Building microscopic soccer balls with evaporating colloidal fakir drops

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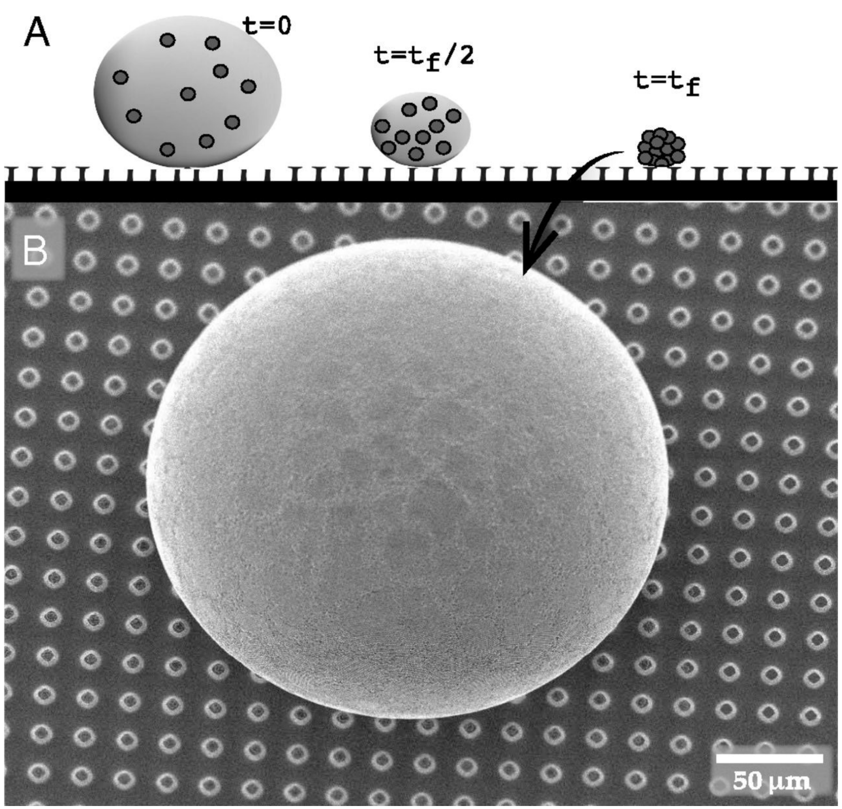
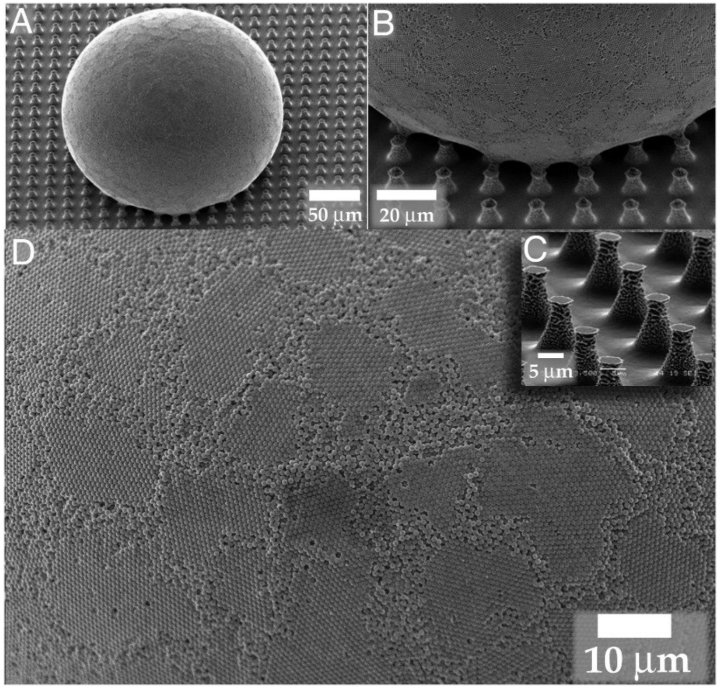


A droplet of colloidal solution is left to evaporate on a superhydrophobic surface.

Avijit Baidya
14.03.15

In this paper

- Evaporation-driven particle **self-assembly** can be used to generate **three-dimensional microstructures**.
- They present a unique method to create **colloidal microstructures** in which we can control the **amount of particles** and **their packing fraction**.
- Evaporation of colloidal dispersion droplets on a special type of superhydrophobic microstructured surface, on which the droplet remains in **Cassie–Baxter state** during the entire **evaporative process**.
- They show how the final particle packing fraction of these balls depends on the dynamics of the droplet evaporation, particle size, and number of particles in the system.



(A) Tilted view of the supraball in contact with the microstructure.(B) Detail of the contact area.
 (C) Magnified view of the micropillars forming the microstructure.
(D) Close-up of the supraball surface. The distribution of crystalline patches resemble the pentagons in a soccer ball.

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Introduction

Evaporation-driven particle self-assembly is an ideal mechanism for constructing micro- and nanostructures at scales where direct manipulation is impossible.

For example, in colloidal dispersion droplets with pinned contact lines, evaporation gives rise to the so-called coffee stain effect (A capillary flow drags the particles toward the contact line to form a ring-shaped stain.).
The convective assembly are used to produce two-dimensional colloidal crystal films. For three-dimensional clusters of microparticles, colloidal dispersion droplets can be dried suspended in emulsions, in spray dryers.

The main drawback of these three-dimensional assembly techniques are the lack of control on both the amount of particles and the particle arrangement in the remaining structures.

Discussion

- To understand the final structure of our present supraballs, it important to understand the dynamics of the droplet evaporation.
- Absence of shell formation suggests that the particles do not influence the droplet evaporation. **They compare the evaporation dynamics to that of a liquid drop that does not contain any particles**. They need to prove this.
- The evaporative mass loss typically governed by the diffusion of vapor molecules in the surrounding air.

  For diffusion-limited evaporation, the rate of volume change of the drop is given by,

$$\frac{dV}{dt} \sim D'R,$$

$D' = D_{va} \Delta c / \rho$, with D_{va} the diffusion constant for vapor in air, Δc the vapor concentration difference between drop surface and the surroundings, and ρ the liquid density.

evaporation rate ∞ R^2

vapor concentration gradient ∞ $1/R$

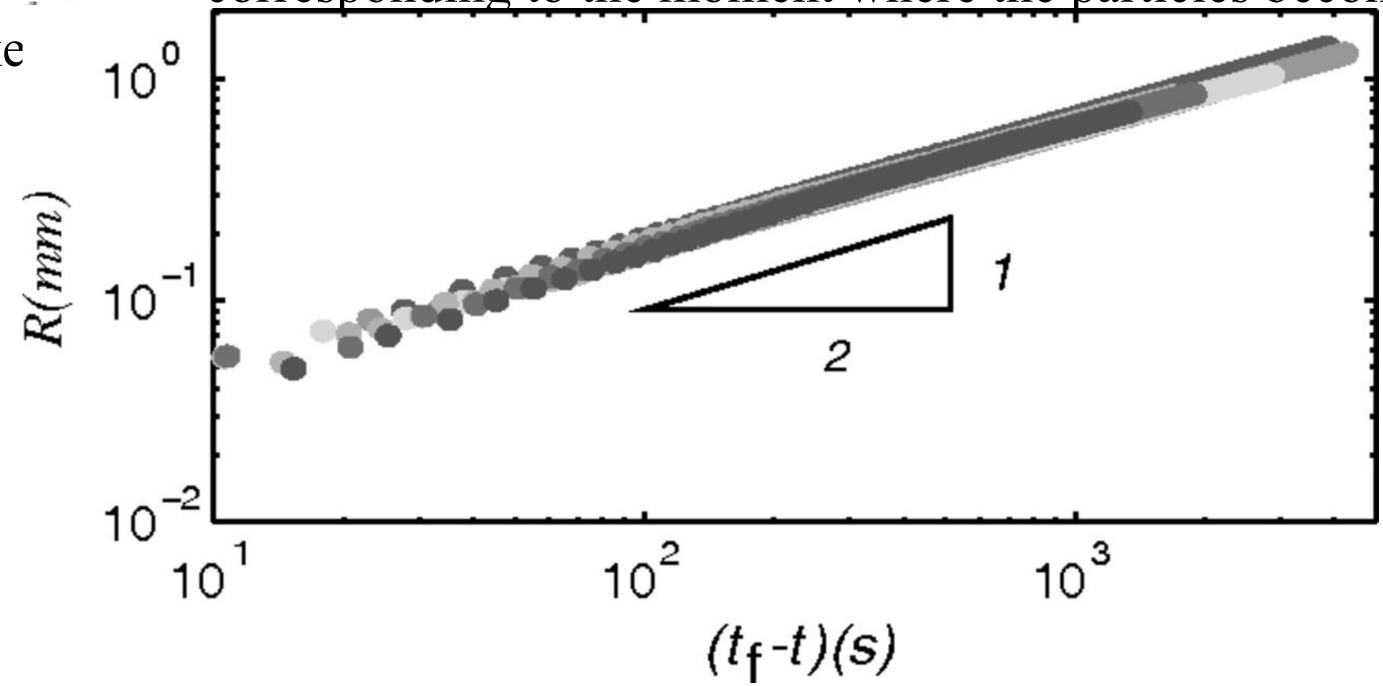
so, total evaporation rate ∞ R

If the droplet evaporates with a constant contact angle, we find that because $V \sim R^3$

$$R(t) \sim [D'(t_f - t)]^{1/2}.$$

Discussion

- Here t_f is the total droplet lifetime in case no particles are present.
- In the present case the drop radius saturates at a finite radius, R_{ball}, at a time $\hat{t} = t_f - R_{ball}^2/D'$, corresponding to the moment where the particles become densely packe



The radius of the droplet plotted against $t_f - t$ with tf the lifetime of the droplet and t the actual time. The triangle indicates the one-half power law, the dots represent the dataset for seven different experiments, where the number of particles was varied. For a certain $\hat{t}$ < t_f the final ball size R_{ball} is reached. The final time was extrapolated as $t_f = \hat{t} + R_{ball}^2/D'$.

This result confirms that the particles do not influence the evaporation process until the final radius R_{ball} is reached.

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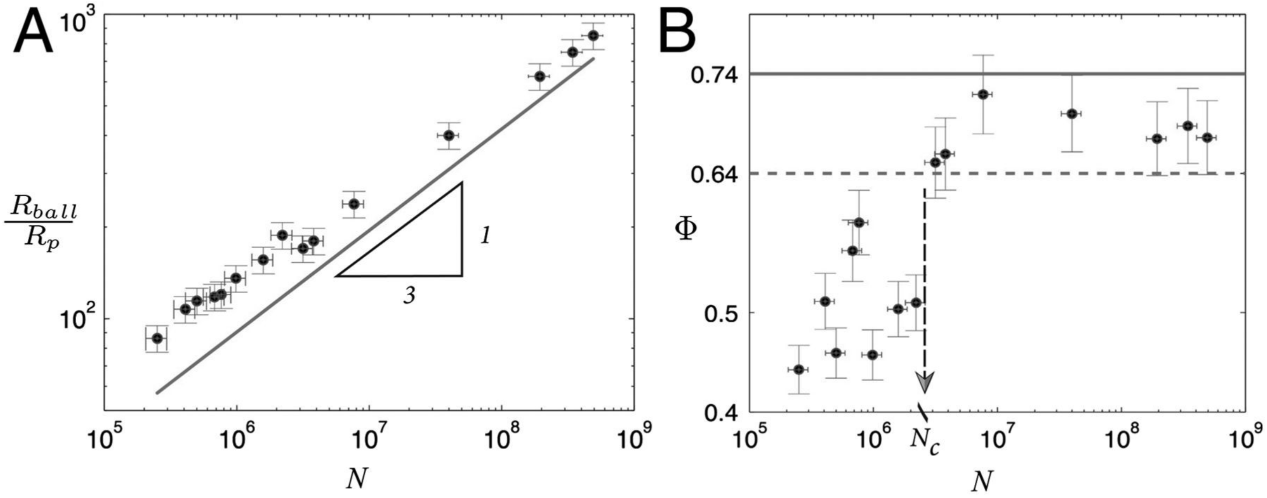
Discussion

- The speed with which the interface is moving inward is given by $dR/dt \sim D/R$. Hence, the interface speed increases dramatically as the droplet shrinks and the maximum speed reached in the experiment will be determined by the final radius R_{ball}.
- The final size of the ball depends on the number of particles inside the drop. In experiment, the ball size was in the range $100 < R_{ball}/R_p < 1000$, with R_p the particle radius. Clearly, the exact final size of the ball will not only depend on the amount of particles in the system but also on their packing fraction.

- The global packing fraction as $$\Phi \equiv N\left(\frac{R_p}{R_{ball}}\right)^3,$$
- The final supraball radius R_{ball} is accurately determined from SEM images. If the packing fractions were identical for all supraballs, $\boldsymbol{R_{ball}/Rp \sim N^{1/3}}$.



A) Supraball to microparticle diameter R_{ball}/R_p plotted against the total amount of particles N in the system

B) The packing fraction Φ strongly depends on N.

Discussion

The critical number of particles $Nc \approx 3 \cdot 10^{6}$ when the packing fraction reaches that of an RCP.

N < Nc a loose, disordered particle packing in the supraball

N > Nc a densely packed, ordered supraball

What causes the transition from ordered to disordered packings, and what determines the critical number of particles?

They compare the timescale on which particles can arrange by **diffusion** to the **hydrodynamic** timescale for the particle transport by convection, given by the inward motion of the liquid-air interface.

- The diffusive timescale, $t_d = Rp^2/D$, Rp = the particle radius and D = the diffusivity of the particles in the liquid.
- The hydrodynamic timescale is $t_h = L/\left| dR/dt \right|$

Here $R(t)$ = droplet radius and L = typical interparticle distance, $L = N^{-1/3} R$

Ratio of both timescales as,

$$\mathcal{A}(t) \equiv \frac{t_d}{t_h} = \left|\frac{dR(t)}{dt}\right|\frac{t_d}{L} = \frac{D'}{D} N^{1/3}\left(\frac{R_p}{R(t)}\right)^2,$$

$A(t)$ increases as the droplet radius becomes smaller during the evaporation until the limit $R = R_{ball}$ is reached.

Discussion

If the cross-over is reached when $R \gg R_{ball}$, from this point in time onward the interface speed is too high, random arrangement, a low packing fraction.
If the cross-over is reached when $R \leq R_{ball}$, dense and ordered, a high packing fraction.

If N is high $(N > Nc)$, this moment is reached relatively early, i.e., well before $A(t) = 1$, and we get an ordered particle packing inside the supraballs. Using that $R_{ball}/Rp \sim N^{1/3}$ and considering $A(t) = 1$, the c[illegible] particles above which we obtain ordered supraballs,

$$N_c \sim \left(\frac{D'}{D}\right)^3.$$

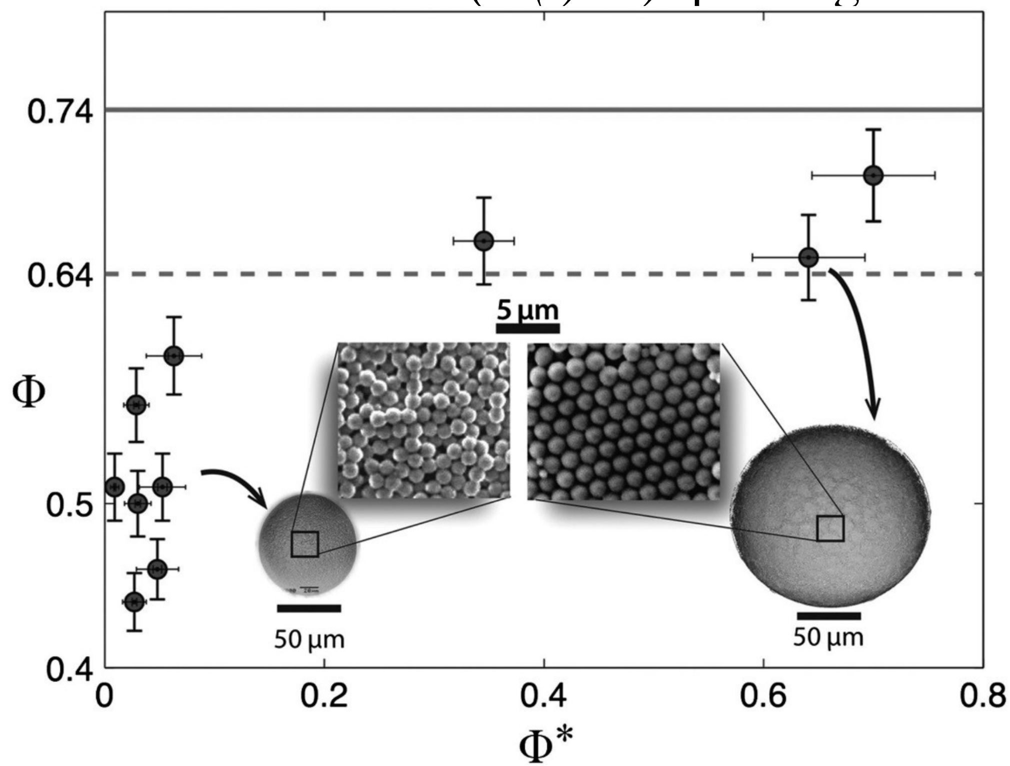
$D' = 3 \times 10^{-10}\, m^2/s$ and $D = 2 \times 10^{-13}\, m^2/s$, $\quad Nc \sim 10^9$

This prediction is two to three orders of magnitudes larger than then experimentally observed Nc.
As they neglected humidity, liquid density, diffusivity of vapor, and saturated vapor concentration.

Discussion

To verify whether the final packing fraction indeed depends on the spacing between the particles the moment the cross-over time is reached, the time-dependent packing fraction as $N(R_p/R(t))^3$.

At cross over time ($A(t)=1$) packing faction= Φ^*



Final packing fraction Φ_f versus the packing fraction at the cross-over time Φ^* .

$R_{ball}/Rp \sim 0.1 * N^{1/3}$, $Nc \sim 10^{7}$

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Conclusion

- A simple technique to create spherical colloidal supraballs relying only on droplet evaporation over a robust superhydrophobic surface.
- The supraballs show a highly ordered structure if the number of particles inside the drop is large.
- Ordered packing depends on the parameters driving the droplet evaporation (through D') and the diffusivity of the particles.
- By controlling the humidity and ambient temperature the supraball packing fraction and hence size can be controlled.

Thank you