Monte Carlo simulation of hard-sphere colloid sedimentation on a hard wall

Federico Lora Gonzalez, June 13, 2012

The settling and packing properties of colloidal suspensions of large hard spheres in an effective gravitational field are investigated by a Monte Carlo constant-NPV simulation. The ratio of an effective gravitational potential to the repulsion/attraction potential in the hard sphere (G/ε) is a critical parameter that determines the surface coverage and packing properties of the system. The surface coverage, Θ, as well as the radial distribution function (RDF), $g(r)$, are calculated at a hard wall for varying suspension volume fractions. Attractive hard spheres ($\varepsilon < 0$) agglomerate before sedimentation, causing Θ to be decreased.

1. Introduction and Background

The phenomenon of self-assembly of colloidal suspensions into crystals is widely used in experimental work to manufacture photonic crystals, opals, thin films, and templates[1,2]. It as been described that for small enough colloidal spheres, self-assembly by sedimentation is a simple, robust process that allows the creation of opals[3]. However, for larger colloids (~1μm), sedimentation does not lead to self-assembly. Instead, functionalization of the colloidal suspension allows for tunable hydrophobicity and particle-particle interaction, which allows for deposition by the Langmuir-Blodgett technique and other methods[4,5]. In this study, a simple model is used to study the self-assembly of these larger colloids. The packing and surface coverage of the resulting colloidal crystal are studied as functions of an effective gravitational potential and suspension concentration (ϱ).

2. System and Methodology

The system of interest is a fluid suspension of hard spheres close to a hard wall in a gravitational field. Particles are assumed to interact with a potential $u_{ij}(r)$ given by:

$$u_{ij}(r) = \begin{cases} \infty & if \ r_{ij} \leq r_0 \\ \varepsilon & if \ r_0 < r_{ij} < r_0 + \delta r \\ 0 & if \ r_{ij} \geq r_0 + \delta r \end{cases} \quad (1)$$

ε is < 0 for an attractive potential, while $\varepsilon > 0$ for a repulsive potential. The particles interact with the wall in a similar fashion, where $u_{wall}(r)$ is given by:

$$u_{wall}(r) = \begin{cases} \infty & if \ r_i \leq r_0 \\ 0.1 * \varepsilon & if \ r_0 < r_i < r_0 + \delta r \\ 0 & if \ r_i \geq r_0 + \delta r \end{cases} \quad (2)$$

The particles also experience a gravitational potential, given by u_g:

$$u_g(z) = |G| z_i \quad (3)$$

The simulation is performed for different values of the ratio $g = G/\varepsilon$, i.e. the ratio of the strength of the gravitational potential to the depth of the particle-particle energy well.

A constant NVT Monte Carlo algorithm was used to simulate the sedimentation process. Particles are randomly placed in a box of side length L, in a layer three particle diameters thick, near the hard wall. Then, the MC algorithm is performed for *n* sweeps: First, a particle is chosen at random. Then, the particle is moved a distance in the range [0,δr_{max}]. The acceptance probability is given by:

$$P_{acc} = e^{-\Delta U / T} \tag{4}$$

where ΔU the change in potential energy after the move. This process is repeated until *n* sweeps are completed. The surface coverage Θ is computed for atoms that sit on the surface, as well as the radial distribution function of atoms on the surface:

$$\Theta = N_{surface} \frac{(\pi r^2)}{L^2} \tag{5}$$

The following parameters were chosen such that the acceptance of the proposed moves was ~10-50%.

Parameter	T	ε	δr	δr_{max}	g	N	ϱ	L	r_0
	3.0	50 or -50	0.01	0.01 to .1	.1 or 5	50	.01 to .3	$\left(\frac{N}{\rho}\right)^{1/3}$	1.0

3. Results and Discussion

A total of twelve simulations were run at differing *g*, ϱ, and ε values, corresponding to strong and weak interactions between particles (g), low to high suspension concentrations(ϱ), and either attractive or repulsive wells between particles (ε) . For each simulation, enough MC sweeps were performed such that the potential energy equilibrated. Then, data was taken for a total of 600,000 MC sweeps. Systems where the effective gravitational potential was higher (g =5) equilibrated considerably faster than those of a lower effective gravitational potential. Representative potential energy curves are shown in figure 1.

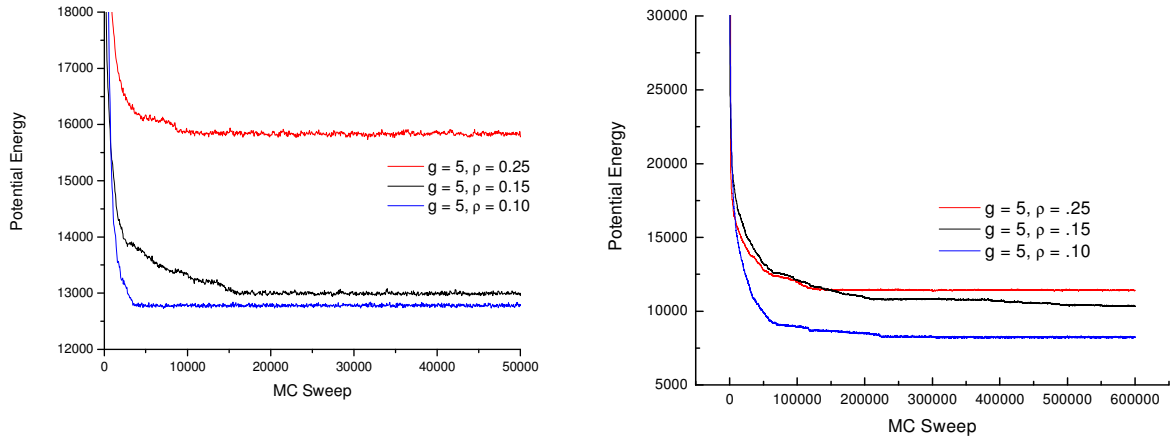

Figure 1(a): Repulsive spheres: Potential energy as a function of Monte Carlo sweep. (b): Attractive spheres

Particles with an attractive potential were prone to agglomeration, as shown by the surface radial distribution function (RDF; Fig. 2) and the surface coverage Θ(z=0) (Fig. 3). For equal suspension concentrations, the systems with attractive potentials show much higher peaks of the RDF at ~$2r_0$ and $4r_0$, but overall lower surface coverage (Fig. 2(b)). For the systems of repulsive potentials, peaks at $2r_0$ and $4r_0$ only appear at the highest concentration, indicating that hexagonal packing occurs only after a critical concentration.

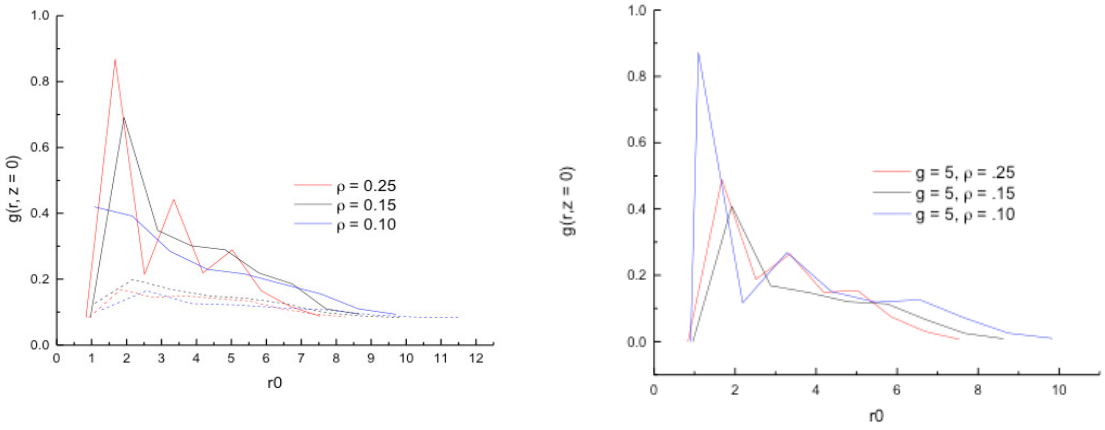

Figure 2(a): Surface radial distribution function (RDF) for repulsive spheres. Dashed lines represent the system with g = 0.1, and solid lines represent g = 5. (b) Surface RDF for attractive spheres

	Repulsive well (ϵ > 0)			**Attractive well (ϵ < 0)**		
ϱ	0.1	0.15	0.25	0.1	0.15	0.25
g = 0.1	.08±.03	.10±.03	.14±.05	0	0	0
g = 5	.62±.01	.80±.01	.78±.01	.57±.01	.46±.01	.55±.01

Figure 3: Surface coverage

The effective gravitational potential is a key component for the packing of spheres on the surface. The interactions between the particles and the surface are short ranged, and do not move the system to close packing. For systems with an attractive potential, the effective gravitational field needs to be stronger for the equivalent system with a repulsive well. In other words, repulsion between spheres promotes the spreading of particles on the surface, whereas attraction between spheres promotes agglomeration. Experimentally, this means that functionalized particles that are stabilized in suspension are more likely to pack more efficiently than those which tend to agglomerate and fall out of suspension. A comparison of these types of particles and the predicted structure from the simulation are shown in figure 4.

Of course, this simple simulation falls short in explain the complex process of colloidal suspension sedimentation, because it ignores all fluid effects, such as capillary forces, buoyancy, and fluid flows, which are known to be key components in the sedimentation of colloidal particles. Much more complex simulations are required to include these effects.

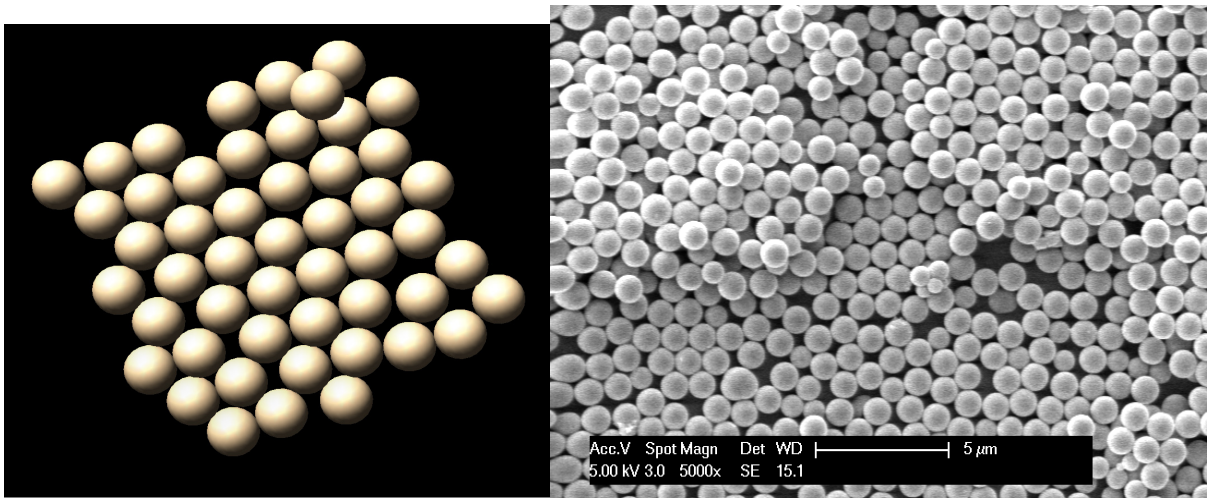

Figure 4: Comparison of simulation and experimental results

References

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