Multiscale Modeling of the Surfactant Mediated Synthesis and Supramolecular Assembly of Cobalt Nanodots

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Multiscale simulations are used to bridge the surfactant templated assembly of individual ~1–10 nm cobalt dots, to their ordering into supramolecular arrays. Potential energy surfaces derived from *ab initio* calculations are input to lattice Monte Carlo simulations at atomic scales. By this process we quantitatively reproduce the experimental cobalt nanoparticle sizes. Crucially, we find that there is an effective short range attraction between pairs of nanodots. Mesoscale simulations show that these attractive interdot potentials are so short ranged that the dots can assemble only into orientally ordered hexatic phases as in the experiments.

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Finite size metal [1–7] and organic [8,9] crystals have been extensively investigated because their optical and magnetic properties vary dramatically with size. A promising way to produce "nanodots" is to mix a reducing agent with a solution of precursor and surfactant. The precursor is immediately reduced to the material of interest, which has limited solubility and attempts to precipitate out. It is empirically known that the surfactant sterically stabilizes the growing nanodot against Oswald ripening, thus controlling nanocrystal size. While solutions of coated magnetic nanoparticles can be used directly, e.g., in MRI [10,11], two and three dimensionally ordered arrays are sometimes preferred, e.g., in photonics. For example, ordered 2D nanodot arrays can be formed by spin casting the solutions on a surface [12,13]. Given these facts, it is clear that a comprehensive model must capture the factors controlling the synthesis of a single dot and also the subsequent supramolecular assembly of dots into arrays. However, to our knowledge no attempts have been made to go from molecular details to a hierarchy of assembly up to the macroscopic. Gelbart and coworkers [14,15] conjectured that surfactant decorated nanocrystals behaved analogously to microemulsions of oil in water stabilized by surfactant. Following this ansatz, the role of surfactant and metal concentration on the sizes of gold nanocrystals could be predicted [14]. Further, they postulated that the nanoparticles assembled into higher order structures if they interacted with a long range repulsion in addition to a short range attraction [15]. Similarly, kinetic Monte Carlo simulations at a macrosystem level allow for the prediction of equilibrium micelle sizes [16]. While interesting, these works do not provide a molecularly detailed understanding of nanodot synthesis and their assembly.

The relevant phenomena in the surfactant mediated nanocrystal growth and assembly occur over disparate length scales, not easily addressed within a single calculation. *Ab initio* calculations, necessary to delineate potential energy surfaces, are restricted to several 10's of moieties. Atomistic simulations, with these *ab initio* potentials as input, are appropriate to model thousands of moieties but cannot simulate large enough systems to capture their mesoscale assembly into μm-cm sized arrays. Mesoscopic models are thus required at this larger scale. Here, we present the first results of a multiscale simulation tool designed to bridge these different time and length scales. Using this approach we quantitatively reproduce the experimentally determined sizes of individual cobalt nanodots. At a larger scale, nanodot assembly into two-dimensional arrays is shown to be akin to the assembly of spheres with very short range attractions.

To make explicit contact with experiment, we select the work of Yin and Wang [7] and investigate the intermolecular interactions between sodium bis(2-ethylhexyl) sulfosuccinate [termed Na(AOT) or surfactant], toluene (solvent), and cobalt (metal). We use all electron spin polarized density functional theory (DFT) based on the generalized gradient approximation [17] to delineate both the ground state and the distance dependent interaction potential between any two moieties. We use 6-311G* basis sets, and the electronic structure calculations are performed using the GAUSSIAN 98 code. Since it is difficult to handle the whole surfactant molecule in this calculation, we divide it into two different parts: (i) the hydrophilic "head" which contains Na, S, and all the oxygens and (b) two hydrophobic "tails." Each tail is a string of (CH_2) groups: for simplicity these are modeled as string of T groups, where each T fragment is equivalent to two catenated (CH_2) groups. Below, we do not show any interactions with a T group since its attractive interactions with any other moiety is comparable to calculation uncertainties. We generate several configurations of a pair of moieties (chosen from head, cobalt, and toluene) at a prespecified separation. Each structure is optimized to get the local minimum energy configuration. The difference between this energy and the sum of the energies of the two moieties in their respective ground states gives the binding energy. Figure 1 shows the intermolecular potential between the different pairs as a function of center of mass separation. In the case of the surfactant head the center of mass is calculated only on the basis of the positions of the Na and SO_3 groups. This reflects the fact that the lowest energy states for all species with the head is always in the vicinity of these groups [18].

These potentials are used as input for Monte Carlo simulations. We discretize space into a simple cubic lattice with a spacing of $a = 2.25$ Å [19]. We make this simplification since off-lattice Molecular Dynamics simulations for the micellization of Na(AOT) in hexane takes ~1 yr CPU time [20]. The a value chosen is comparable to the position of the minimum in the cobalt-cobalt potential. We expect this to be a reasonable choice since cobalt is crystallized at the temperature of interest ($T^* = k_B T/\varepsilon_{\text{Co-Co}} = 0.05$, ~483 K). We *a priori* therefore expect to be incorrect in reproducing the crystal symmetry of the cobalt. For all other pairs of moieties, however, the hard core is larger than 2.25 Å, thus allowing us to sample both attractive and repulsive interactions even on this lattice. We sample interactions at lattice points, and thus we employ a discretized version of the continuous potential. Additional motivation for this simplification comes from our previous work which suggests that lattice models with such discretized potentials quantitatively reproduce the thermodynamics of off-lattice systems, so long as molecular sizes are larger than the spacing of the underlying lattice [21]. The surfactant, Na(AOT), is modeled as $T_3H_2T_4$: here each T was equivalent to two (CH_2) units and H is a head fragment. No torsional or bond bending potentials are incorporated in the Na(AOT) [19]. All interactions involving a H or a Co are truncated at 4.5 Å. All interactions with the T groups and the toluene-toluene interaction are modeled as hard cores (a T group has a hard core diameter of 4.67 Å while that of toluene is 4.30 Å. For T-H and H-toluene interactions they are 3.5 and 3.4 Å, respectively). While we sacrifice quantitative accuracy in making some of these computationally expedient assumptions, we expect our results to be qualitatively, and even semiquantitatively, accurate.

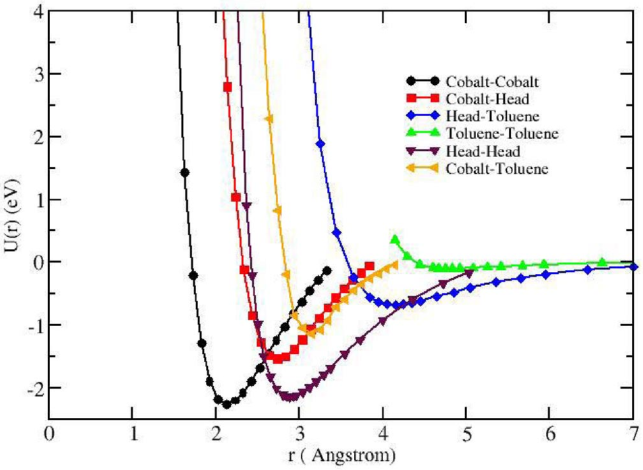

FIG. 1 (color online). Potential energy of interaction in units of eV as a function of separation distance between different moieties (in units of Å) derived from the DFT calculations.

We use the grand canonical ensemble Metropolis Monte Carlo method [22] with periodic boundary conditions in all three directions. Simulations on lattices of size, 40^3, 60^3, and 80^3 yielded similar results, implying that finite system size effects are minimal. In a typical simulation on the 40^3 lattice the numbers of Co atoms (=384; volume fraction = 0.006) and of toluene molecules (=3400; volume fraction = 0.72) are kept fixed, and these moieties are moved only by random displacement. At low temperature, the random displacement of Co is hardly ever accepted since they are all in clusters. To improve the efficiency of this move we use the aggregation volume biased Monte Carlo method (AVBMC), exactly as has been successfully employed to perform Gibbs ensemble simulations of gas-crystal equilibria [23]. For these AVBMC moves the "inside" volume is a sphere of side 4. The number of surfactant varies in the simulation, and their insertion and deletion are controlled by their specified chemical potential. For the surfactants we use reptation and chain addition and destruction following the configurational bias method [24]. Typical simulations involve 500×10^6 MC moves: 12.5% random moves for solvent (acceptance ~36%), 12.5% AVBMC moves for Co (acceptance ~10%), 45% reptation moves for the Na(AOT) (acceptance ~1%), and 30% insertion/deletion events (acceptance ~0.001%). All thermodynamic properties are calculated following the histogram reweighting method [19].

We first examine the spatial distribution of Co, toluene, and H and T moieties in a given micelle. It is clear that, as in the experiments, the Co are in the center of the micelle. These are sequentially surrounded by H, T, and then solvent [Fig. 2(c)]. We start the simulations in two different fashions: (i) the cobalt particles are distributed at random and (ii) we start with a conformation equilibrated at a much higher temperature ($T^* = 0.5$). In the first case, we find that the aggregates quickly form, but they are extremely polydisperse (~ 20%) [Fig. 2(a)]. However, after 500×10^6 MC steps we find that the size distribution of metal clusters is narrow (polydispersity ~ 5%), the number of micelles has decreased, while their sizes have increased [Fig. 2(b)]. We find that the two different starting states end up with the same number of dots and practically indistinguishable size distributions. These results, in combination, establish the robustness of the MC results. For parameters chosen to mimic the experiments [7] we obtain nanocrystal sizes of 4.7 nm with an equilibrium polydispersity of 5% in satisfactory agreement with experiment where crystals are distributed in the range of 4–9 nm [7]. Our results stress the validity of the experimentally based conjectures that (i) the surfac-

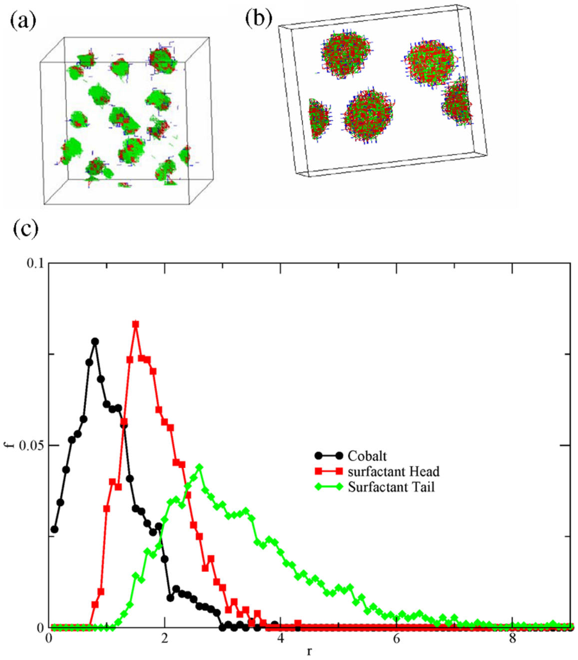

FIG. 2 (color online). (a) Snapshot of nanoclusters decorated by surfactant. Co is on the inside surrounded sequentially by heads, tails, and solvent (solvent not shown). This snapshot is after 10×10^6 MCS. (b) Same as (a) but after 500×10^6 MCS. No further changes occur over an additional 500×10^6 step MCS run. (c) Spatial distribution of Co, H, and T for micelles in (b). r is in units of lattice constant: to obtain real distances r should be multiplied by 2.25 Å.

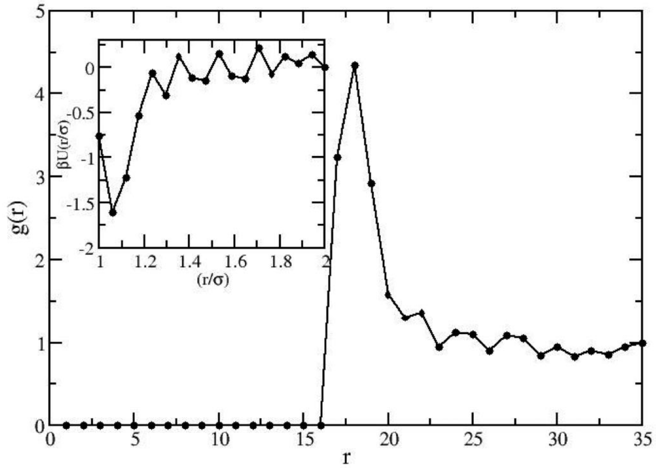

FIG. 3. $g(r)$ of the nanoclusters. Inset: $\beta u(r)$ between two nanoclusters obtained from inverse Metropolis MC simulations with random displacements of spheres. The potentials were updated after 8.13×10^5 cycles: each cycle is one attempted move per sphere. We stop when the $g_{\text{target}}(r)$ is reproduced to within 1%. Distances are normalized by the nanocluster diameter, σ.

tant templates the growth of the metal dots and (ii) that the uniformity of nanodot size is attributed to the slow exchange of metal atoms between micelles, permitting size "equilibration" [3].

To understand the molecular basis for the supramolecular assembly of these nanodots into 2D arrays, where size scales of μm-cm need to be considered, we construct the $g(r)$ for the centers of mass of a pair of nanoclusters decorated by surfactant. Figure 3 clearly shows that the $g(r) = 0$ for distances smaller than 17 lattice units (~38Å), the mean diameter of a nanocluster. Further, $g(r) = 1$ practically for all distances outside the immediate vicinity of contact. This result shows that the nanodots do not aggregate strongly,; i.e., they are stabilized against Oswald ripening by the T which are solvated by the solvent. Two facts reiterate this notion. First, even when the micelles are in close proximity, metal particles continue to exchange between different micelles. However, on average, one micelle never grows at the expense of another at equilibrium. Second, metal nanoclusters without decorating surfactant agglomerate irreversibly.

We employ the $g(r)$ values to deduce an effective distance dependent interaction, $\beta u(r)$, between two nanodots. To construct this $\beta u(r)$, which precisely reproduces these $g(r)$, we perform inverse Monte Carlo simulations [25,26]. In this step we coarse grain away any detailed description of the surfactant decorated micelles and model them as spheres of radius unity. Further, we treat the spheres as time invariant in size and monodisperse, reasonable approximations close to equilibrium. The r values in the $g(r)$ are then normalized by the sphere diameter (17 lattice units ~ 38Å) to reflect this coarse graining. Since each nanodot on average occupies $\sim 17^3$ lattice sites, this coarse graining step reduces the computational effort by at least a factor of 17^6. We begin with a dilute system of spheres which are at the same density as in the simulation of micellization described above (1230 spheres in a box of size 60^3, where lengths are in coarse grained units; i.e., 1 length unit ~ 38 Å). Our simulation box size is 60×38 Å ~ 0.25 μm, in the right range to consider the supramolecular assembly of these nanodots. Initially, the interaction potential between pairs of coarse grained spheres is set to $\beta u(r) = -\ln g(r)$. We now perform a Monte Carlo simulation with this $u(r)$ and update the $\beta u(r)$ as follows: [26] $[\beta u(r)]_{\text{new}} = [\beta u(r)]_{\text{old}} + f \times \ln[\frac{g(r)}{g_{\text{target}}(r)}]$, where $g_{\text{target}}(r)$ is the target value of the radial distribution function between the nanodots, $g(r)$ is the corresponding function obtained using the current estimate of $\beta u(r)$, and $f = 0.1$. A few iterations (~10) of this process ensure that a converged $\beta u(r)$ vs r results (see the inset to Fig. 3). Note that the potential is somewhat attractive ($\beta u(r) \approx -1.5$) close to contact and then goes to zero with increasing r. This relatively weak attraction close to contact, which is comparable to thermal energy (1 in the same units), arises since the presence of a dot creates a zone from which other dots are excluded. Since this exclusion driven attraction is

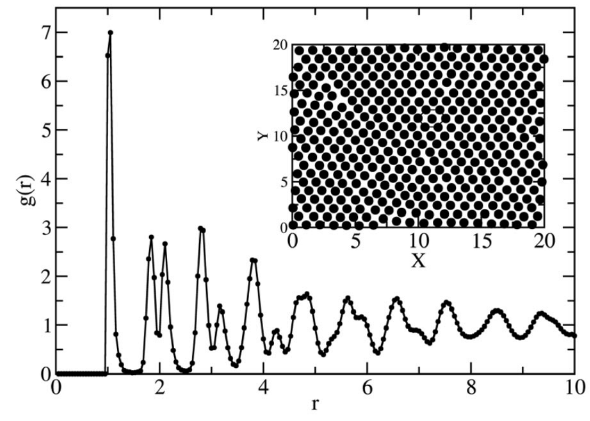

FIG. 4. $g(r)$ of two-dimensional arrays of nanodots. Inset: a snapshot of the two-dimensional array of nanodots. We consider 380 spheres in a box with a lateral dimension of $L = 20$ on a side with periodic boundary conditions in both dimensions.

relatively weak, we conjecture that the nanodots should show little sign of binding irreversibly. Note that this form of the potential does not possess a long range repulsion between particles, postulated by Gelbart to be the origin of long range assembly of dots [15].

We perform 2D MC simulations on these coarse grained spheres using the $\beta u(r)$ in Fig. 3 to understand the experimentally observed ordering of these nanodots cast on substrates. As expected from past work [27,28] the relatively short range of the attractive interdot potential prevents them from undergoing a liquid-gas phase separation with increasing concentration. Rather, they form an orientally ordered hexatic phase (Fig. 4, main figure) with increasing concentration and into hexatic crystals at even higher filling fractions [7]. A representative example is shown in Fig. 4 (inset) for a filling fraction $\eta = (\pi/4) \times N_s/L^2 \approx 0.76$ (N_s is the number of spheres and L is the box size) where hard disks are expected to form an orientally ordered hexatic phase. These results are very reminiscent of the ordering of the cobalt nanodots in the experiments [3,6] and strongly suggest that a combination of long range repulsion and short range attraction is unnecessary in this context. Rather, the physics of two-dimensional assembly of nanodots into ordered arrays is equivalent to the behavior of spheres with short range attractions.

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[18] We found that the $u(r)$ derived from two particles adequately represents the properties of larger nonmetallic clusters, e.g., for Ar. This is not the case for metals. For Co the binding energy between two cobalt atoms is ~ -2.25 eV. When we use this value to predict the properties of 13 atom clusters, we obtain a binding energy ~ -6.75 eV per atom, larger than even the experimental bulk value ~ -4.38 eV. This stresses the importance of many body repulsions for metallic systems. Consequently, we are incorrect in using two body potentials in the case of cobalt. However, we operate at temperatures where Co atoms are strongly bound to other Co atoms. Further, we use a lattice description that is relatively insensitive to changes in the structure and packing of Co in each nanodot. We therefore suggest that the use of this potential probably does not qualitatively alter the results we obtain from our simulations; however, we are currently working to verify this conjecture by incorporating these many body effects.
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