

Supplementary information

Loosely Packed Monolayer Coffee Stains in Dried Drops of Soft Colloids

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Preparation of pNIPAM microgel spheres

pNIPAM microgels were prepared by the method reported by Pelton and Chibante¹. 0.25g N- isopropyl acrylamide (Sigma Aldrich) and 0.025g N,N'-Methylenebis acrylamide (Sigma Aldrich) were dissolved in 15ml of DI water (Milli-Q Integral 3/5/10/15 system, M-Millipore). The mixture was degassed and stirred under N_2 atmosphere on a temperature controlled magnetic stirrer. Once the temperature of the mixture reached 70° C, 20mg of potassium persulfate initiator, dissolved in 5ml of DI water was added to the reaction mixture. Polymerization reactions was allowed to continue under constant stirring in N_2 atmosphere at 70° C for 7-8 hours. At the end of 8 hrs, reaction was terminated and the mixture was allowed to cool overnight. Thus prepared particles were subjected to several cycles of centrifugation and redispersion in DI water. Concentrated sediment at the end of 3 cycles was refrigerated and stored for further use.

The concentration of particles in mother solution, is determined by drying the dispersion of known weight on a high precision microbalance. Several dilutions of this parent solution was prepared in DI water for subsequent use in evaporative self assembly experiments discussed in main text. Dynamic light scattering and zeta potential measurements were performed using particle size analyzer, nanopartica SZ-100, from Horiba Scientific. Hydrodynamic radius of the particles determined by dynamic light scattering is 294 ± 6 nm at 25° C. Electrophoretic mobility measurements indicate a negative zeta potential of about -44 mV for the microgels. Smoluchowsky model was used to deduce the zeta potential. Measured zeta potential corresponds to approximately 5.94×10^3 number of elementary charges present on the surface of colloidal particle.

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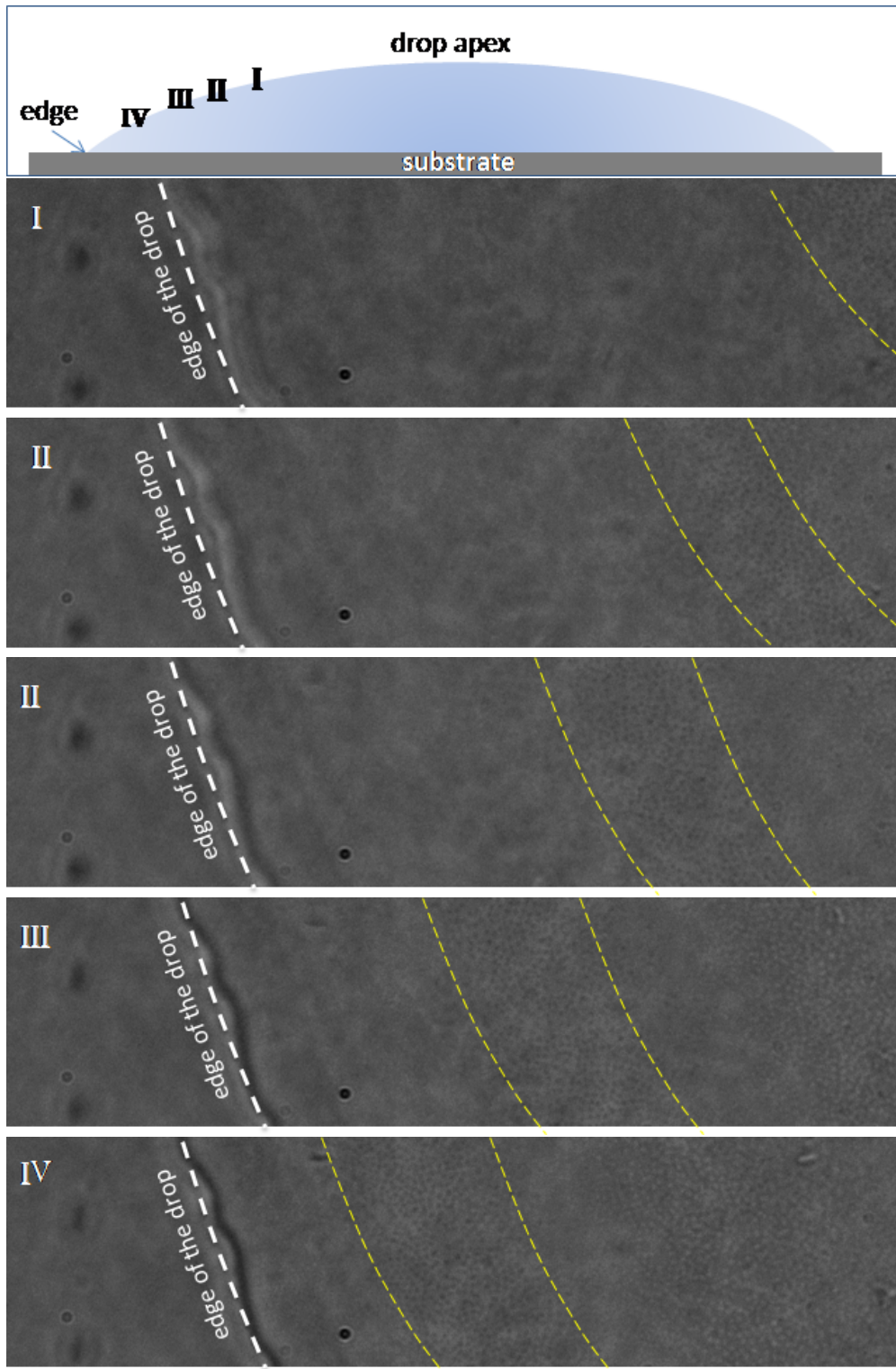


Figure S1 A schematic representation of sessile drop is shown on top panel. Different locations on the interface is numbered from I-IV. Optical microscopy images focusing only on the respective locations of the interface is shown in following panels numbered I-IV. Only A patch of particles within the two dotted line area is under focus for a particular height of the objective

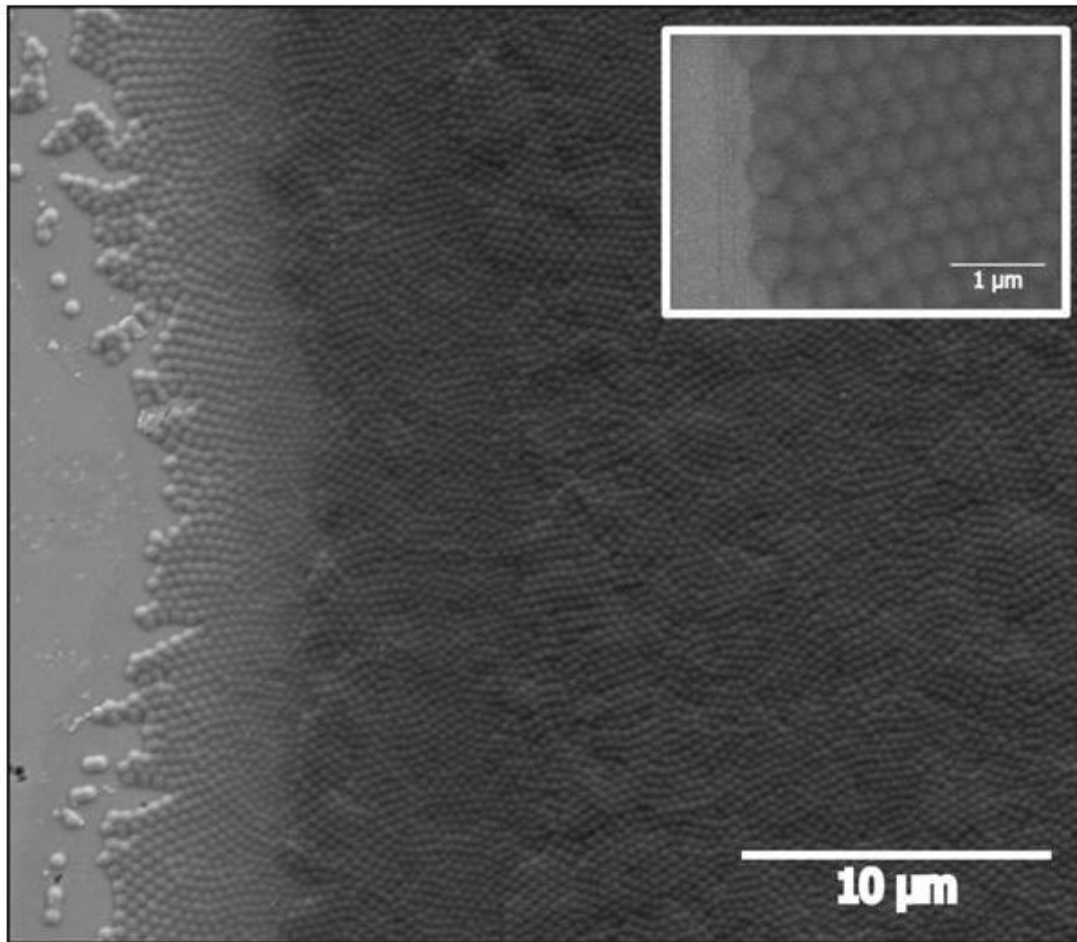


Figure S2 SEM image of a multilayer ring formed by pNIPAM microgels at high concentration.

Construction and analysis of Voronoi polygons

Voronoi cells are polygons which are locus of all points relatively close to a particular lattice site compared to any other site in a two-dimensional lattice. For ordered arrangement of particles in hexagonal symmetry, all the Voronoi cells will be hexagons of same area. In a disordered phase, the Voronoi cells acquire random geometries with widely varying area, resulting in a higher standard deviation. Small strips of $30\mu\text{m} \times 30\mu\text{m}$ area were chosen at $250\mu\text{m}$ interval along a line drawn across the stain through the center. These

areas were further subdivided and analyzed using in-house developed MATLAB code. Area of each bound Voronoi polygon was calculated and deviation of each area from the average was deduced. One can easily relate this standard deviation to the order/disorder present in a system by defining Areal Disorder (AD), as discussed in the main text .

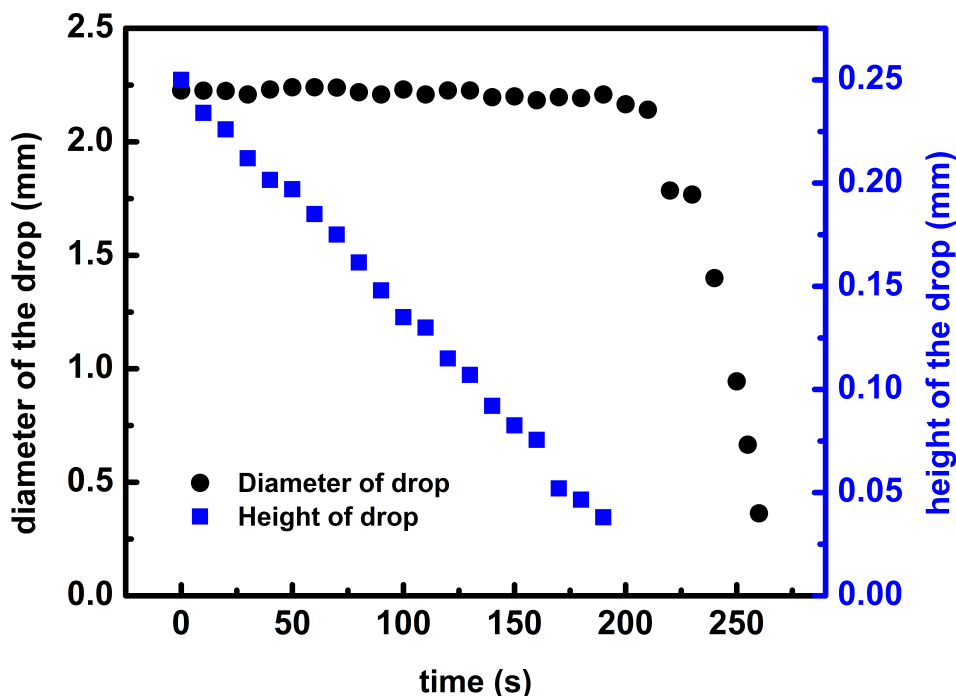


Figure S3 Variation of contact radius (black filled circles) and height of the drop (blue filled squares) with time for a 0.01 wt% pNIPAM microgel dispersion placed on glass.

Calculation of center-to-center distance from different interactions between microgel particles.

Microgel particles used for this work have a core-corona architecture. These particles contain negative charge on their surface as is evident from zeta potential measurements. These result in electrical double layer repulsion and steric repulsion between the particles. These interactions also prevent the particles from flocculating in bulk.

When these microgel particles are present at the water-vapor interface, attractive capillary interactions emerging due to interfacial perturbations also contribute towards the final deposition patterns of the microgel particles^{2,3}. The resultant interaction between

the particles are estimated by assuming two body potentials. The repulsive electrostatic dipole-dipole type interaction between charged microgel particles situated on the water-vapor interface at a center-to-center separation ‘ $2s$ ’ is given by,

$$V_{dipole} = \frac{2}{4\pi\epsilon_0} \left(\frac{Ze}{\epsilon_r \kappa} \right)^2 (2s)^{-3} \quad (1)$$

where Z is the number of electric charge on a single colloidal particle, e is the charge of a single electron, ϵ_0 and ϵ_r are the permittivity of free-space and relative permittivity of water respectively⁴. κ^{-1} is the Debye screening length of the system and is given by,

$$\kappa^{-1} = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{2N_A e^2 I}} \quad (2)$$

where k_B is the Boltzmann constant, T is the temperature in Kelvin scale. N_A is the Avogadro number and I is the ionic strength of the system.

The steric interaction between two core-shell particles is dependent on the dimensions of core (R) and shell (δ), and the concentration of adsorbed polymer in the shell (c) and the center-to-center distance, $2s$, between the particles and is given by,

$$V_{steric} = \frac{4\pi c^2 k_B T}{3v_w \rho^2} \left(\frac{1}{2} - \chi \right) \left[\delta - (s - R) \right]^2 \left[3R + 2\delta + (s - R) \right], \quad (3)$$

where v_w is the molecular volume of the solvent, ρ is the density of the polymer, and χ is the Flory-Huggins interaction parameter between the polymer and solvent⁵.

During the final stages of evaporation, when the microgel spheres touch the substrate, the water-vapor interface get perturbed due to the presence of particles leading to the emergence of long-range immersion capillary forces between the particles. The strength of these immersion capillary forces are determined by the center-to-center distance between the particles, equilibrium contact angle θ , particle radius R , radius of horizontal projection of the contact line r_c , height of contact line above the level of liquid film h_c and the angle determining the slope of water meniscus at the contact point Ψ_c ⁶. The immersion capillary interactions are estimated by using the following expression.

$$V_{cap} = -2\pi\gamma \left(2h_c R \cos\theta - r_c h_c \sin\Psi_c + r_c^2 \right) \quad (4)$$

where γ is the surface tension of the water-vapor interface.

We estimated the typical magnitudes of V_{steric} , V_{cap} and V_{dipole} assuming that the shell of the microgel is 50% less dense compared to the bulk pNIPAM polymer, and it extends

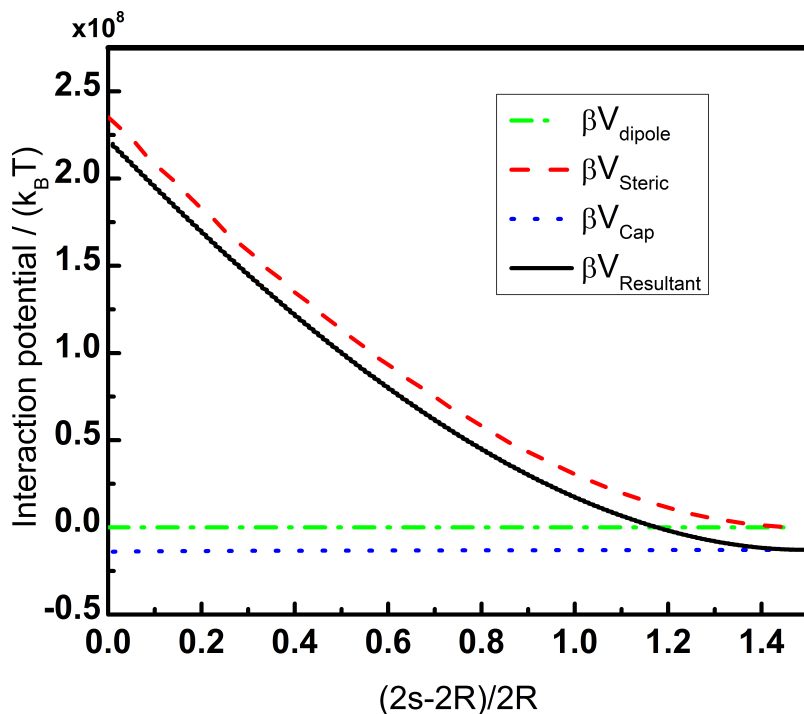


Figure S4 Dependence of attractive capillary, repulsive steric and electrostatic interactions on surface to surface distance of the particles.

to a distance of 1.5 times the core radius, from the core surface and these are reasonable assumptions typically used in the literature^{5,7}. The Flory Huggings interaction parameter for pNIPAM water system is known to be 0.25 at 298K⁸. For hydrophilic particles such as pNIPAM containing microgels, θ could be taken to be 20° ⁷. For all calculations, R is taken to be 271 ± 9 nm, which is the core radius obtained from SEM image analysis. Using these values we obtained the center-to-center distance between the particles, at which the steric repulsion is counter balanced by the capillary attraction, to form two-dimensional crystalline structures to be $1.18 \pm 0.04 \mu m$. Electrostatic and Van der Waals interactions are very small at these particle separations and only prevail at shorter length scales. Therefore our calculations show that the steric and immersion capillary forces control the distance between the particles. When number of particles in the drop is increased, particles mutually repel each other resulting in a compression of the outer low density regions of the shell. We presume that this crowding and mutual repulsion of particles result in changing the distance between particles when concentration is increased.

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