

(1)

where $l_i$, $a_i$, and $b_i$ are roughly proportional to the density of the solvent, nanoparticle of type A (NanoA), and nanoparticle of type B (NanoB) at lattice site $i$, respectively. Each binary variable can equal 0 (low density) or 1 (high density), however, a single lattice site cannot be occupied by more than one species.

The sum ($\sum_{\langle ij \rangle}$) in Equation 1 includes only adjacent lattice cells. A similar qualitative picture emerges when longer range...
attractions are included.\[39\] The cells attract one another with a strength that depends on the occupation of the two cells. The strength of the interactions between adjacent cells occupied by the liquid is determined by the energy density of the liquid and is given by \(e_l\). Similarly, when two adjacent cells are occupied by NanoA or NanoB they attract one another with a strength determined by the nanoparticle interfacial energy given by \(e_{ab}\). Adjacent cells that are occupied by different species also attract one another. The strength of NanoA–liquid, NanoB–liquid, and NanoA–NanoB attractions are given by \(e_{al}\), \(e_{bl}\), and \(e_{ab}\), respectively. The last term on the right hand side of Equation 1 describes the effects of the chemical potential, \(\mu\), that is used to establish the average concentration of liquid and vapor cells at equilibrium.

The dynamics of the model used here are stochastic, both for fluctuations in solvent density and for nanoparticle diffusion. The full description of the stochastic moves can be found elsewhere.\[31,32\] In short, an attempt is made to convert a randomly chosen lattice cell \(i\) that is not occupied by a nanoparticle, from liquid into vapor (or vice versa), \(I_i \rightarrow \{1–l\}\). These moves are then accepted with a Metropolis probability \(p_{acc} = \min[1, \exp(\Delta H/k_BT)]\), where \(k_B\) is the Boltzmann constant, \(T\) is temperature, and \(\Delta H\) is the resulting change in energy computed using the Hamiltonian given by Equation 1. Nanoparticles execute a random walk on the 2D lattice, biased by their interactions with each other and with liquid cells. Their movement is also accepted with the same Metropolis probability, but only if the region into which the nanoparticle moves is completely filled with liquid. The solvent density in the lattice cells overtaken by this displacement is regenerated in the wake of the moving nanoparticle. This final constraint mimics the very low mobility of nanocrystals on a dry surface.\[10\] A single Monte Carlo step consists of an attempt to change the value of all liquid/vapor cells (note that the sum of the liquid and vapor cells is conserved) followed by \(N_{move}\) attempts to move all nanoparticles.

All the simulations reported below start from a non-equilibrium initial condition where the lattice is entirely filled with liquid and nanoparticles. This initial condition seems appropriate for experiments of a thin liquid film containing nanoparticles that completely wet the substrate. The nanoparticles acquire a random position inside the simulation box at a given coverage and molar ratio. Periodic boundary conditions are imposed in both directions, \(\mu\) is fixed at a value for which the equilibrium state is vapor, and the dynamics of nanoparticle assembly, nanoparticle phase separation, and solvent evaporation are followed.

In all the simulations reported, the following parameters are fixed: \(e_l = e_{al} = 9/4\) and \(e_{ab} = 7/4\) in units of \(\ell_0\). These parameters are chosen to ensure that the interactions between nanoparticles are screened by the solvent\[30–32\] such that the self-organization of nanoparticles occurs only when the solvent evaporates.\[21,31,32\] This implies that \(e_{al} = e_{bl} > e_l\). Furthermore, \(e_{bl} > e_{ab} = e_{al}\) is taken to model the more polarizable core of the nanoparticles compared with that of a corresponding liquid patch with similar dimensions.

In a two-component system, the cross interactions between the two species determine the equilibrium superstructure within the self-assembled domains. Three cases are studied where \(e_{ab} = 6/4\), \(e_{ab} = 9/4\), and \(e_{ab} = 10/4\). These model parameters lead to equilibrium superstructures that correspond to phase separation between nanoparticles of type A and B, to an amorphous state, and to an ordered, checkerboard-like superstructure, respectively. These different situations are referred to as ‘amorphous’, ‘binary’, and ‘checkerboard’ phases, respectively. All simulations are performed for a box size of \(512 \times 512\) cells. The time is reported in units of Monte Carlo steps. This time unit can be translated to ‘real’ time using a simple relation between the diffusivity of the nanoparticles and the size of the typical solvent correlation length, \(\xi.\)[31]

In Figure 1, snapshots of simulated non-equilibrium trajectories at early, intermediate, and late times are projected. The total coverage is 10 % and \(g_a = g_b = 0.05\), where \(g_a\), \(g_b\) are the 2D densities of NanoA and NanoB, respectively. The chosen trajectories differ from one another only in the strength of \(e_{ab}\). The upper, middle, and lower panels correspond to \(e_{ab} = 6/4\), \(e_{ab} = 9/4\), and \(e_{ab} = 10/4\), respectively. At early times \((t = 1\) in units of Monte Carlo steps), nanoparticles fill random cells in the simulation box. The remaining cells are filled with liquid. The evolution of this non-equilibrium initial state towards equilibrium is driven by the value of the chemical potential, which favors evaporation. At relatively short times \((t = 64\), long-wavelength fluctuations of the solvent density lead to evaporation of the thin liquid layer, and nanoparticles assemble to form distinct, disk-like aggregates, similar to the case of a single component system.\[31\]

After the solvent has evaporated, domains continue to grow (left panels at \(t = 65536\), and the system is driven to the equilibrium structure of a single large disk. This is a result of the fact that the liquid still wets the boundaries of the nanoparticle domains due to the attractions between the solvent and the nanoparticles. In this case the domains remain mobile throughout the growth dynamics since the energetic cost of moving a nanoparticle into the surrounding solvent is comparable to \(k_BT\). This occurs when a wetting layer remains thermally stable at the edges of a nanoparticle domain, \(\mu + e_{al} > 1 + 2e_{ab}/k_BT\). In this case the solvent drives the uniform aggregation of the nanoparticles, while growing domains are free to rearrange and coalesce.

As expected, the order within each domain (superstructure) depends on the coupling strength between the nanoparticles of type A and B. When \(e_{ab} = e_l = e_{al}\) (middle panels) an amorphous structure is formed within each domain, and the nanoparticles are randomly packed. Within this limit the self-organization process can be reduced to that of a single component system described elsewhere.\[31\]

When \(e_{ab} < e_l = e_{bl}\) (upper panels) the system tends to phase separate into domains that are rich in nanoparticles A and domains that are rich in nanoparticles B. It is interesting to note that the separation between nanoparticles A and B within each domain is nearly complete, despite the fact that the system is still far from its equilibrium structure of a single large
This indicates that the time scale for domain growth is not limited by the phase separation of the nanoparticles. When $e_{ab} > e_a = e_b$ (lower panels), the system forms a checkerboard structure within each domain. In this limit, a thermodynamically stable superstructure is obtained when each nanoparticle is surrounded by the other type of nanoparticle. Each domain (disk) is characterized by several defects, a result of the fact that the number of nanoparticles A and B differ in each aggregate. Due to this limitation, the number of defects per domain is large in comparison with the previous case where $e_{ab} < e_a = e_b$. As the size of the domain increases, the number of defects decreases, which is consistent with the increase of the ratio of volume to surface area. Perfect ordering can be achieved only when the system is close to its equilibrium structure, a structure that forms on a very long timescale.

One notable difference between these three cases is the average size of the domains. The typical size of the domains is clearly smaller when $e_{ab} > e_a = e_b$. This is also the case at higher nanoparticle coverage when the system forms ribbon-like morphologies (see Fig. 3 below). This suggests that the mechanism of domain growth depends on the nature of the interdomain superstructure. To better understand this aspect of the growth dynamics, the mechanism for coarsening for the three values of $e_{ab}$ has been studied. The results are illustrated in Figure 2, which depicts the time evolution of the average number of nanoparticles in an aggregate ($N(t)$) along with the average number of nanoparticles of type A ($N_A(t)$) and B ($N_B(t)$). A particle is connected to an aggregate if, along any direction, it is in direct contact with the aggregate. The average size of a domain is related to the number of particles in an aggregate via the standard proportionality $R(t) \propto N(t)^{1/2}$. Following a transient period in which $N(t)$ is nearly conserved, it suddenly grows due to the evaporation of the solvent. At later times, $N(t)$ grows as $t^{a}$ for all cases shown. This result is consistent with growth by a cluster diffusion mechanism, in which domains grow solely by coalescence,[43] and which is similar to the growth mechanism found for a single component system.[31]

While qualitative features of growth dynamics are common to all three model systems studied, the exponent $a$ depends on the value of $e_{ab}$. When the system is driven to form a checkerboard superstructure $a \approx 1/5$, while for the other two cases...
$a = 1/3$. This, along with the fact that perfect ordering in the case of a checkerboard structure is achieved only near the equilibrium structure, implies that the formation of an ordered superlattice is significantly slower than the formation of an amorphous state. It is not surprising, therefore, that most previous studies of assemblies of multicomponent nanocrystals have resulted in amorphous materials.\[27–30\] This excludes the study of Redl et al.\[26\] where the best binary superlattices were generated by controlling the solvent evaporation rate, such that the evaporation was very slow.

The different values of the exponent $a$ also suggest that the mechanism for coarsening depends on the interdomain superstructure. For $a = 1/3$, the mechanism for island diffusion is uncorrelated evaporation/condensation.\[44\] The diffusion of domains occurs by annihilation of a nanoparticle on one end of the cluster and the creation of a nanoparticle at the other end at the same time. For $a = 1/5$ the mechanism is periphery diffusion,\[45\] in which nanoparticles diffuse on the periphery of the domain. In this case, the shape of the domain changes slightly as nanoparticles diffuse along the boundaries. An analysis of the diffusion of single aggregates reveals exactly the above mechanisms for the corresponding cases. These different mechanisms can be related to the energetics of the system. The stronger interactions between nanoparticles of type A and B ($e_{ab} > e_a = e_b$) result in tightly packed aggregates that contain lower amounts of solvent confined between them. Thus, only nanoparticles at the wet periphery of the aggregates are mobile. When the interactions between nanoparticles of type A and B are weaker ($e_{ab} \leq e_a = e_b$), the solvent can wet the entire aggregate and the nanoparticles are mobile everywhere.

At a higher coverage under similar evaporation conditions and with similar nanoparticle mobilities, domains are anisotropic and percolate through the lattice. This is illustrated in Figure 3, where snapshots from simulated non-equilibrium trajectories at early, intermediate, and late times are projected. The total coverage is 40 %, so that $g_a = g_b = 0.2$. Similar to the previous case of lower coverage, the chosen trajectories differ from one another only in the strength of $e_{ab}$. The upper, middle, and lower panels correspond to $e_{ab} = 6/4$, $e_{ab} = 9/4$, and $e_{ab} = 10/4$, respectively. Under these conditions, the evaporation of the solvent simply triggers the self-organization. Domains continue to grow after the solvent has nearly disappeared since their interface remains wet throughout the growth process. The size of the domains is mainly determined by the diffusion rate of the nanoparticles.

In Figure 4, a few representative simulation trajectories under heterogeneous evaporation conditions for a total coverage of 20 % are plotted. The transition from homogeneous to heterogeneous evaporation limits can be tuned by changing $\mu$ or $T$\[31\]. For the results reported here, the temperature (in comparison to the homogeneous case) has been modified to ensure that the evaporation is heterogeneous in space. The upper, middle, and lower panels correspond to $e_{ab} = 6/4$, $e_{ab} = 9/4$, and $e_{ab} = 10/4$, respectively. The initial conditions used are similar to those for the homogeneous evaporation case (left frames), namely, nanoparticles fill random cells in the simulation box and the remaining cells are then filled with liquid.

The evolution of this non-equilibrium initial state towards equilibrium is dramatically different from the homogeneous evaporation case. Here, the solvent remains locally metastable on the surface and evaporation occurs not by long-wavelength fluctuations, but by nucleation and growth of vapor bubbles. This is depicted at relatively short times ($t = 64$), where large vapor holes are formed for all three cases shown, and the density of the solvent is clearly heterogeneous on a relatively
large length scale. At longer times, the shapes of the terminal structures in these trajectories are determined primarily by the relative time scales of evaporation, \( \tau \), and nanoparticle motion, \( \tau_D = \xi^2 / D \), where \( D \) is the nanoparticle diffusion coefficient in solution. If nanoparticles are sufficiently mobile to track the fronts of the growing vapor nuclei, their aggregate patterns will be shaped by the structural history of evaporation.\[31\] On the other hand, when the mobility of the nanoparticles is low compared with evaporation, the resulting morphologies are fractal-like and originate in dynamics that are locally similar to diffusion-limited aggregation.\[46\]

The formation of the superstructures within each domain depends on the value of \( \epsilon_{ab} \). Similar to the case of homogeneous evaporation, when \( \epsilon_{ab} < \epsilon_a = \epsilon_b \) (upper panels), the system tends to phase separate into domains that are rich in nanoparticles A and domains that are rich in nanoparticles B. The last time frame shown, where the system is already effectively frozen (stick case, see Rabani et al.\[31\]), clearly indicates that the binary phase separation is far from completion. In comparison to the case of homogeneous evaporation under similar conditions (upper left panel of Fig. 3), structural changes in each domain are much slower as a result of the very low mobility of the domain edges. In the homogeneous evaporation case, coalescence and growth of domains occurs mainly after the solvent has approached its equilibrium density, and thus, the system has enough time to relax to its equilibrium superstructure. Here, the system has a narrow time window during the evaporation process itself to relax to the equilibrium superstructure. For the case shown in Figure 4, this time frame is too short to complete the binary phase separation.

A similar picture emerges for the case of \( \epsilon_{ab} > \epsilon_a = \epsilon_b \) (lower panels), where the system tends to form a checkerboard structure within each domain. In this case, the time window of evaporation is long enough to achieve local order. Unlike the previous case where the system tends to phase separate and nanoparticles move on length scales typical of the size of the domains, here the spatial motion required to establish equilibrium is on a much smaller length scale, typical of the size of the nanoparticles themselves. Despite this, the resulting morphologies are still characterized by many defects compared with the homogeneous evaporation limit under similar conditions, and the relaxation of these defects occurs on a very long time scale.

In Figure 5, representative morphologies at long times when the system is already effectively frozen and for different ratios of \( \tau / \tau_D \) are plotted. The upper and lower panels represent the case where the system phase separates and when it forms a checkerboard superstructure, respectively. The ratios of \( \tau / \tau_D \) from the left to right are 500, 3000, 30 000, and 270 000. For the lowest value of \( \tau / \tau_D \), the system forms a fractal-like structure, and rod-like structures are formed for the other cases shown. This is consistent with the results reported for a single component system.\[31\] When the system tends to phases separate (upper panels of Fig. 5) the ratio \( \tau / \tau_D \) can be used to monitor the dynamics of the phase separation as the system is driven towards equilibrium. As the value of \( \tau / \tau_D \) is increased, the sizes of the domains that are rich in nanoparticles of type A (B) increase. However, a complete separation between nanoparticles of type A and B under the current conditions requires even larger values of \( \tau / \tau_D \) than those studied here. The situation is somewhat different when the system is driven to form a checkerboard superstructure, as shown in the lower panels of Figure 5. Even at a relatively small value of
As the value of $s/t_D$ is increased, the time window wherein the nanoparticles are mobile is increased, and defects that are observed at low values of $s/t_D$ are annealed. At the largest value of $s/t_D$ shown in Figure 5, the density of defects is quite low.

Self-assembly is an extremely useful tool to fabricate novel materials with unique physical properties. Experimentally, it has been widely used in materials science over the past decade. However, our understanding of the self-assembly process in general, and of out-of-equilibrium self-assembly in particular, is still limited. A significant step towards a universal description of out-of-equilibrium self-assembly on the nanometer-scale has recently been suggested for a single-component system. In this work, a similar approach has been developed to describe the out-of-equilibrium self-assembly of binary mixtures of nanoparticles.

Two distinct ordering mechanisms have been discussed, which correspond to homogeneous and heterogeneous limits of the evaporation dynamics. When the evaporation is spatially uniform, the coarsening of the 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 and phase separation are determined by nanoparticle diffusion. The mechanism for coarsening depends on the strength of the cross-particle interactions and on the amount of liquid confined within the domains. At later times, the average domain size grows as a power law given by $R(t) \propto t^\alpha$. This is consistent with growth by a cluster-diffusion mechanism, in which domains grow solely by coalescence. When the system is driven to phase separation, the scaling exponent is found to be $\alpha = 1/3$ and the mechanism for island diffusion is uncorrelated evaporation/condensation. When the system forms a checkerboard superstructure, coalescence occurs by periphery diffusion which leads to $\alpha = 1/5$.

Alternately, when the evaporation is heterogeneous in space and the domain edges are effectively frozen when the evaporation is complete, the systems form network- or fractal-like structures. The shapes of the terminal structures are determined primarily by the relative time scales of evaporation, $\tau$, and nanoparticle motion, $t_D$. If the nanoparticles are sufficiently mobile to track the fronts of growing vapor nuclei, their aggregate patterns will be shaped by the structural history of evaporation, which leads to network-like morphologies. On the other hand, when the mobility of the nanoparticles is low compared with the rate of evaporation, the resulting morphologies are fractal-like. Self-organization and ordering within the domains occurs only in a narrow time window during the evaporation process itself. When the system is driven to phase separate, nanoparticles move on length scales typical of the size of the domains, and separation between nanoparticles of type A and B requires very slow evaporation rates. In the other case, when nanoparticles form a checkerboard structure, the spatial motion required to establish equilibrium is on a much smaller length scale, typically of the size of the nanoparticles themselves. Thus, local ordering can be achieved at faster evaporation rates. However, annealing of the local defects does require slow evaporation rates as well.

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