Cluster Structure and Corralling Effect Driven by Interaction Mismatch in Two Dimensional Mixtures

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(Received 2 May 2005; published 20 January 2006)

The formation of clusters with crystal-like order in two dimensions is studied using Monte Carlo simulations. We find that the necessary conditions to induce the formation of clusters of one component is to add a second component that has a larger size and that has a long-range soft repulsive interaction with its own kind but not with the other one. The clusters of the small particles are found to be surrounded by a network of quasi-one-dimensional arrangements of the larger particles. The degree of order of the clusters is found to depend on the concentration of the larger particles. The findings explain recent experimental observations on lipid-poloxamer mixtures and they provide guidelines for how to form ordered clusters of nanoparticles in two dimensions.

DOI: 10.1103/PhysRevLett.96.028701 PACS numbers: 89.75.Fb, 81.16.Rf, 82.35.Np, 82.60.Qr

The formation of domains of ordered particles on surfaces is a major challenge in a large variety of nanotechnological applications [1–3]. It also presents an important fundamental question of how the range and type of interparticle interactions in mixtures can lead to the formation of clusters with a high degree of order for one of the species. Nanoparticles on surfaces, or interfaces, are not strictly two-dimensional systems. Can one take advantage of the third dimension to tune the interparticle interactions to obtain cluster with high degree of order? In this Letter we demonstrate that in binary mixtures of small and large particles, size mismatch between particles and a long range soft repulsive interactions between the large particles are sufficient (and may be necessary) conditions to induce the formation of clusters of the smaller particles with varying degree of internal order. The combination of these interparticle interactions is possible due to the presence of the third dimension.

Recent experimental observations [4] on lipid monolayers spread at the water-air interface show that the adsorption of triblock copolymers, with one hydrophobic block end-capped at both ends with hydrophilic blocks, induces the corralling of the lipids into clusters with crystalline order. This phenomenon is observed at very low lipid surface densities and it is accompanied with a jump of the lateral pressure. The questions that we address are: (i) what are the specific interactions in this system that lead to the formation of crystal-like lipid clusters, and (ii) what are the generic interparticle interactions in (quasi)-two-dimensional systems that will lead to the formation of clusters with a desired degree of order?

Experimental observations of mixtures of nanoparticles of different sizes spread at surfaces show the formation of a large variety of different crystalline phases at high densities [5]. Computer simulations of mixtures of two-dimensional Lennard-Jones particles predict similar behavior [6]. However, there is no evidence that these types of mixtures can form clusters with high order of only one component [7]. The studies on the lipid-polymer mixtures suggest that the role of the polymer is to induce a long range repulsion that is responsible for the corralling and the jump on the lateral pressure. In this Letter we study what are the fundamental conditions necessary to induce corralling and the formation of clusters with high degree of order, using Monte Carlo simulations on simple model systems.

To represent qualitatively the gas-liquid-solid two-dimensional phase behavior observed in lipid (l) monolayers at the water-air interface we treat the lipid-lipid interactions with a Lennard-Jones (LJ) potential of the form $u_{ll} = 4\epsilon[(\sigma_{ll}/r)^{12} - (\sigma_{ll}/r)^6]$, where σ_{ll} is a measure of the effective size of the lipid and ϵ is the strength of the interaction. This simplified potential does not account for the internal degrees of freedom of the hydrocarbon chains in the lipid, and thus it should be thought of as a potential of mean-force determined by the proper averaging of the chain conformations. On the other hand, this potential, in its generic form, could properly represent the effective interactions between two nanoparticles. To summarize, we choose this potential for its simplicity, generality, and because it captures the phase behavior of the one component system.

The two blocks of the polymers interact in the following way. The hydrophobic blocks interact with themselves and also with the hydrophobic tails of the lipid molecules. The hydrophilic blocks interact only with other hydrophilic blocks of the polymer on the water side of the interface. The two types of interactions are different since the hydrophilic blocks are in a good low molecular weight solvent environment. For the hydrophobic blocks of the polymer we consider a LJ interaction, to follow the same line as for the lipid-lipid interactions. The polymer-polymer (LJ) hydrophobic interactions are irrelevant due to the strength and range of the hydrophilic-hydrophilic repulsions shown below. The range and strength of the hydrophobic polymer-lipid interaction, $\sigma_{\rm pl}$ and $\epsilon_{\rm pl}$, are different than the lipid-lipid interaction. The size mismatch is incorporated to represent the very different order that can be achieved upon two-dimensional packing of pure hydrocarbon methylenic tails (lipids) and the propylene oxide that comes from the polymer. The effect of the strength of the interactions is one of the parameters that we study. This interaction scheme could be applied for a binary mixture of nanoparticles, where $\sigma_{\rm pl}$ and $\epsilon_{\rm pl}$ would represent the large-small particle range and strength of the mixed interactions.

For the polymer-polymer interactions the most important contribution arises from the hydrophilic blocks. Since they are in a good solvent environment, these interactions are repulsive and their range is of the order of the polymer size. We can calculate the potential of mean force between two polymer chains attached to a surface when their tethering points are at a distance d from each other. This is obtained by calculating the following ensemble average [8]

$$\beta u_{mf,\rm pp}(d) = -\ln\langle \exp[-\sum_{ij} \beta u_{\rm mm}(r_{ij}; d)]\rangle_{\alpha_1,\alpha_2}, \qquad (1)$$

where the sum runs over all the pairs of monomer-monomer (mm) intermolecular interactions, when the distance between tethering points is d, and the brackets represent an average over all the conformations of polymers 1 and 2, $u_{\rm mm}(r_{ij})$ is the mm (purely repulsive) LJ potential. The way we calculate the mean-force potential is by generating a very large set of independent conformations for each polymer chain, α_1 and α_2. For each distance d we calculate all the pair interactions between monomers of polymer 1 and monomers of polymer 2 and average over the complete set of conformations.

The different interactions in the mixture are shown in Fig. 1 for two different chain lengths of the hydrophilic block of the polymer. The main features of the potentials are: (i) the size mismatch between the hydrophobic parts of the lipid and the polymer and (ii) the long range *soft* repulsive potential between the hydrophilic blocks of the polymer, whose range depends upon the hydrophilic block chain length. While we only show two examples, whose chain lengths are relevant for the experimental systems [4], it is clear that the range of the soft potential will scale as the radius of gyration of the chains, i.e., as $N^{3/5}$, for the good solvent case treated. We fit the soft repulsive potential with a double exponential, since it is more convenient for carrying out the simulations.

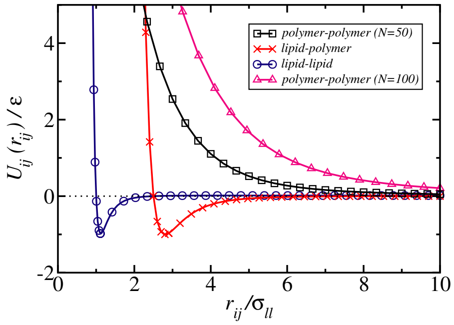

FIG. 1 (color online). The effective interactions between the particles, with the different contributions as shown in the inset and described in the text.

Using the described model system we have carried out extensive Monte Carlo (MC) simulations under the following conditions. We start with a pure lipid system under dilute conditions. After equilibration of the one component system, we simulate the adsorption of the polymer and equilibrate the polymer-lipid mixed system. Thus, we consider a canonical ensemble for the lipids and grand canonical for the polymers, i.e., fixed number of lipids, polymer chemical potential, surface area, and temperature [9]. We have simulated systems with many different sets of parameters for the interaction potentials. From the simulations results we find that the strength of the polymer-lipid attractions is irrelevant for the formation of clusters. The necessary conditions for the formation of clusters of lipids surrounded by a networklike structure of the polymers (corralling) are the size mismatch between the two particles and the presence of the long range soft potential between the large particles. The minimal value for the size ratio is 1.5, for $\sigma_{\rm lp}/\sigma_{\rm ll} \leq 1.5$ there is no clustering regardless of the other parameters, i.e., the two species mix completely or phase separate into two macroscopic phases.

The next question is what is the internal structure of the clusters. To this end we show in Fig. 2 snapshots from six different simulations. The snapshots are characteristic of the equilibrium structures in each of the cases. Each snapshot corresponds to a different value of the chemical potential of the polymers. Thus, as we increase the chemical potential the equilibrium density of adsorbed polymers increases. The first snapshot is for the pure lipid. In this case we see a typical low density structure of the two-

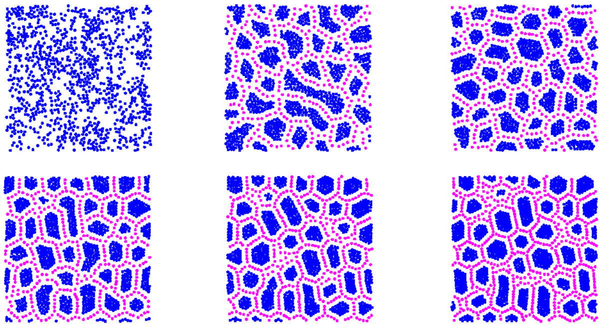

FIG. 2 (color online). Snapshots of the equilibrium structure of the mixtures for different polymer chemical potentials. The dark (blue) particles represent the lipids while the light (magenta) ones represent the polymers. The simulations correspond to the case of polymer with $N = 100$. The initial density of lipids is $\rho_l\sigma_{\rm ll}^2 = 0.32$, while the chemical potentials of the polymers are, top row no polymer, $\mu/\varepsilon = 70$ and 80; bottom row $\mu/\varepsilon = 100$, 120 and 150.

dimensional fluid. In all the other cases, the adsorption of the polymer induces the "corralling" of the lipids into clusters. The polymers form a percolating network surrounding the lipids clusters. As the polymer concentration (chemical potential) increases there is an increase in the density of the lipids within a cluster and in the ordering within the cluster. The shape of the clusters also becomes more polygonlike with sharper vertices, reflecting the more ordered structures.

To quantify the degree of order within a cluster, we use the local hexatic order parameter defined by [10]

$$|\Psi| = \frac{1}{N}\sum_{l}|g_6(l)| \quad \text{with } g_6(l) = \frac{1}{n(l)}\sum_{j}\exp[6i\theta_{lj}], \quad (2)$$

where θ_{lj} is the angle between the vector connecting the l and j particles and a reference axis, the sum j runs over all the nearest neighbors of molecule l, and $n(l)$ is the total number of neighbors of l. The first sum runs over all molecules l that are not at the boundaries of a cluster, $n(l) \geq 3$, and N is the total number of nonboundary lipids. With this definition we have that $\Psi = 0$ for a disorder structure while $\Psi = 1$ for a perfect hexagonal arrangement. Therefore, the larger the value of Ψ the more hexagonal order (crystal) in the cluster. Figure 3 shows the hexatic order parameter as a function of the polymer chemical potential for two different chain lengths. There is a large increase in ordering as the chemical potential increases. For the pure lipids the hexatic order is very close to zero, as expected for a low concentration two-dimensional fluid. However, as more polymers adsorb the corralling into clusters results in higher local density of lipids surrounded by boundaries of the polymers. This translates in higher packing order since that is the optimal structure of high density fluids. Interestingly, the degree of ordering is the same for the two different molecular weights as shown by the scaling of the chemical potential in the figure. The formation of the clusters and the degree of ordering in the clusters do not depend on the initial conditions of the simulations. We have checked many different initial conditions, including several different lipid densities, within the range of low to intermediate densities, and we observed the formation of the clusters with the same structure. The same results are obtained by performing simulations at constant number of lipids and constant number of polymers starting from a completely random initial configuration of both species. Therefore, we are confident that the clusters are equilibrium structures of the system. It should be mentioned that the size of the formed clusters depends on the amount of lipid and adsorbed polymer.

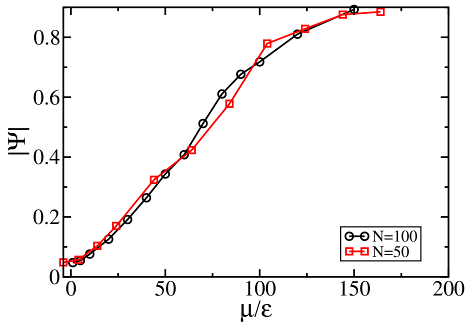

FIG. 3 (color online). The hexatic order parameter as a function of the polymer chemical potential for two different polymer chain lengths. Note that each point in the figure represents a long simulation. The two curves are found to scale when the chemical potential of the $N = 50$ case is transformed by $\mu/\varepsilon = (\mu_{50}/\varepsilon - 3) * 2$ which shows a linear relationship with $N = 100$.

As mentioned above we find that the necessary conditions for the formation of clusters is size mismatch and the long range soft repulsions of the larger particles. As shown in Fig. 3, the crystal-like order is determined by the concentration of polymers that adsorb. Experimentally one can control the number of particles that adsorb by increasing its bulk concentration. In the experimental lipid-polymers systems, the manifestation of the amount of polymers adsorbed is expressed in the lateral pressure increase that is measured [4]. In Fig. 4 we show the variation of the pressure as a function of the polymer chemical potential. There is an increase in the pressure as the polymer chemical potential, i.e., adsorbed amount, increases. This is in agreement with the experimental observations in which there is a very large jump on the pressure, accompanied by crystal-like order of the corralled lipids, which would correspond to a chemical potential of order 100 in Fig. 3. Moreover, the results from Figs. 4 and 3 can be used to design the level of ordering desired within the clusters. Namely, what are the conditions of the solution from which the polymers adsorb that will lead to a certain pressure increase upon adsorption and as a result clusters with a desired degree of order?

Throughout the discussion we have been referring to the systems studied as lipid-polymer mixtures. However, the model that we have studied is generic and therefore the conclusions apply for many different systems. In particular, we can use our findings to design mixtures of nanoparticles that can be induced to form domains with high degree of internal order, even at low concentrations. Thus,

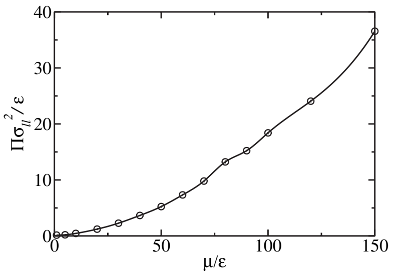

FIG. 4. The two-dimensional pressure as a function of the polymer chemical potential for $N = 100$.

it is very important to understand the physical reasons for the observed behavior. Namely, why the specific combination of interactions lead to cluster formation and not macrophase separation and what the modifications are that can be made on the particles to obtain the desired interaction potential.

Let us consider the two components of the interactions that we find necessary for cluster formation. First, the size mismatch between the particles by itself would lead to macrophase separation for the conditions studied here (results not shown). Second, the long range soft repulsive interactions, without size mismatch, would result in complete mixing between the two species, since in this way the system minimizes the repulsions. Therefore, the two interactions have opposite tendencies regarding mixing of the species. The optimal structure resulting from these two competing tendencies is to form clusters for the attracting (small) particles, surrounded by a networklike structure of the large particles. These structures optimize the small particles attractions, while the formation of the boundary domains by the long range interacting particles is a compromise that relaxes some of the repulsions but enables a larger gain by the small particles in their attractive interactions. This is the reason that in most cases, see Fig. 2, the boundary domains are quasi-one dimensional.

How should we choose the additives in order to induce the corralling of nanoparticles? First, we need to select the additive particles to be larger in size to fulfill the size mismatch. Second, the long range soft repulsion can be achieved by end grafting polymers to the large particles. The specific choice of the polymer chain length has to be such that the radius of gyration is a few times the size of the large particle. Finally, in order to achieve the desired effect, it is important that the polymers responsible for the soft long range repulsion interact with other polymers but do not interact with the small particles. The mixtures of lipid-poloxamers have a natural separation due to the presence of the air-water interface that separate the hydrophobic attracting parts from the long range repulsions of the hydrophilic blocks. In the case of nanoparticles one would need to attach the polymers to the region of the large particles that is not in contact with the surface (interface) or with the small particles. This can be achieved by using the recently developed method of synthesizing ordered domains within a nanoparticle [11].

To summarize, we have shown that the necessary conditions to form clusters in binary mixtures of particles with a structure in which the large particles corral the small ones are size mismatch between the particles and a long range soft repulsive interaction between the larger particles. The structure of the corralled clusters depends upon the concentration of large particles. We find that with a large enough concentration of large particles, crystal-like order is observed on the clusters. Our predictions are in agreement with experimental observations of lipid-poloxamer mixtures and serve as a basis for the design of clusters of ordered nanoparticles in two dimensions.

This work is supported by the National Science Foundation, under Grant No. CTS-0338377.

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