

EVAPORATION-DRIVEN ASSEMBLY OF COLLOIDAL PARTICLES

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Summary We use a combination of numerical simulations and theoretical models to study the packing selection problem for the experiment of Manoharan *et al.* [1].

INTRODUCTION

In a recent experiment by Manoharan *et al.* [1], a small number N of spherical particles (diameter of about one micron) located at the surface of an oil droplet self-assemble due to the evaporation of the droplet. Such process leads to final packings of spheres which are unique and, for $N \leq 11$, equivalent to the minimal second moment clusters as studied by Sloane *et al.* [2]. Because such simple experimental process could be used to generate building blocks of a given number of particles at the micron or even nanometer scale, it is of fundamental interest to determine the parameters responsible for the packing selection.

NUMERICAL SIMULATIONS

We first use numerical simulations to reproduce the packings of Manoharan *et al.* [1]. The simulations are performed using The Surface Evolver [3], program designed to calculate minimum energy configurations of deformable surfaces. The N solid spheres are modeled by N droplets of large surface tension, typically 10 to 100 times larger than that of main droplet, in order to penalize deformation of their interface and effectively force them to remain spherical throughout the drying process. Steric constraints are enforced by adding a repulsive part to the energy, acting between the centers of gravity of each sphere; the final packings are found to be independent of the details of such repulsive energy. Finally, the contact angle condition on each sphere is explicitly enforced by choosing the unique value of the droplet-particle interfacial tension which is appropriate in order to satisfy Young's law at the contact line. A typical initial condition is illustrated in Figure 1 in the case of 12 spheres.

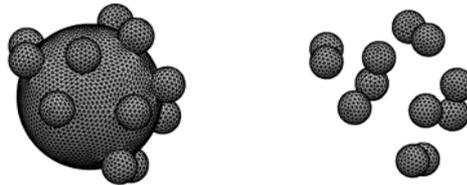


Figure 1: Typical initial configuration for the numerical simulations in the case of 12 spheres. Left: both the spherical particles and the droplet are visualized; right: only the particles are shown. The contact angle in this case is 90° .

Finally, we reproduce the effect of droplet evaporation by decreasing the volume of the droplet in a quasi-static fashion. The results of the simulations, which take up to almost a week for $N = 11$, are presented in Figure 2 [4]. The simulations are found to reproduce well the final packings of Manoharan [1]. However, contrary to what observed experimentally in [1], we observe a smooth evolution of the sphere packings towards the minimum-moment packings of [2]. We attribute such difference to friction between spheres and contact angle hysteresis in the experiments.

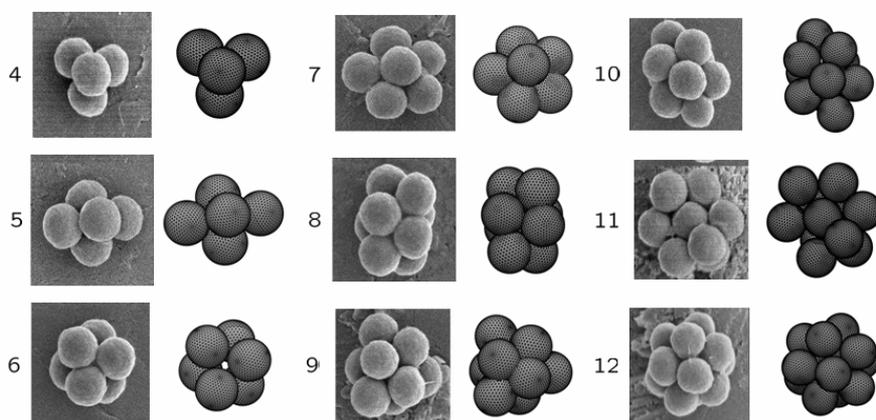


Figure 2: Comparison between the experimental packings of Manoharan *et al.* (2003) [1] (left) with the results of our simulations (right) as a function of the number of spheres.

THEORETICAL CONSIDERATIONS

We now study theoretically the packing selection problem.

Critical packing. If $N = 1$, the droplet shape will trivially remain that of a spherical cap throughout the drying process and there is never any capillary force on the colloidal sphere. If $N \geq 2$, the droplet shape will be spherical as long as its volume is large enough (Figure 3a) but there exists a critical volume V_C below which excluded-volume interactions can no longer be ignored (Figure 3b). The volume of the spherical droplet at this point can be characterized in the following fashion. The steric interactions between particles located on the surface of a sphere can also be thought as the steric interactions between (1) the "cone of influence" of each particle, defined as the cone originating from the droplet center and tangent to the particle (illustrated in Figure 3b), or (2) the interactions between the intersection of each of these cones with the spherical cap droplet, i.e. circles. Consequently, packing spherical particles on the surface of a sphere is essentially equivalent to packing circles on a sphere, which is a mathematical problem with a rich history [5,6]: for small N , the circle packings are unique and correspond therefore to unique packings of particles at the critical volume. Furthermore, by geometrical arguments, it is easy to show that the corresponding critical packing of particles are also independent of the solid-liquid contact angle [7]; in contrast, the droplet volume at this critical packing depends naturally on the contact angle.

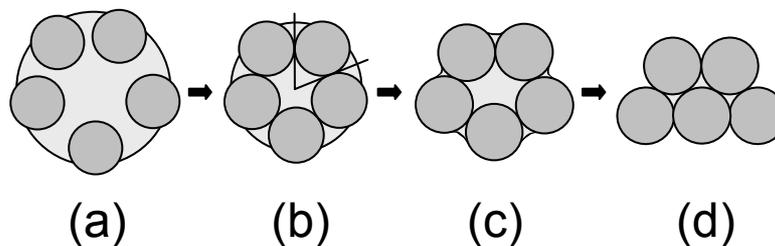


Figure 3: Schematic representation of the drying process for $N \geq 2$.

Deformations below the critical packing. Below the critical volume V_C characterized above, deviations of the droplet interface from a spherical cap lead to the appearance of capillary forces on each particle (Figure 3c). In the limit where the drying rate is small, each particle will remain at equilibrium throughout the drying process and contact forces need to exist between pair of particles in order to balance instantaneously the capillary forces. The main theoretical question to be answered is: how do the spheres rearrange when the droplet volume is reduced below its critical value? Although intuitively one might think that in order to answer this question, the full surface energy minimization problem has to be solved, we have found that in fact the various constraints associated with the spherical packings are sufficient to entirely determine the sphere rearrangements. Indeed, suppose the droplet volume is reduced by a small amount. The spheres will rearrange in a way that satisfy (1) the droplet volume constraint (one equation), (2) the contact condition for each touching pair of spheres (n_C equations, where n_C is the number of contacts) and (3) force balance on each sphere. The latter give rise to nontrivial constraints; since there are fewer contact forces (n_C) than there are components of the capillary forces ($3N$), the latter cannot be arbitrary and only a few of the capillary forces can be chosen independently [7]. Counting the number of constraint equations, we found that the number of constraints is exactly equal to the number of unknowns up to $N=18$, and therefore the rearrangement of the particles is unique and completely determined by the geometry of the spherical packing. Using such procedure, we were then able to construct a model program which starts from the spherical packing, decrease the droplet volume by small increments and calculates the corresponding incremental particle rearrangement consistent with all the constraint until final equilibrium is reached. This model successfully reproduces most of the final packings illustrated in Figure 2, but at a much lower computational cost than the full simulations.

CONCLUSION

We have presented a study of the packing selection problem for the experimental results of Manoharan et al. [1] using a combination of numerical and theoretical analysis. Further work on this problem will concentrate on packings obtained with spheres having variations in their wetting characteristics.

References

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