Stratification in Binary Colloidal Polymer Films: Experiment and Simulations

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Classification of Ordering of Surface Particles

We use the approach of Krinninger *et al.*,[1] which is a two-dimensional version of the widely used Steinhardt order parameters for crystalline ordering. In brief, it evaluates the q_6 order parameter for every particle in an experimental AFM image or in a simulation snapshot. For each particle, all particles within a distance of 1.2 particle diameters are considered its neighbours. Then for each particle with at least three neighbours, we calculate the *l=6* Steinhardt order parameter q_6, using only the angle in the plane, θ, and keeping ϕ constant, because we are working in two dimensions.[2] A particle with four neighbours in a perfect square arrangement around a central particle has q_6 = 0.586, whereas one with six neighbours in a perfect hexagonal arrangement has q_6 = 0.741. Thus, using q_6, we classify particles as follows. The range q_6 is split into three ranges: disordered (0 to 0.5), square ordering (0.5 to 0.65), and hexagonal ordering (> 0.65).

Langevin Dynamics Simulations

The simulations used a box height of H/d_S = 150 for α = 2 and 750 for α = 7. The number of simulated particles varied between 60,000 and 150,000. The evaporation speed v_{ev} was -0.1 d_S/t_0, with t_0 being the standard LAMMPS time unit. We set the LAMMPS Langevin dynamics parameter λ = 0.01 for the small particles, which are taken to have a unit mass in LAMMPS units. Then the Langevin drag coefficient for the small particles, ξ = 100. Taking a reduced temperature T^*= 100 results in a diffusion constant for the small particles of $D_S = 1\ d_S^2/\ t_0$. Hence the Péclet numbers for the small and large particles are Pe_S = 15 and Pe_L = 30 for α = 2, and Pe_S = 75 and Pe_L = 525 for α = 7.

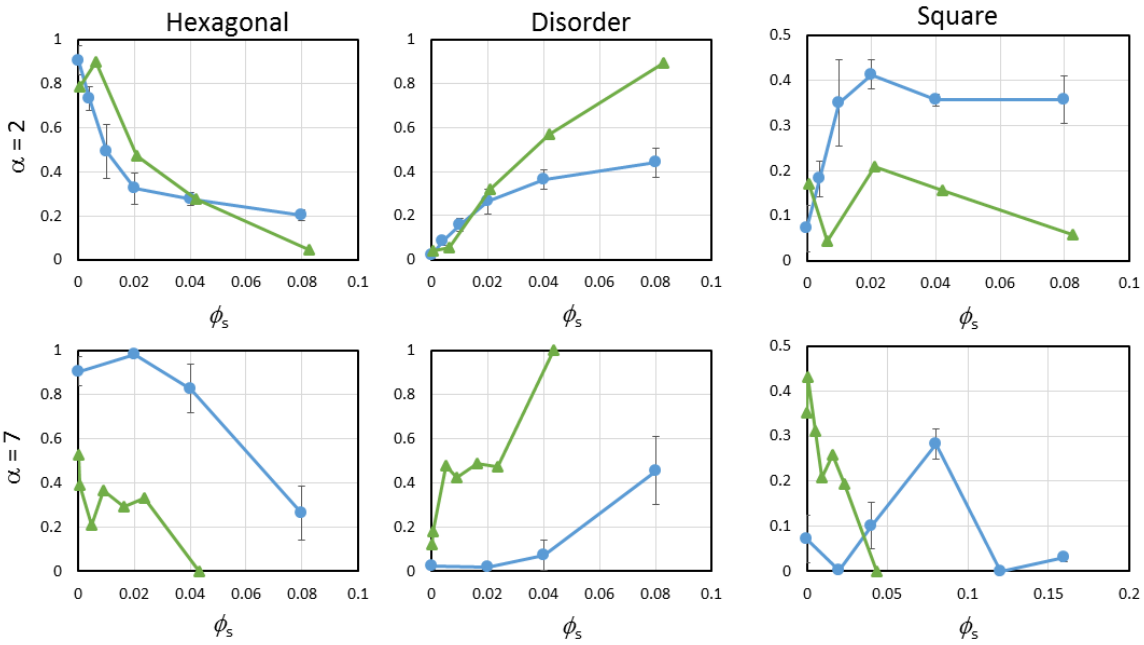

Figure S1. Fractions of hexagonal order (left column) and disorder (middle column) obtained from both experiments and simulations for two different size ratios of particles: α = 2 (upper row) and α = 7 (bottom row). Green triangular symbols denotes the simulation results. Blue round symbols denote experimental results. The total initial volume fraction of particles was ϕ_{tot} = 0.4 for simulations and experiments.

When we compare the simulations and experiments in Figure S1, we see generally good agreement. But there are two factors that lead to a greater amount of disorder in the simulations. One factor is that the simulations do not predict as much square order as is found in the experiments. A second factor for disagreement between simulations and experiments is that the simulations find stratification of small particles at the top surface, even for volume fractions as low as ϕ_S = 0.024. With the onset of stratification of the small particles at the top, there is a significant number of large particles that do not have neighbours within the required distance of 1.2 large particle diameters. When this is the case, the particle in question is regarded as 'disordered', which leads to greater disordering in simulations compared to the experiments.

Table S1. Summary of the Initial Concentrations and Final Analysis of the Langevin Dynamics Simulations

$\alpha = 7$

ϕ_S	ϕ_L	ϕ_S^F	ϕ_L^F	P^{fin}	w (d_S)
0.00034	0.3964	0.000552	0.6363	47	-
0.0049	0.393	0.008	0.63	60	1.86
0.0089	0.3992	0.014	0.626	72	2.37
0.016	0.39	0.0254	0.606	88	2.99
0.024	0.382	0.0371	0.594	105	7.68
0.044	0.361	0.07	0.579	167	-

$\alpha = 2$

ϕ_S	ϕ_L	ϕ_S^F	ϕ_L^F	P^{fin}	w (d_S)
0.00057	0.395	0.00093	0.643	345	-
0.00623	0.39	0.01	0.633	381	-
0.0215	0.388	0.034	0.609	452	0.086
0.041	0.35	0.067	0.569	484	0.4
0.081	0.31	0.13	0.5	614	1.67
0.121	0.27	0.196	0.44	745	4.46
0.16	0.24	0.259	0.388	938	4.24
0.188	0.188	0.316	0.314	958	3.26

Table S1 summarises the initial (first two columns) and the final (third and fourth columns) volume fractions of particles in the Langevin dynamics simulations. Note that as the small particles are numerous at a given volume fraction, increasing the amount of small particles at a constant total volume fraction increases the final pressure, P^{fin} (fifth column). Pressure is expressed in units of k_BT/d_S^3 and the width, w has units of d_S. (The value of w was obtained by fitting Equation 5 to the experimental data.) In the final column, the dash indicates that profiles were not fit because there was no stratification. When $\alpha = 7$, and $\phi_S = 0.044$ (last row in the first section of the table), there is a thick layer of small particles with a high and approximately constant density. In this case, the dash indicates that an exponential function could not be fit to the data.

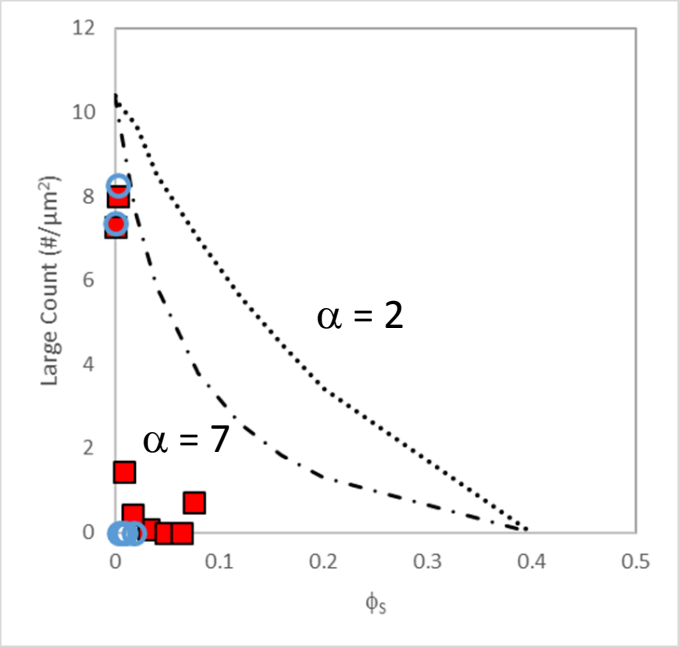

Figure S2. Counts of large particles per unit area, *N*, in simulations of particle mixtures with $\alpha = 2$ (filled red squares) and $\alpha = 7$ (open blue circles) as a function of the volume fraction of small particles, ϕ_S. In all simulations, the total volume fraction of particles is 0.4 (concentrated regime). The dotted line ($\alpha = 2$) and the dashed line ($\alpha = 7$) show results from the simple geometric model given in Eq. 3.

References

1. P. Krinninger, A. Fischer and A. Fortini, *Physical Review E,* 2014, **90**, 12201.
2. P. Steinhardt, D. Nelson and M. Ronchetti, *Physical Review B*, 1983, **28**, 784.