Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

To create a discontinuous potential that would result in a monotonically increasing function would have required the potential to be cut off at a range that would prevent a charge on one colloid from interacting with both charges on a neighboring colloid. The maximum cut off distance for a monotonically increasing function was calculated to be 0.762σ by placing two dipolar discs adjacent to each other with perpendicular dipoles, as shown in Figure 1

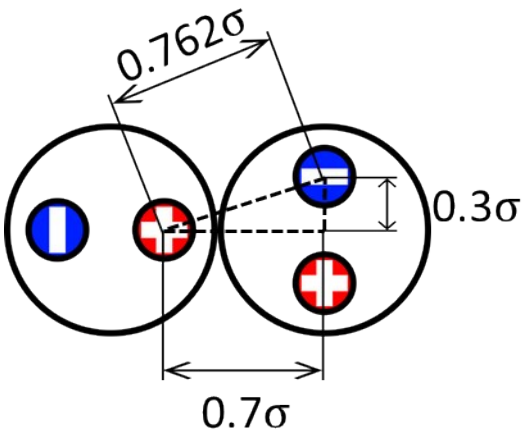

Figure 1: Maximum discontinuous potential range to create a monotonically increasing function.

This maximum cut off distance is shorter than the length necessary for charges to interact when colloids are aligned side-by-side (1σ) and in staggered chains (0.87σ).

A second option for developing a potential that would be monotonically increasing as a function of the distance between charges would be to have only the closest charges on two neighboring colloids interact during the dynamics simulations. This could be accomplished by performing a check on every charge-charge interaction that occurs between two colloids: calculating the distance between all charges on the two interacting colloids, and then neglecting the charge-charge interaction if there is a closer pair of charges for those two colloids. There are two drawbacks to this method. The first is the computational cost that is

added by calculating the charge-charge distance for each collision. The second drawback is that this method would overestimate the interaction energy of discs arranged in a staggered chain or a hexagonal close packed lattice. This can be seen in the work by Schmidle et al., where the cut-off range chosen for the discontinuous potential used (0.99σ) effectively serves to limit the interactions occurring between colloids to attractive interactions only for two dipolar discs arraigned head-to-tail, or three discs in a staggered chain. The effect is that the discs have a greater tendency to arrange in staggered chains in the simulations, as opposed to what would be seen in experiments.

If we relax our constraint of trying to create a monotonically increasing function for the total interaction energy of two colloids calculated from the discontinuous potential ($U_{total,DMD}$) as a function of the distance between nearest charges, we create a potential that can more accurately capture the equilibrium behavior of small clusters of colloids. The angle average total interaction energy U_{total} is plotted below in Figure 2: a) Total interaction energy between two colloids for all possible orientations and distances between the center of the colloids verses the distance between the closest attractive charges on (top) two discs, (middle) one rod and one disc, or (bottom) two rod as calculated by the discontinuous potential (green) and the Yukawa potential (blue). (b) Total interaction energy between two colloids in a head-to-tail configuration verses the distance between the closest attractive charges on (top) two discs, (middle) one rod and one disc, or (bottom) two rods as calculated by the discontinuous potential (purple) and the Yukawa potential (red). as a function of the distance between nearest attractive charges as calculated by the discontinuous potential (green) defined in Equations (2-4) and the Yukawa potential (blue) defined in Equation (5). Also shown are the total interaction energy for two colloids aligned in a head to tail configuration as

a function of the distance between nearest attractive charges as calculated by the discontinuous potential (purple) and Yukawa potential(red).

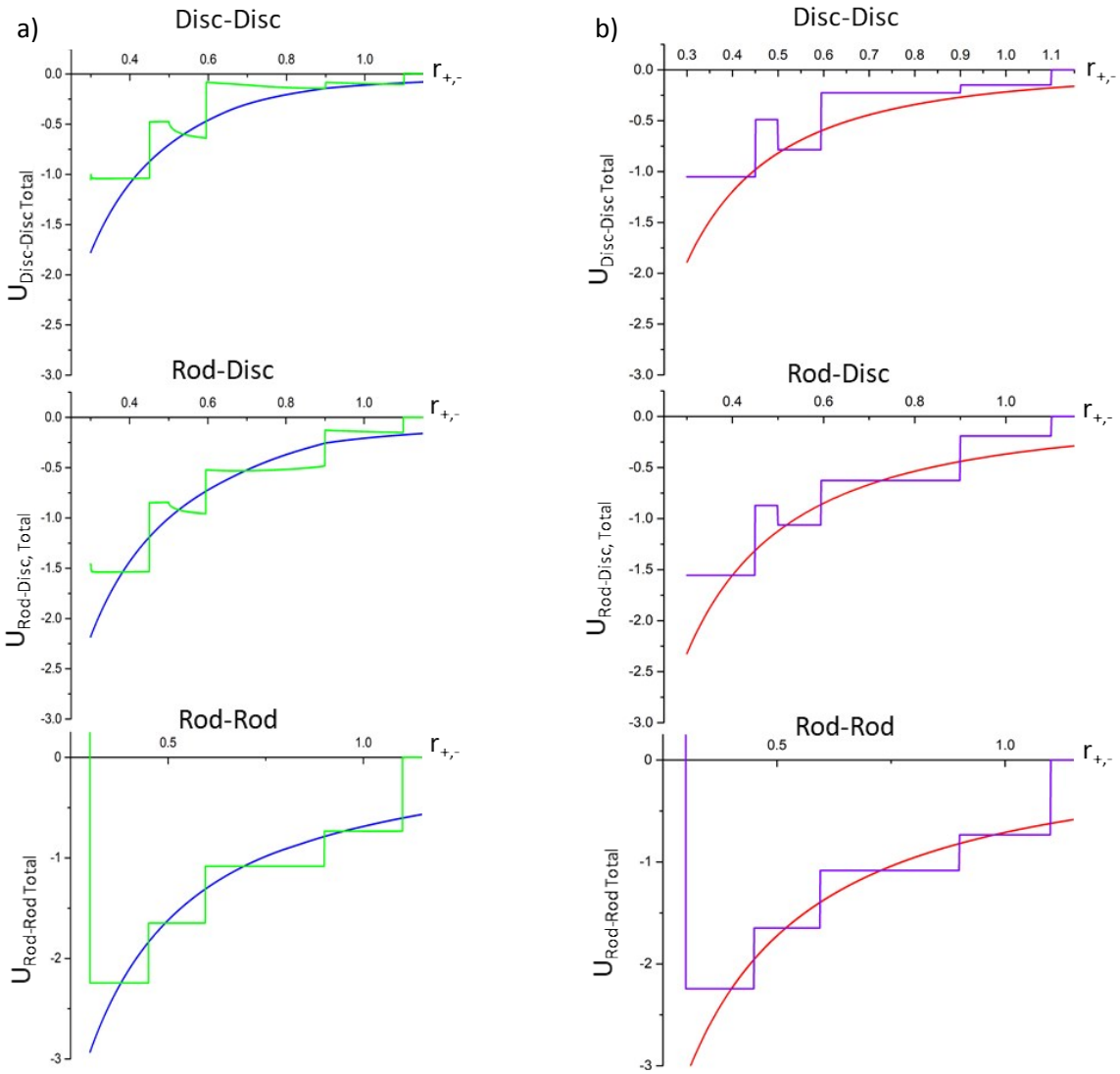

Figure 2: a) Total interaction energy between two colloids for all possible orientations and distances between the center of the colloids verses the distance between the closest attractive charges on (top) two discs, (middle) one rod and one disc, or (bottom) two rod as calculated by the discontinuous potential (green) and the Yukawa potential (blue). (b) Total interaction energy between two colloids in a head-to-tail configuration verses the distance between the closest attractive charges on (top) two discs, (middle) one rod and one disc, or (bottom) two rods as calculated by the discontinuous potential (purple) and the Yukawa potential (red).

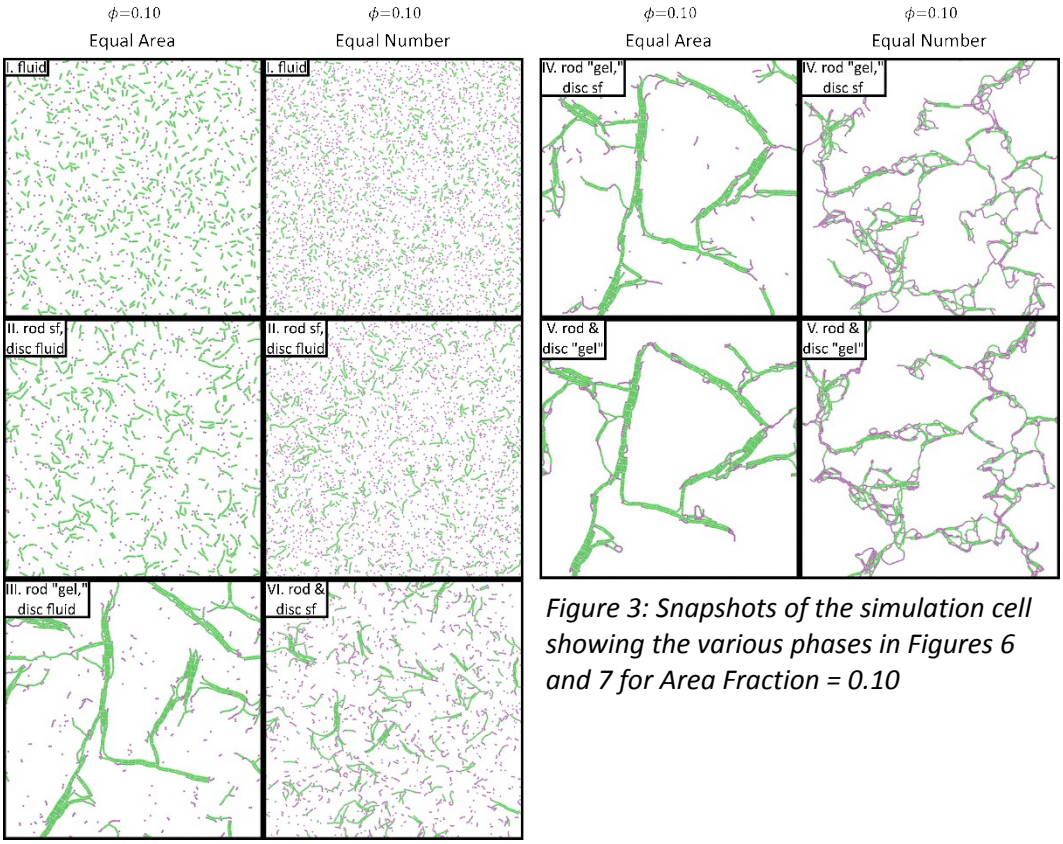

Figure 3: Snapshots of the simulation cell showing the various phases in Figures 6 and 7 for Area Fraction = 0.10

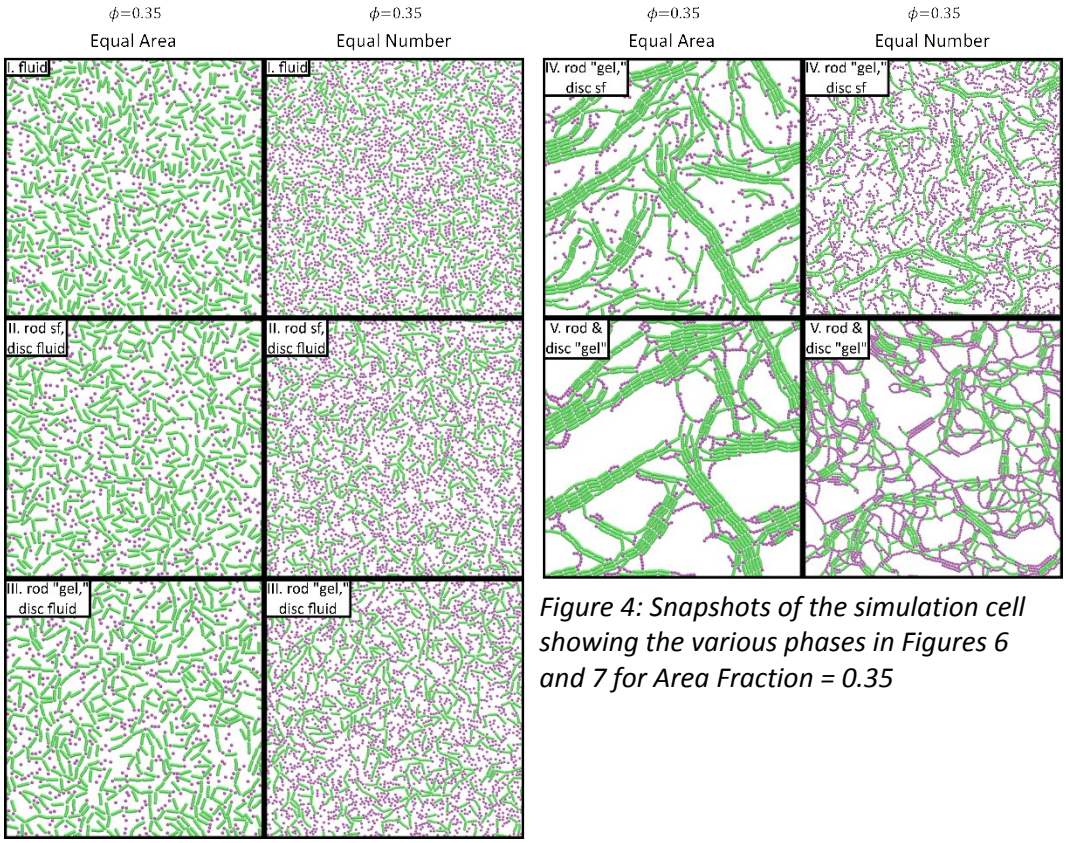

Figure 4: Snapshots of the simulation cell showing the various phases in Figures 6 and 7 for Area Fraction = 0.35

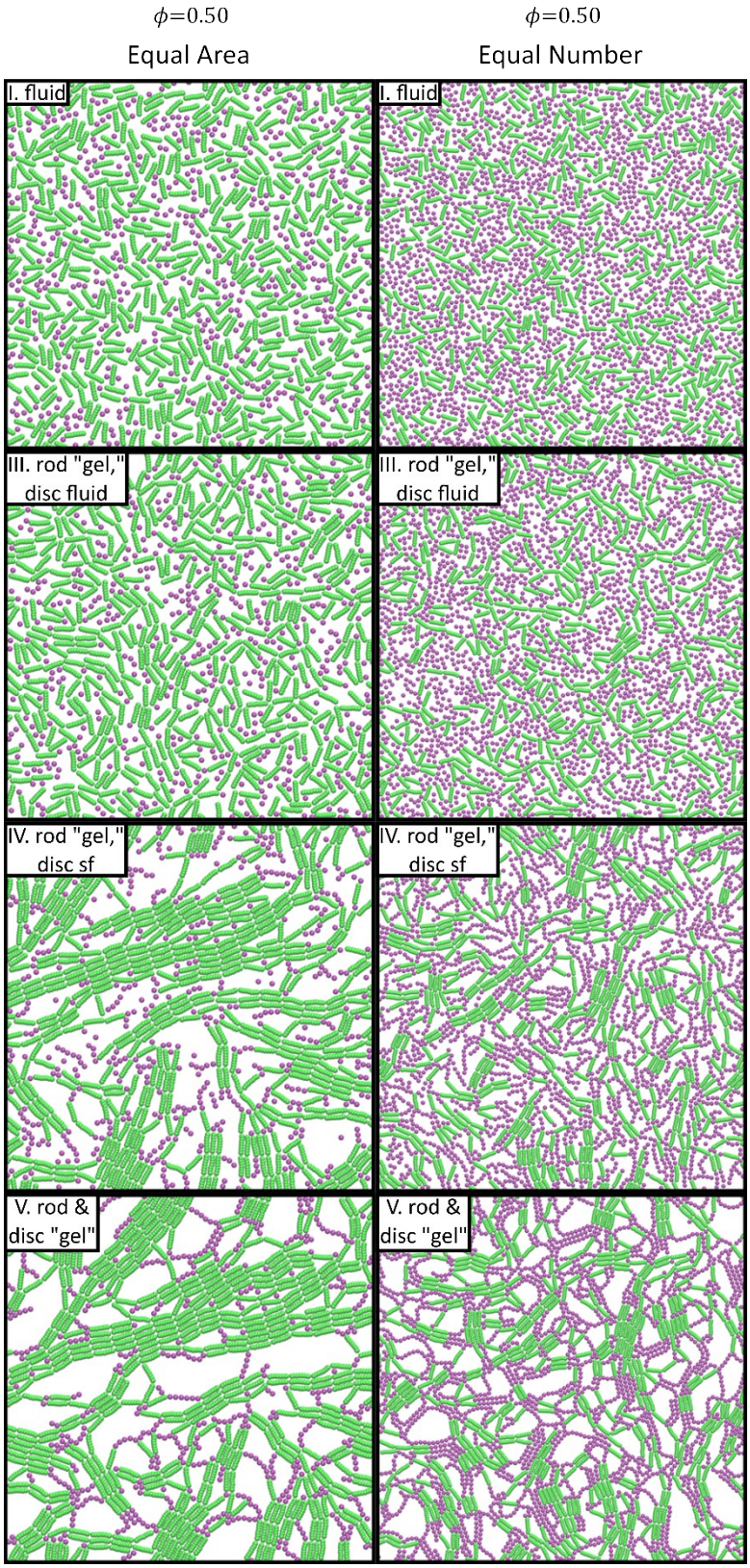

Figure 5: Snapshots of the simulation cell showing the various phases in Figures 6 and 7 for Area Fraction = 0.50