(Preliminary report) Crystallisation in colloidal gels

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H. Tsurusawa

Our focus

Our first paper, “Gelation as condensation frustrated by hydrodynamics and mechanical tension”, has demonstrated scanning the entire process of gelation in a single particle level. The paper focused on the early stage of gelation, especially percolation and coarsening process. The process of dynamical arrest of gels were not successfully observed because of the problems of materials and methods as follows.

Here, we optimise the procedure to observe the very late stage of gelation and elucidate the mechanism of dynamical arrest of gels.

Materials and Methods

Colloids

The colloid in our first paper has diameter of 3.0 micrometer and Brownian motion time of 5 sec. This colloid is optimised for observing the early and middle stage of gelation since we focused on the mechanism of percolation and coarsening instead of dynamical arrest. Since this colloid is moving slow and sensitive to density mismatch, the observation time is practically limited within about 1hour (~720τ).
To observe the late stage of gelation, I newly prepared a colloid with diameter of 2.1 micrometer. This colloid has Brownian motion time of 2 sec.

Polymer

I newly prepared a polystyrene with molecular weight of 3.8 MDa, whereas the polystyrene in the first paper has M.W. of 8.4 MDa.

Solvent and density match

The solvent is a mixture of cis-decalin and CHB. Density is matched by salt-reservoir and its precision is within 0.3wt% of cis-decalin ($\Delta\rho < 0.1\%$).

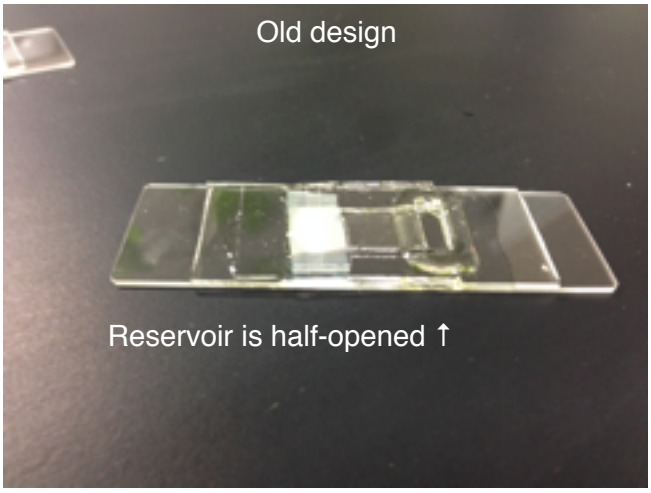
Salt-reservoir cell

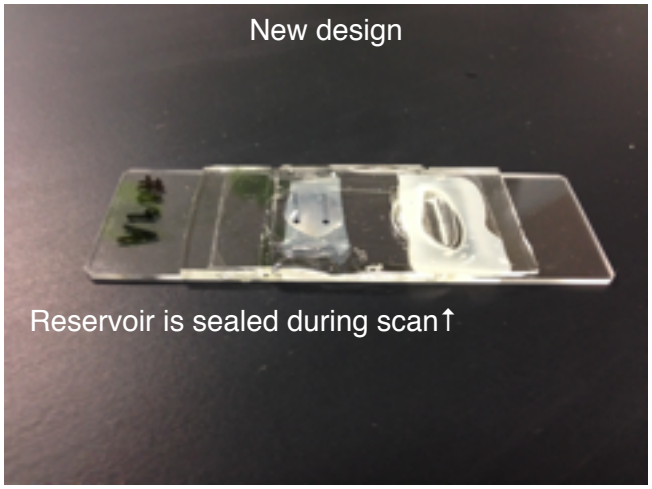
The design of salt-reservoir cell is updated for long-term observation. The previous design causes two problems,

1) Temporal increase of density mismatch.
   The solvent in a bottom cell is evaporating. Since the evaporating rates of cis-decalin and CHB are different, the density of the bottom cell gradually mismatches with the top cell.
2) Back flow from a bottom cell.
   Evaporation proceeds within several hours. This causes long-term back flow to the top cell.

These two problems originate from the open structure of the bottom cell. So, the design and the procedure of salt-reservoir experiment were updated as follow.

1) The top cell contains colloid (+) polymer (-) salt. The bottom cell contains solvent (+) polymer (-) salt. The bottom cell is half-opened.
2) The solution in the bottom cell is exchanged to the solvent (+) polymer (+) salt to initiate aggregation.
3) The bottom cell is immediately sealed by cover glass and araldite glue.
4) Confocal microscope starts scanning colloidal aggregation processes.

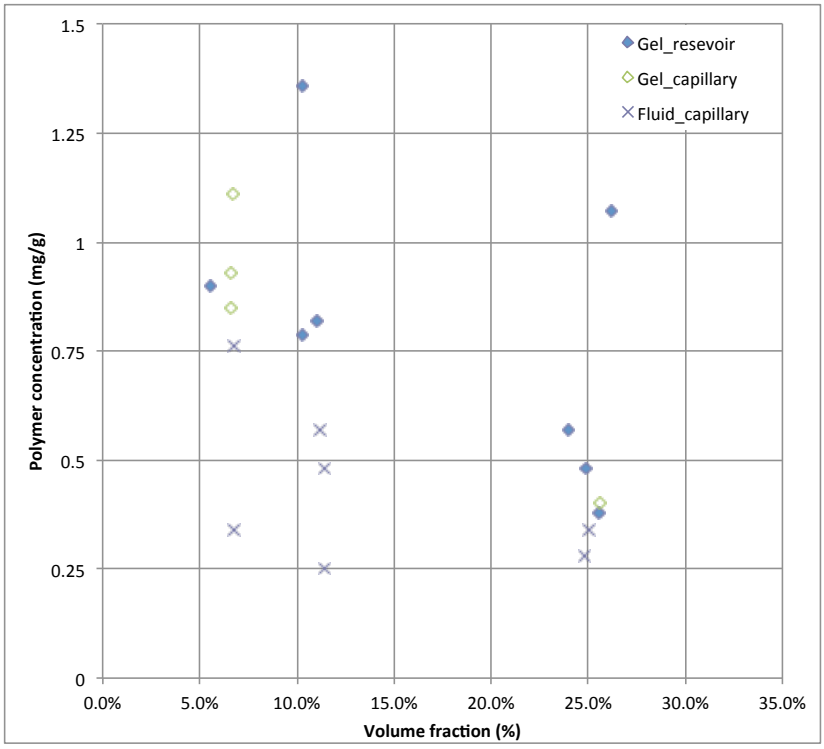




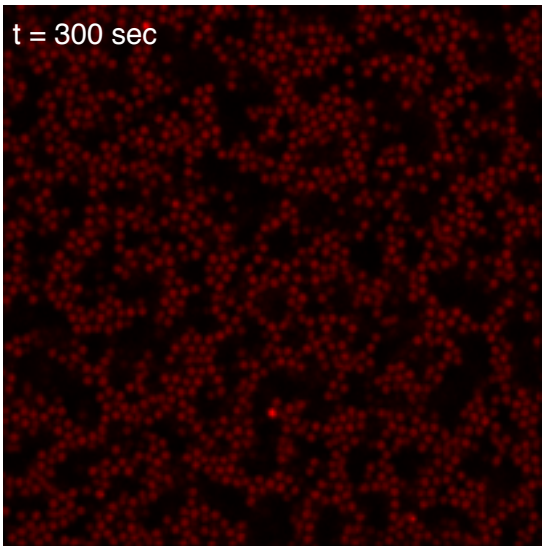
The third step is newly added. By using this procedure, the gels are little affected by gravity nor flow. We can reliably observe gelation processes for more than 5 hours (>10,000 τ).

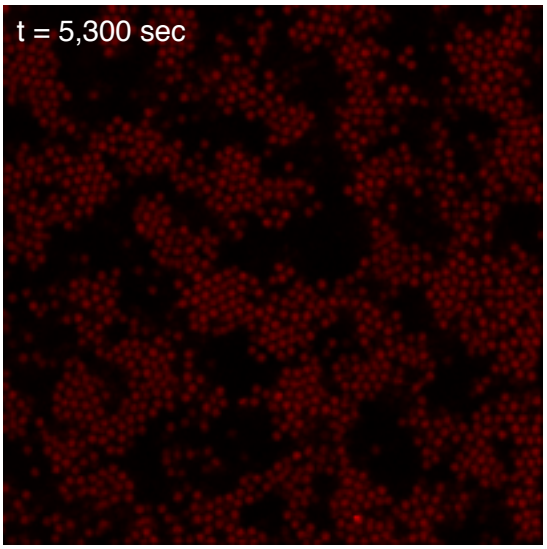
Phase diagram

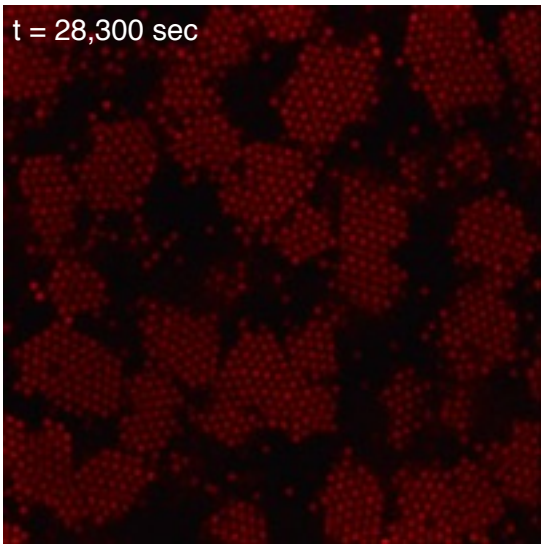
Phase diagram by both capillary and reservoir methods is shown below.



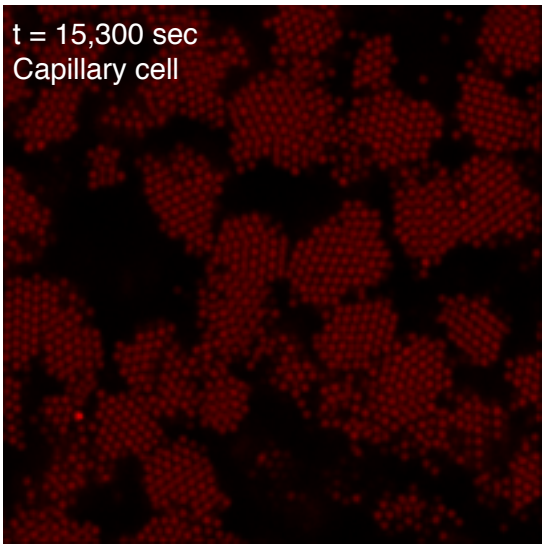
Crystallisation in AR-Res06A (The most important scan).
AR-Res06A has Φ = 25.5% and Cp = 0.38 mg/g. This sample point is very close to the gelation boundary. As aggregation started, the colloids immediately percolated and then coarsening process proceeded. At t = 5,300 sec, arms of the gel started crystallisation. The crystalline domains monotonically grow. At t = 28,300 sec, the gel became “percolated crystals” with their dynamics arrested.





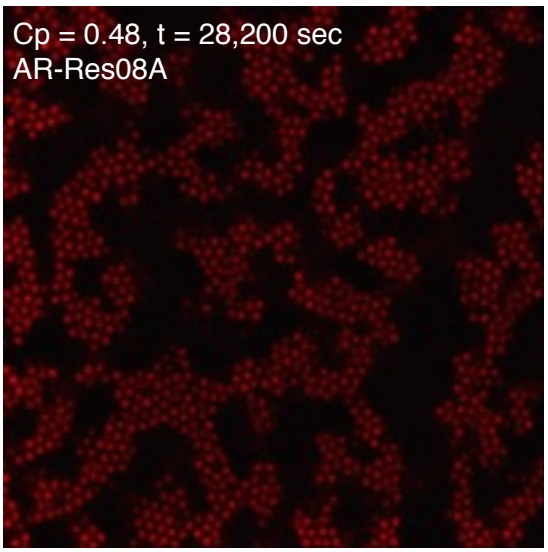


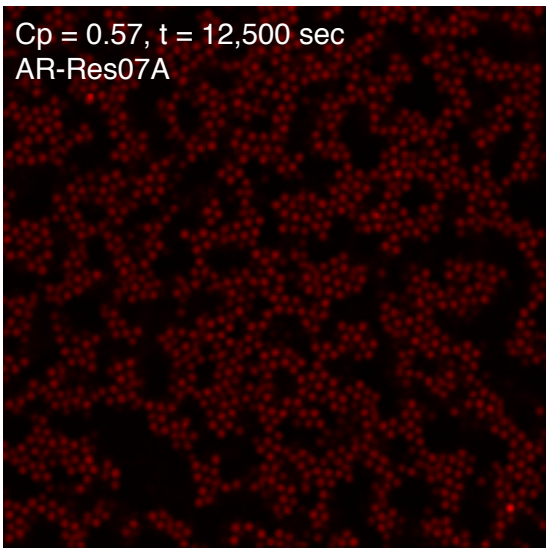
Confirming crystallisation by capillary method
To confirm the result of AR-Res06A, I prepared a sample (AR-Res18CapB) by capillary method. AR-Res18CapB has Φ = 25.6% and Cp = 0.40 mg/g, almost the same as AR-Res06A. Salt was added into the sample bottle and the sample was incubated into a capillary cell sealed by UV glue. To cancel slight density mismatch, the capillary was put vertically and scanned by confocal microscope 15,300 sec after preparing the cell. As shown below, the colloids crystallised. This result confirms crystallisation in AR-Res06A.

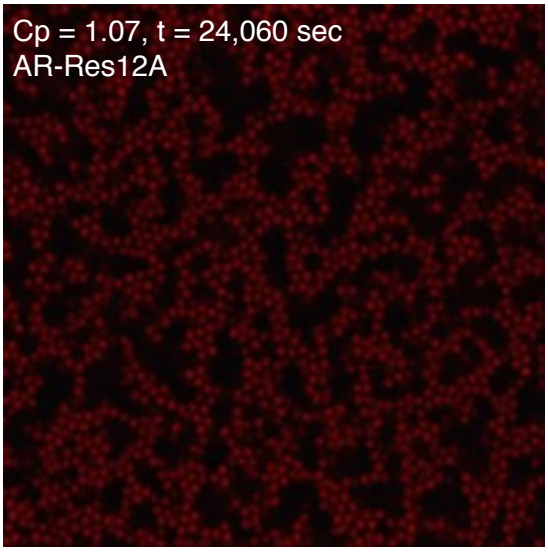


Cp-dependency at Phi = 25%

Fig.4 shows Cp-dependency on crystallisation. As Cp increases, the crystalline order of the final state decreases. Our first paper showed accumulation of mechanical tension in gels. So, we may suggest that stronger attractions frustrate crystallisation in gels. The results of Cp-dependency suggest that crystallisation competes with mechanical tension.

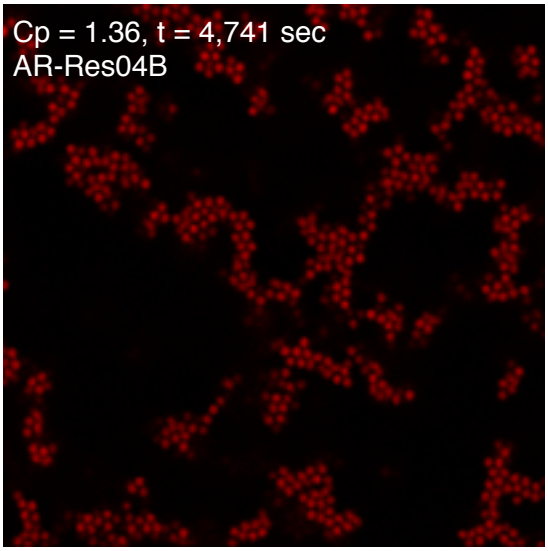


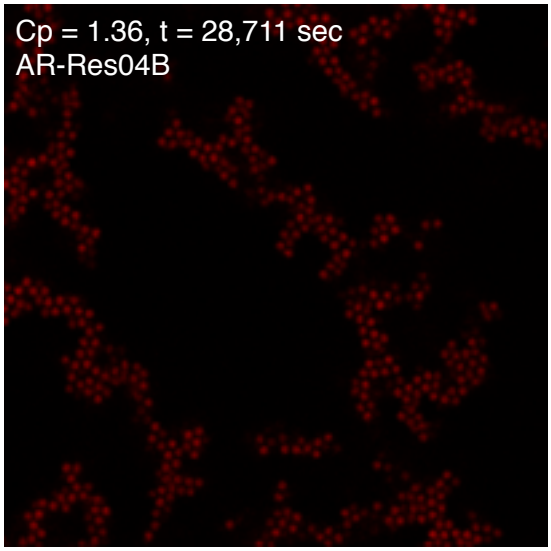


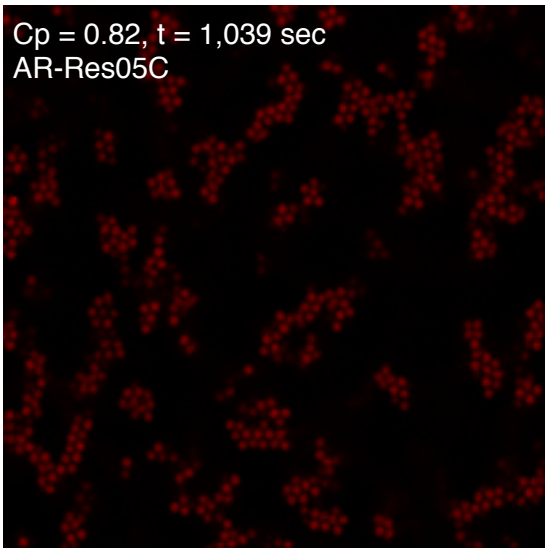


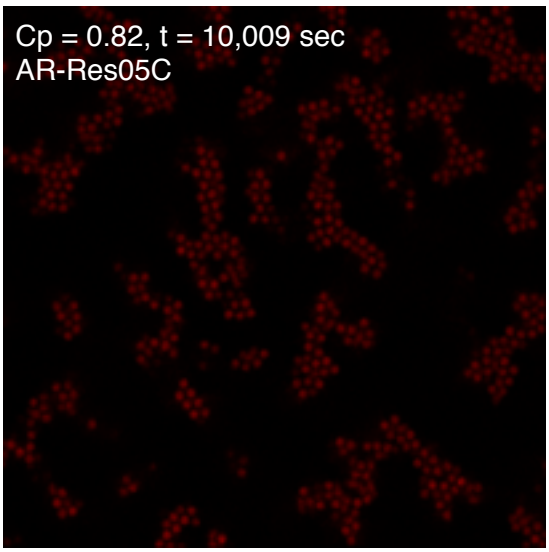
Gelation at Φ = 10%

The processes of dynamical arrest of gels with Φ ~ 10% are observed in AR-Res04B (Cp = 1.36) and AR-Res05C (Cp = 0.82). As gelation proceeds, crystalline order increased. As Cp increases, the crystalline order at the final stage decreases (right ???). Growth of crystalline order may cause dynamical arrest of gels at Φ ~ 10%. But I can not find crystal gels, as shown in AR-Res06A, at Φ ~ 10%.









Conclusion

We observed the entire processes, for over 20,000 sec (10,000 τ), of dynamical arrest of gels. We demonstrated that colloidal gels with weak attractions can crystallise. Cp-dependency suggests that crystallisation is frustrated by mechanical tension and gels are dynamically arrested when mechanical tension balances with the driving force of crystallisation. We found no evidence to support glass transition model.