Phase Behavior of Janus Colloids Determined by Sedimentation Equilibrium

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Supporting Information

Sedimentation equilibrium analysis at different system sizes

A question that arises in almost every simulation study is the effect of the system size on the results obtained. In particular, phase behavior studies have the complication of interfacial regions (regions that transition one phase into a different one) possibly making up a big percentage of the system being analyzed[1]. As explained in the main text, we approach this obstacle by reducing the interface to a minimum, but still allow it to exist. In this section we are interested in testing if the size of the system we use, both by making the simulation box smaller along the long axis (i.e. the "z" axis) or bigger along the cross section area of the interface.

Figure S1 shows sedimentation equilibrium results for systems at $\alpha=100°$ and $\varepsilon/kT=0.9$. The system sizes explored are $n=1200, 2400, 3600$ and 4800 for simulation cross section size $L_x=20.50a$ and $L_y=21.30a$ and $Ga/kT=1.04, 0.52, 0.347$ and 0.26, respectively. A second set of simulations $n=4800, 9600, 14400$ and 19200 for simulation cross section size $L_x=41.00a$ and $L_y=42.60a$ and the same gravity forces as the first set. The first set of system sizes are meant to explore if the system size has an effect on the observed coexistence properties by changing the sedimentation length (kT/G), and thus the vertical resolution of the sedimentation equilibrium analysis. The second set of system sizes is the same as the first set, but doubling the horizontal dimensions of the simulation box. This set is meant to test the effect of the size of the interfacial area on the observed coexistence properties.

Fig S1a shows the height averaged density profiles, Fig S1b shows estimated osmotic pressure as a function of height and Fig S1c shows the equation of state for all system sizes explored. Density profiles and osmotic pressure profiles both show the wider simulation box results are indistinguishable to results with the smaller simulation box of the same gravitational potential. Given the difference in gravitational force applied to the different systems, density profiles and osmotic pressure profiles do change when the sedimentation length is changed. When results are summarized in the equation of state plot in Fig S1c, we see all results collapse to single curve. From density profiles shown in Fig S1a, a point can be made for systems with a very short sedimentation length. It can be seen that only a few data points can be seen for the $Ga/kT=1.04$ system sizes. This low resolution can result in poor estimation of coexistence densities. In general, we changed the gravitational force in our simulations to ensure good sampling of densities of both phases around interfacial regions.

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References

1. D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications*, Elsevier Science, 2001.

Figure S1
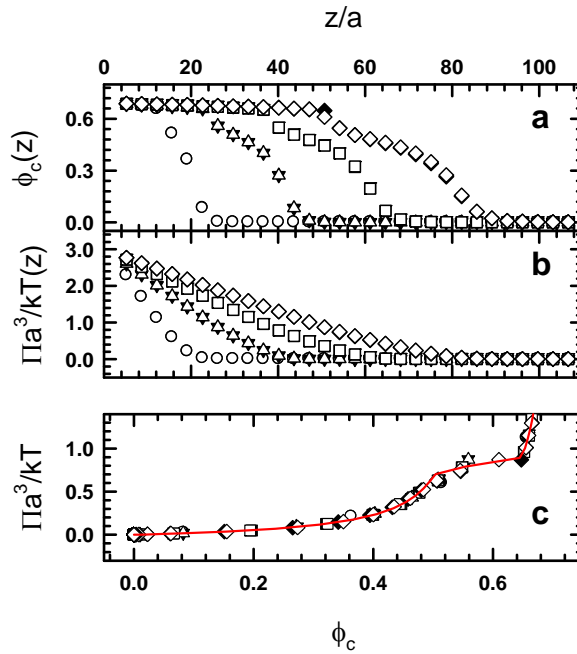
System size effects in sedimentation equilibrium analysis. (a) height averaged density, ϕ_c, as function of height. (b) normalized osmotic pressure, $\Pi a^3/kT$, as function of height, z. (c) equation of state from simulation results, shown in symbols, and from fitting to a sigmoidal functional form (see main manuscript text), shown in solid red line. Spheres interact with potential energies given in Eqs (1)-(5) for $\alpha=100°$, $\varepsilon/kT=1.0$ for different gravitational forces, Ga/kT, and system sizes, n, as follows: White symbols correspond to a simulation box size, $L_x=20.25a$ and $L_y=21.04a$ with gravitational forces and system sizes: $Ga/kT=1.04$ and $n=1200$, circles; $Ga/kT=0.52$ and $n=2400$, triangles; $Ga/kT=0.347$ and $n=3600$, squares; $Ga/kT=0.26$ and $n=4800$, diamonds. Black symbols correspond to a simulation box size, $L_x=40.50a$ and $L_y=42.08a$ with gravitational forces and system sizes: $Ga/kT=1.04$ and $n=4800$, circles; $Ga/kT=0.52$ and $n=9600$, triangles; $Ga/kT=0.347$ and $n=14400$, squares; $Ga/kT=0.26$ and $n=19200$, diamonds.