

How particle stiffness determines interfacial self-assembly



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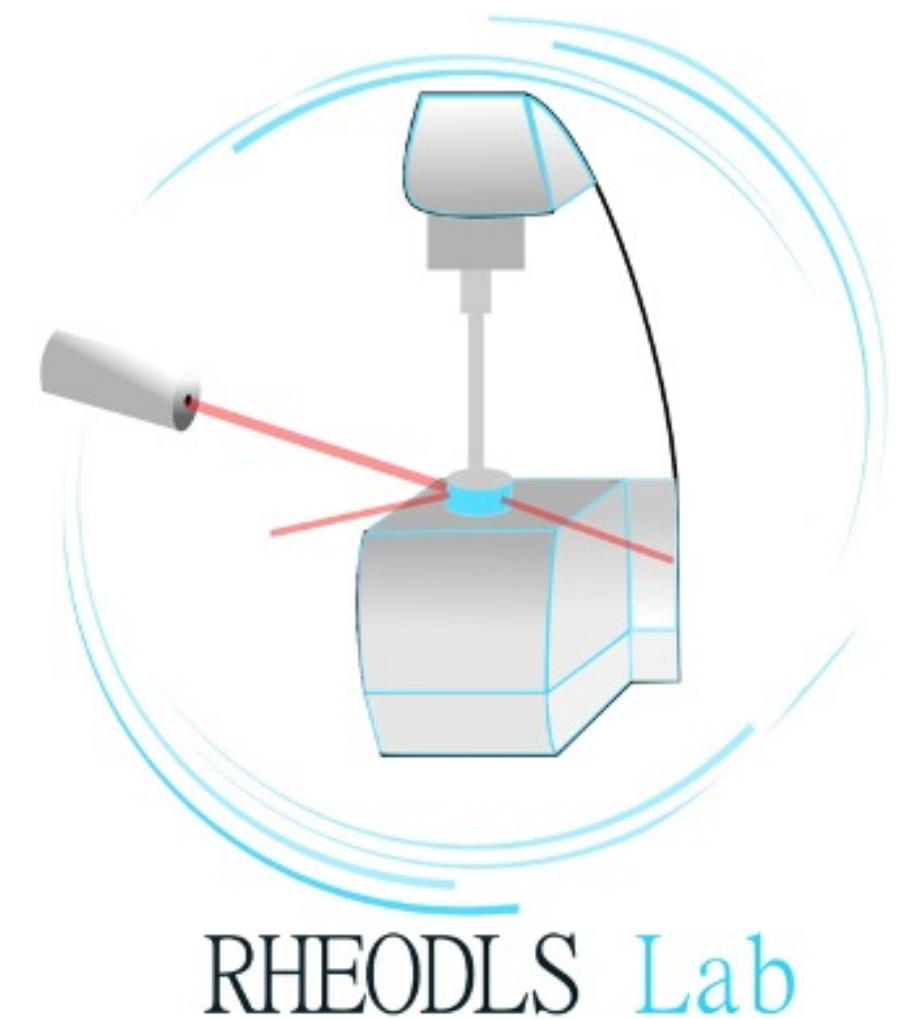
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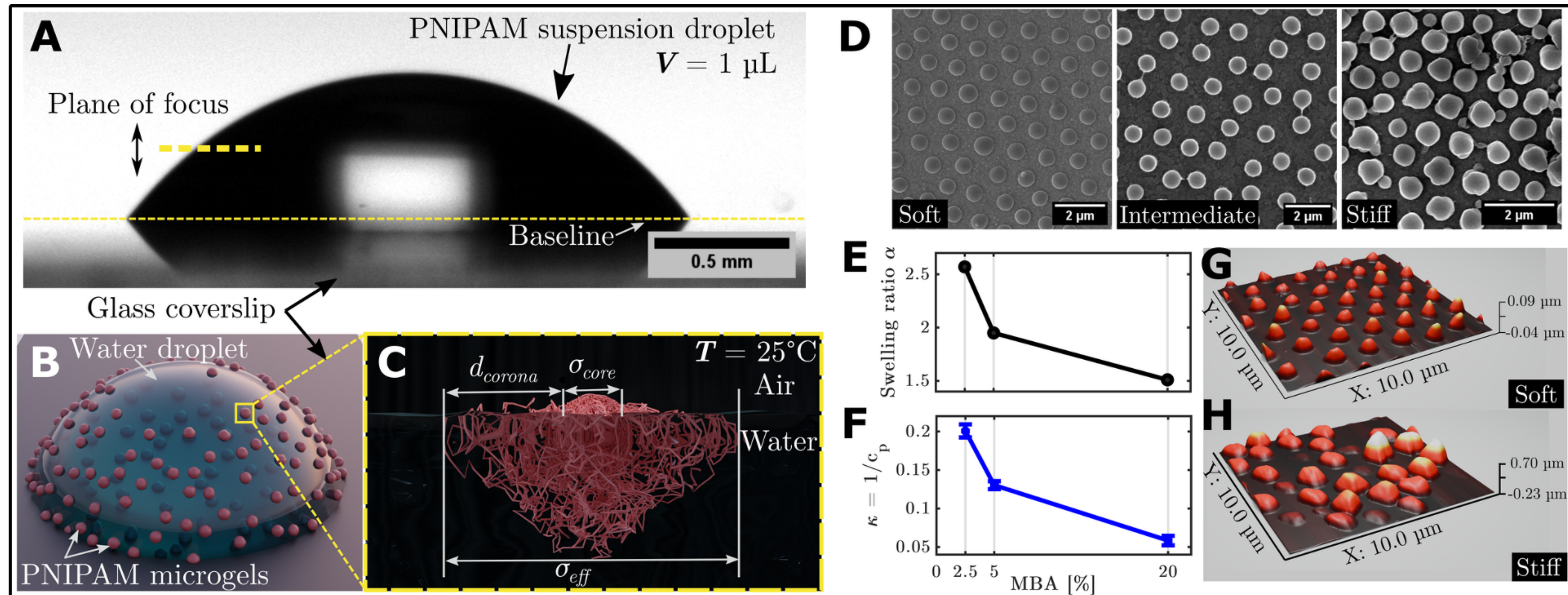
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SWPNIOE, SNU, Delhi NCR, September 11-12, 2026



RHEODLS Lab

Drying aqueous colloidal microgel (PNIPAM) suspension droplets

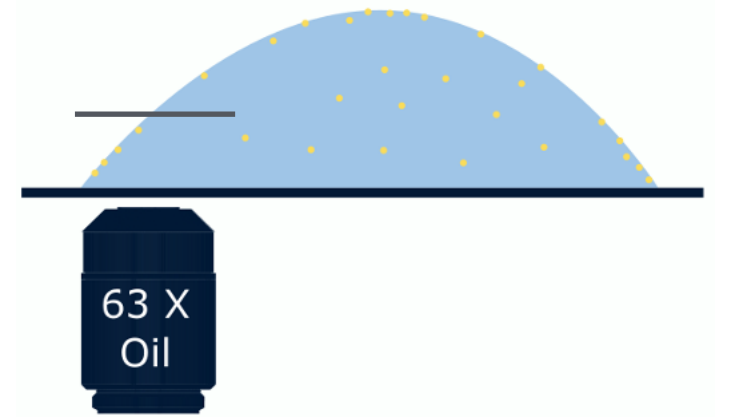


Particles are amphiphilic, their stiffness was controlled by controlling MBA concentration

Stiffest particles are the least deformable and compressible

Stiffer particles have shorter coronas and are more polar

Self-assembly of **soft** particles at air water interface



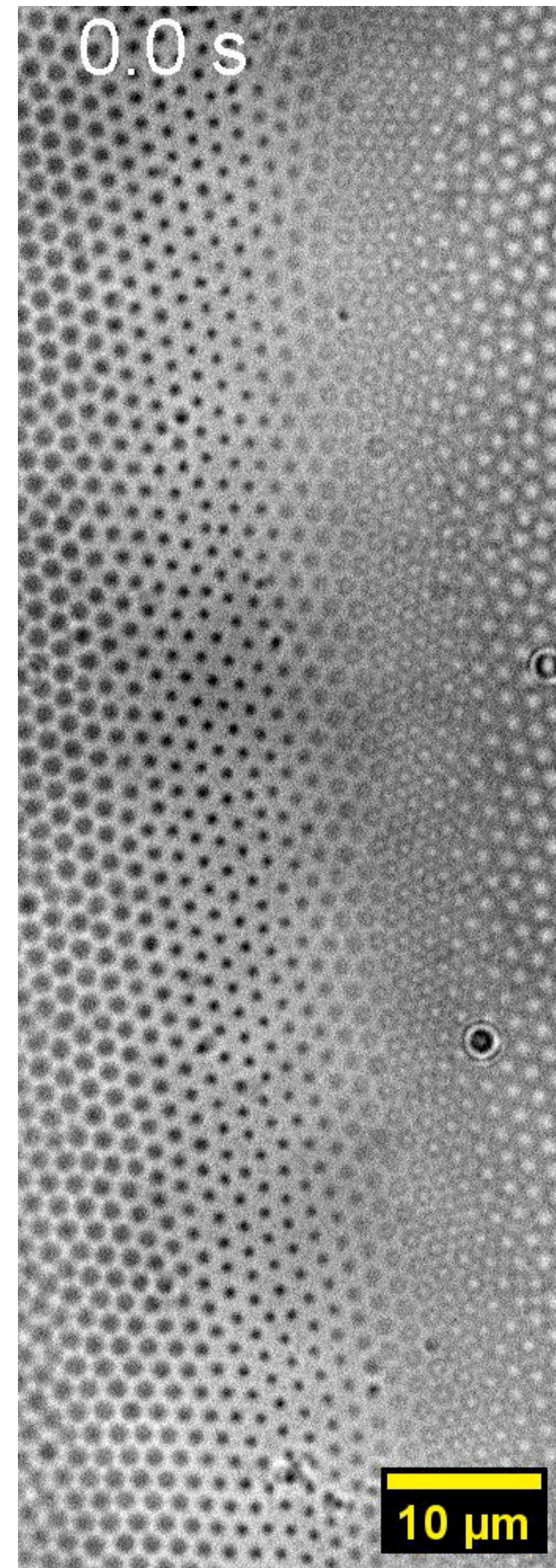
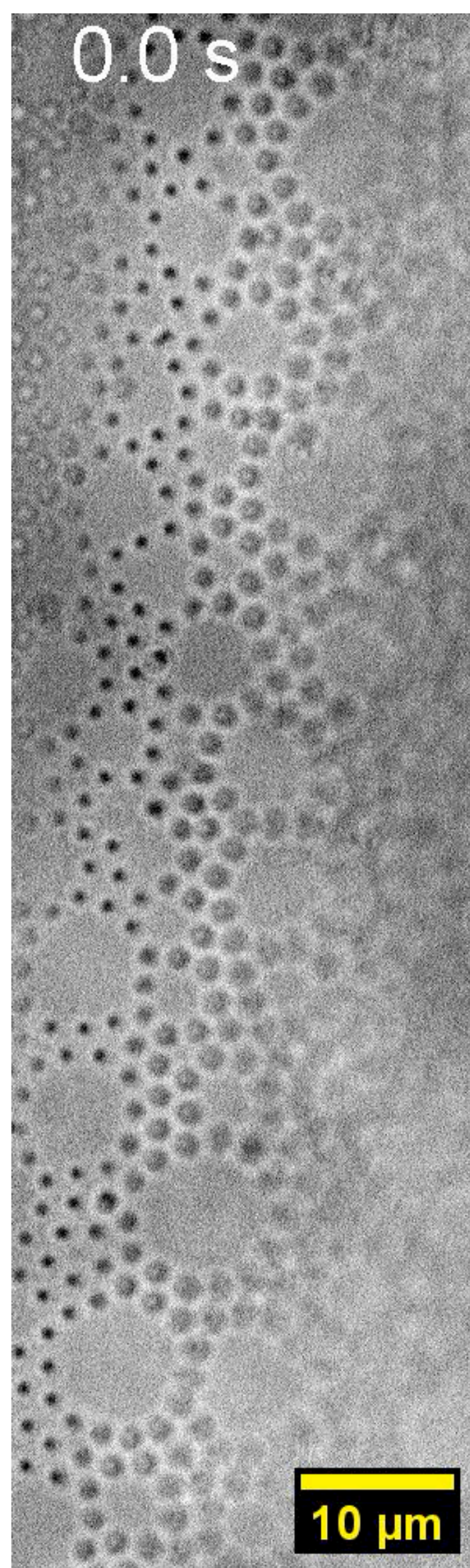
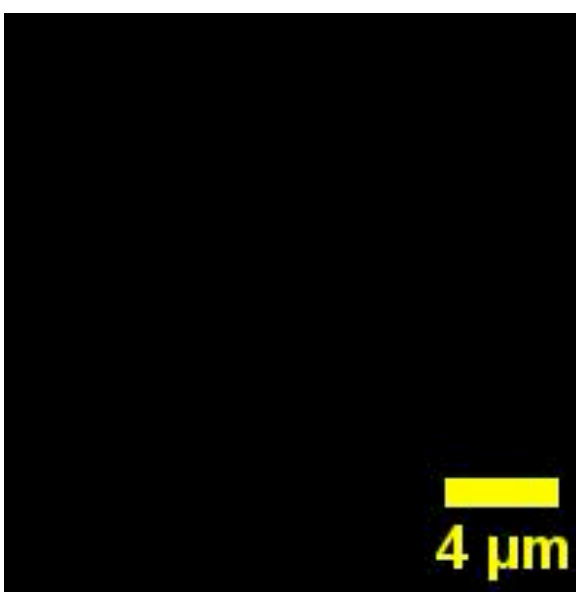
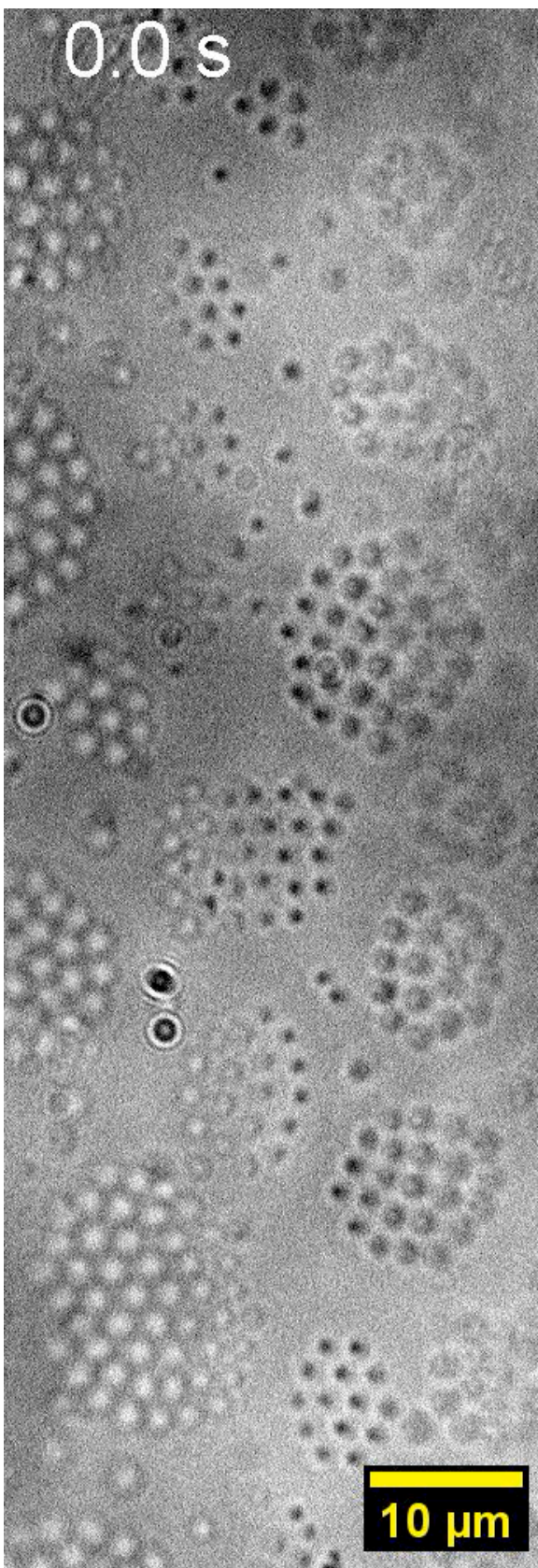
Low surface density:
Colloidal clusters that coalesce

Intermediate surface density:
Circular voids surrounded by 2D chains (2D foams)

High surface density:
Hexagonal lattices

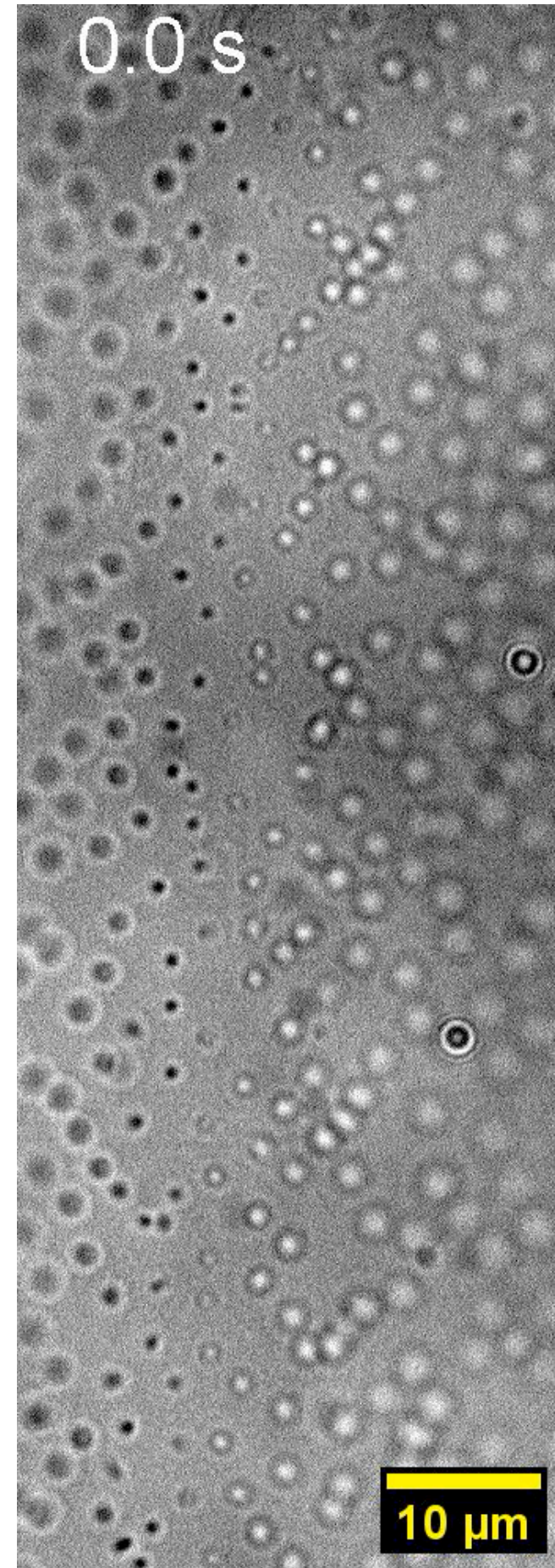
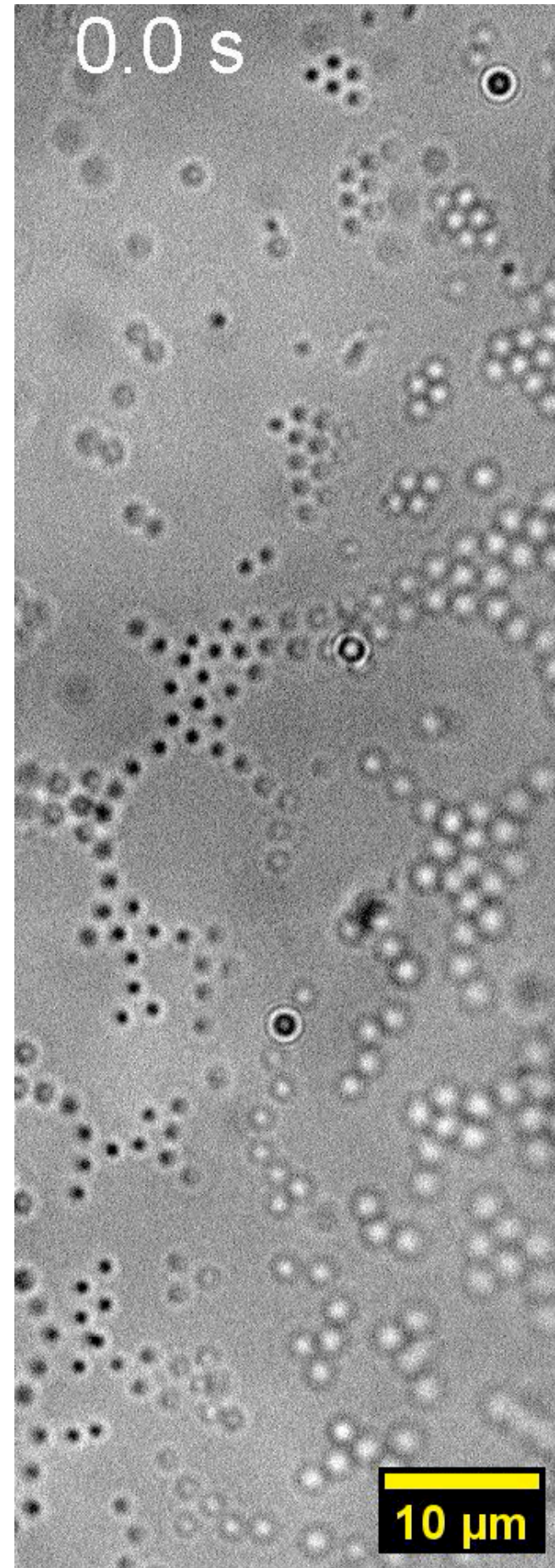
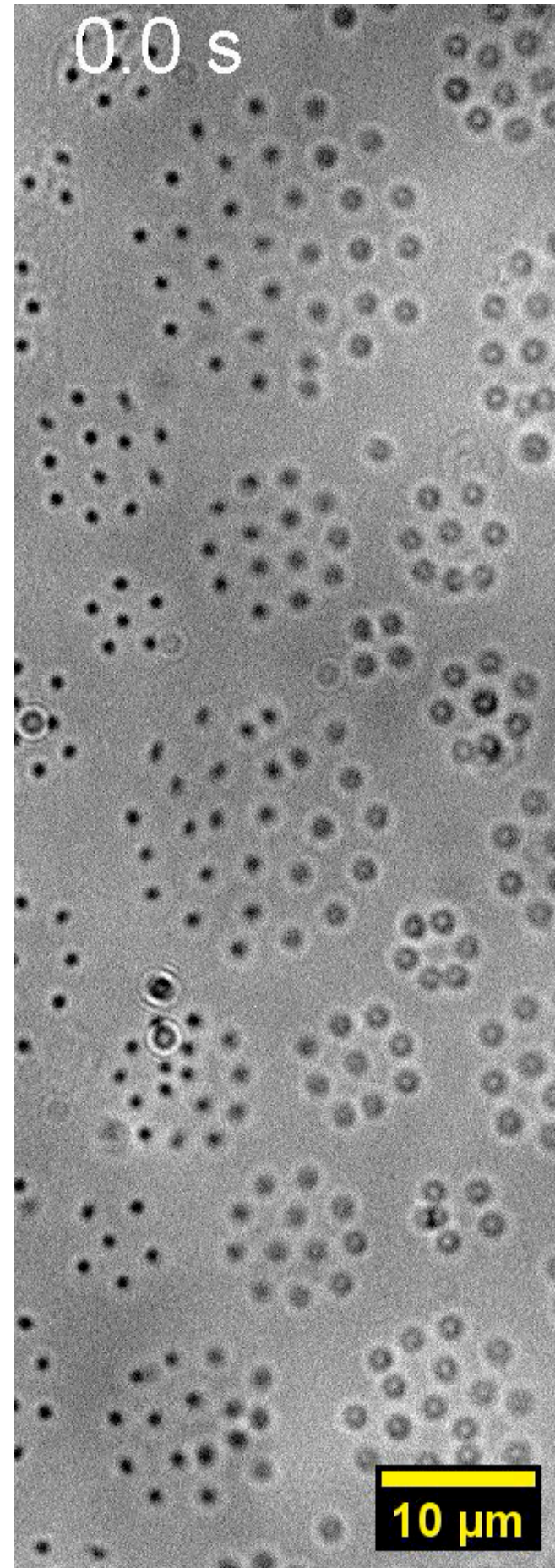
Particles separated by an average distance greater than particle size: **steric repulsion??**

Ordered clusters: **capillary attractions?**



Increasing area fraction at the interface due to drying

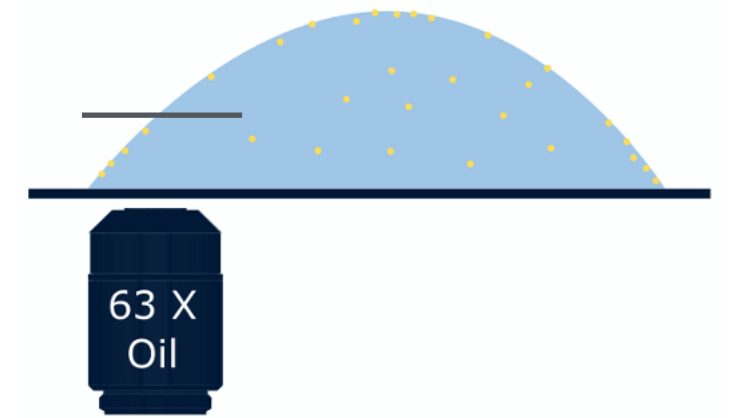
Self-assembly of particles of **intermediate stiffnesses** at air water interface



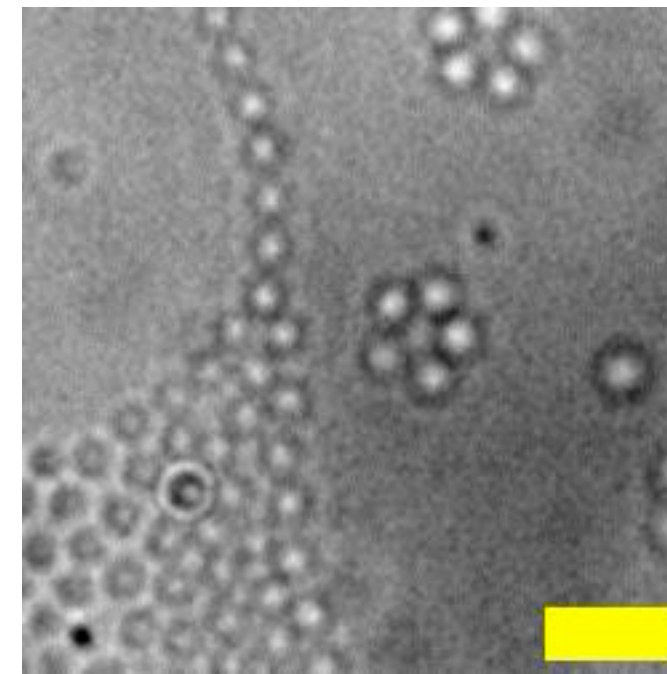
Low surface density:
Very loosely packed hexagonal lattices

Intermediate surface density:
Disordered 2D foams

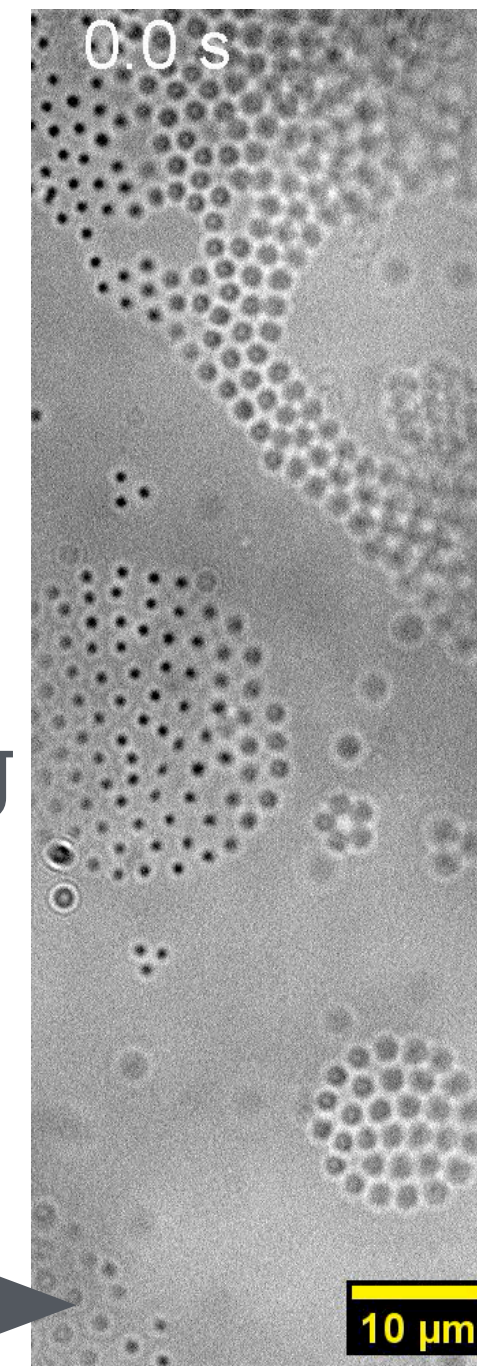
High surface density:
Chain-like structures



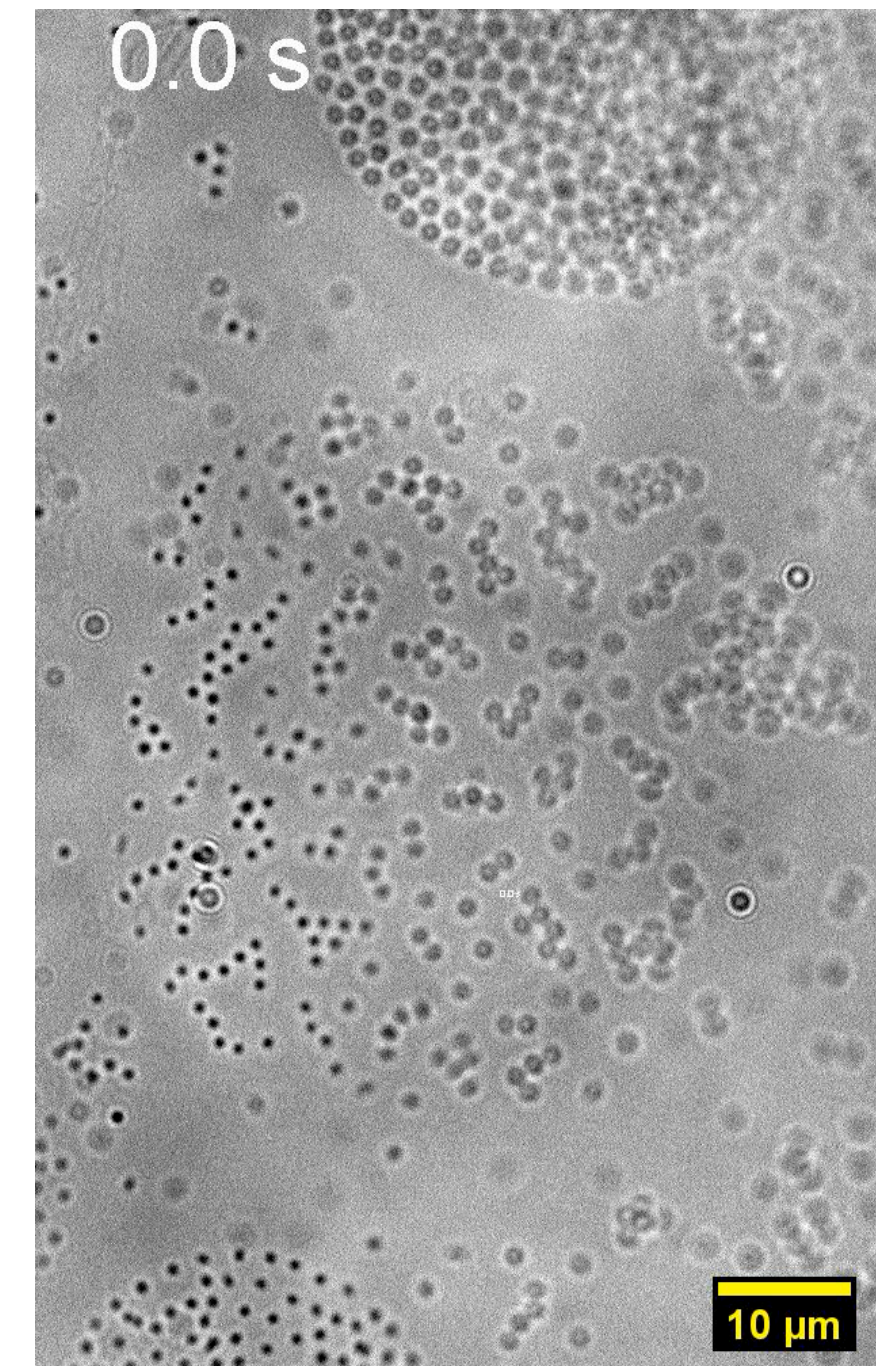
Exotic microstructures



Clusters merging
with foam



Clusters inside foams

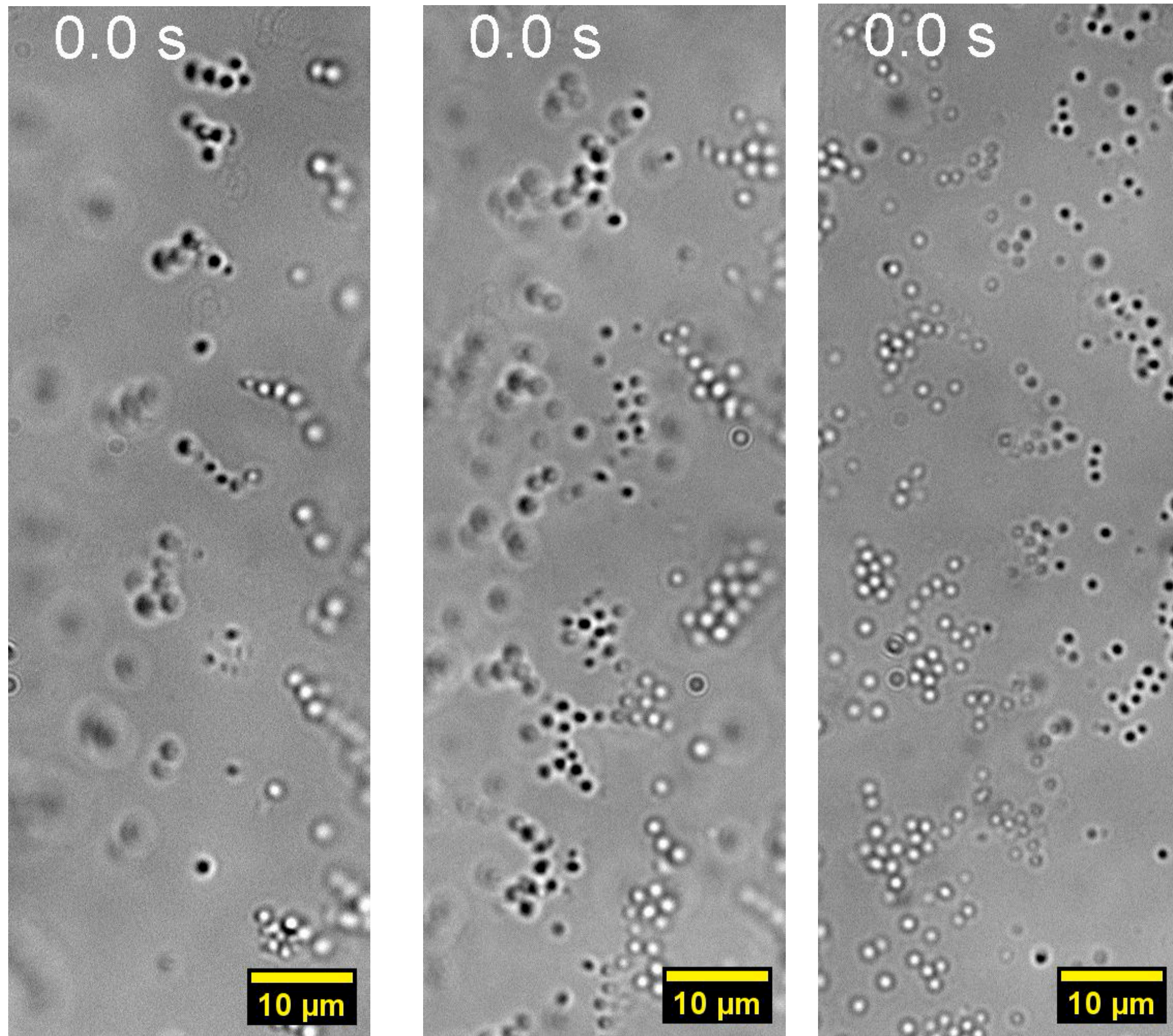


Order
coexisting
with
disorder

Increasing area fraction at the interface due to
drying



Self-assembly of **stiff** particles at air water interface



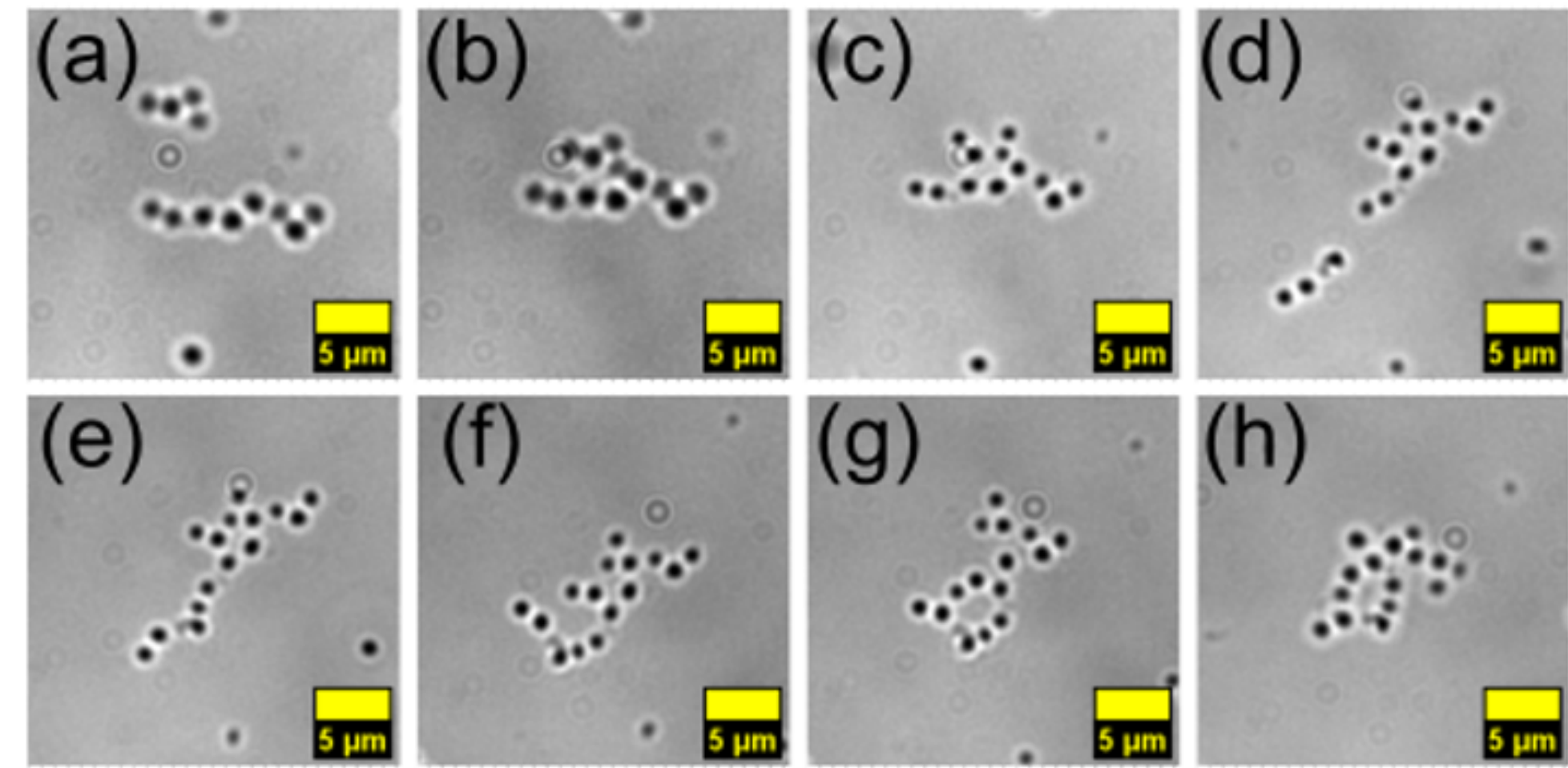
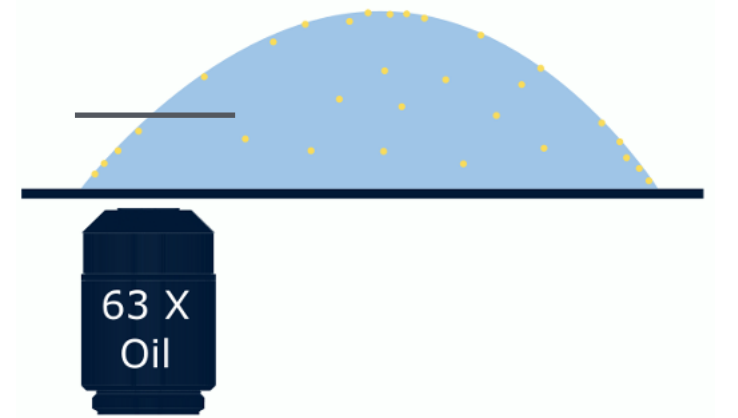
Increasing area fraction at the interface due to drying



Low surface density:
Chains

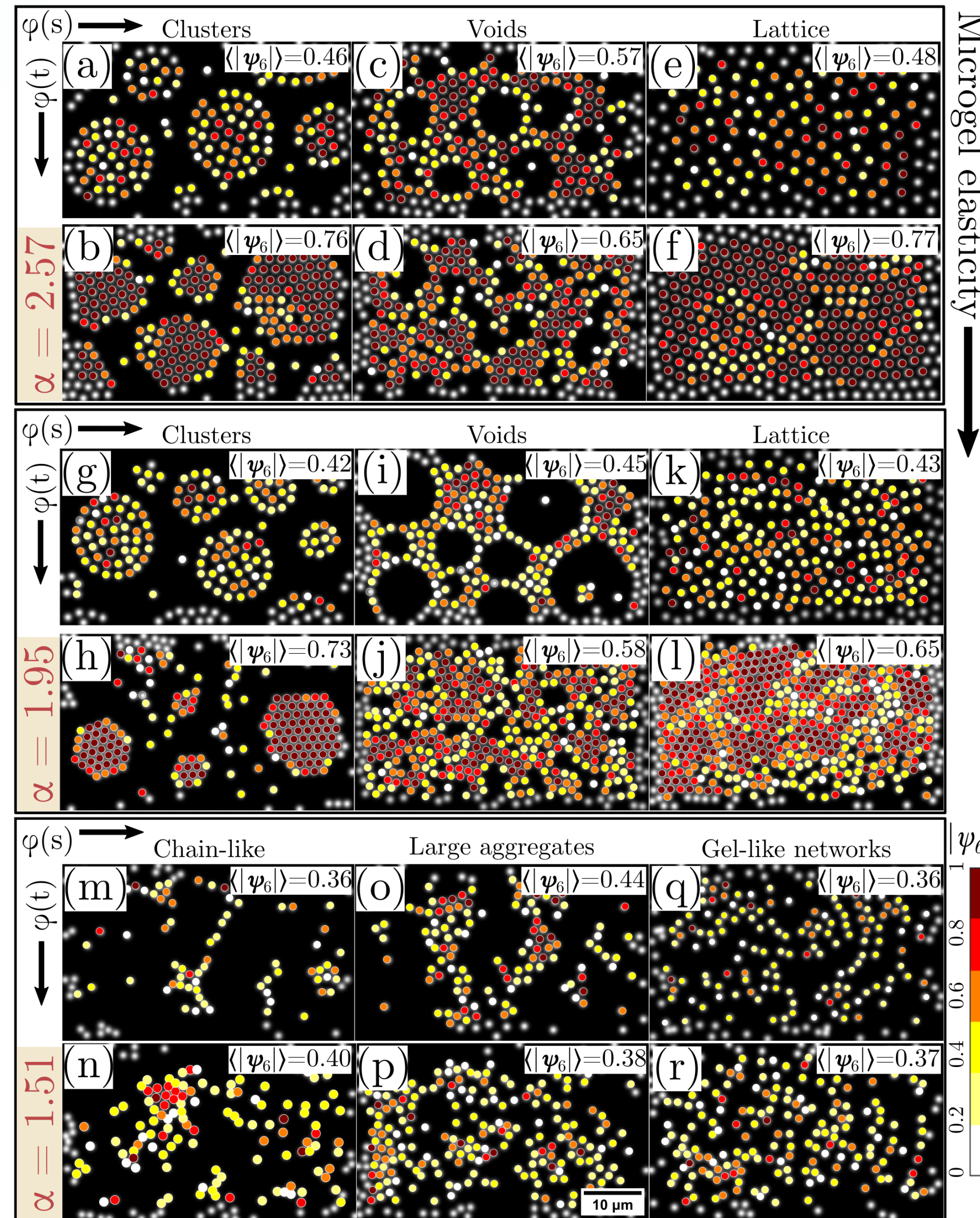
Intermediate surface density:
Chains compactify via mergers and rearrangements

High surface density:
Highly disordered structures, some gel-like strands



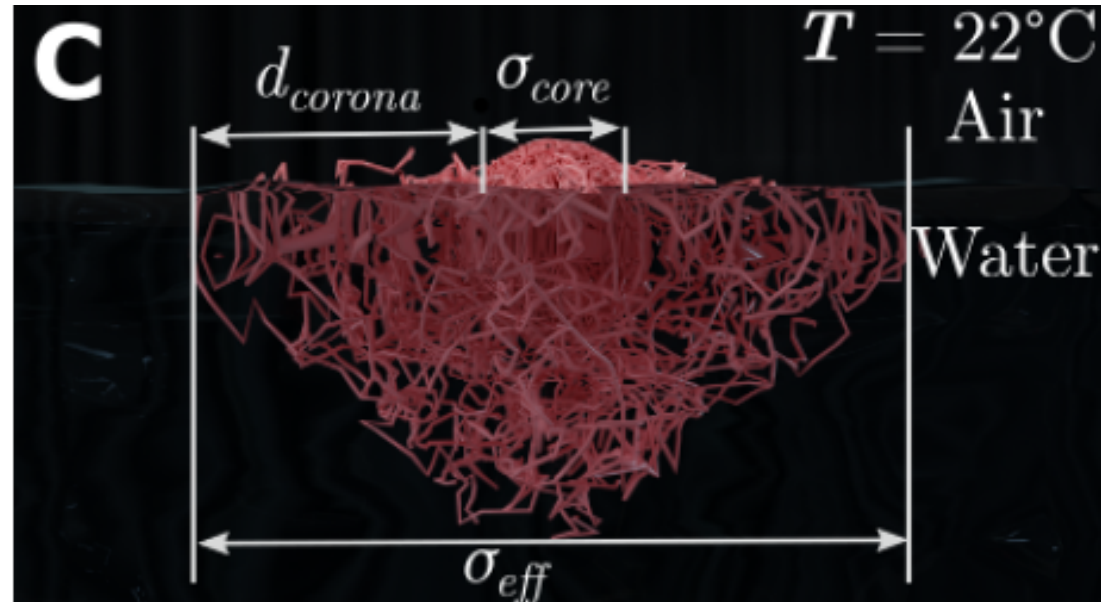
Time-lapse images of mergers and rearrangements

Can we guess what the inter-particle interactions could be?



Observation	Implication
Soft particles are separated by a distance greater than their diameters	Short range repulsion is present: Steric repulsion?
Soft particles form ordered clusters.	Relatively long-range attraction should be present: Capillary attraction?
Soft particles are separated by a distance greater than their diameters	Presence of a secondary minimum
Ordered clusters are circular	Line tension is present Long range repulsion (dipolar?)
Ordered clusters, voids and non-closed packed hexagonal lattices coexist	Frustration? Competing length scales?
Stiff particles form linear and chain-like aggregates	Short range attraction Hydrophobic interaction?

Searching for an effective inter-particle potential

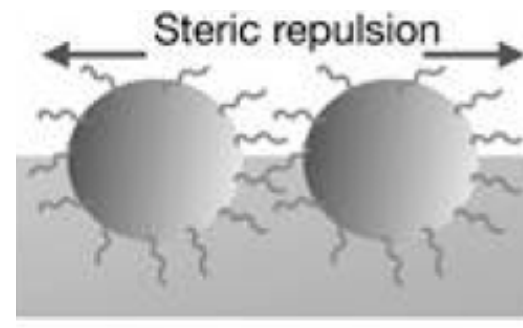


$$U(r) = \begin{cases} \infty, & r \leq \sigma_c, \\ U_h + U_s + U_c + U_d, & \sigma_c < r < 8\sigma_c. \\ 0, & r \geq 8\sigma_c \end{cases}$$

When particles are very close: **hydrophobic attractions** interactions dominate:

$$U_{hydrophobic} = -W_o \exp[-h/\sigma_o]$$

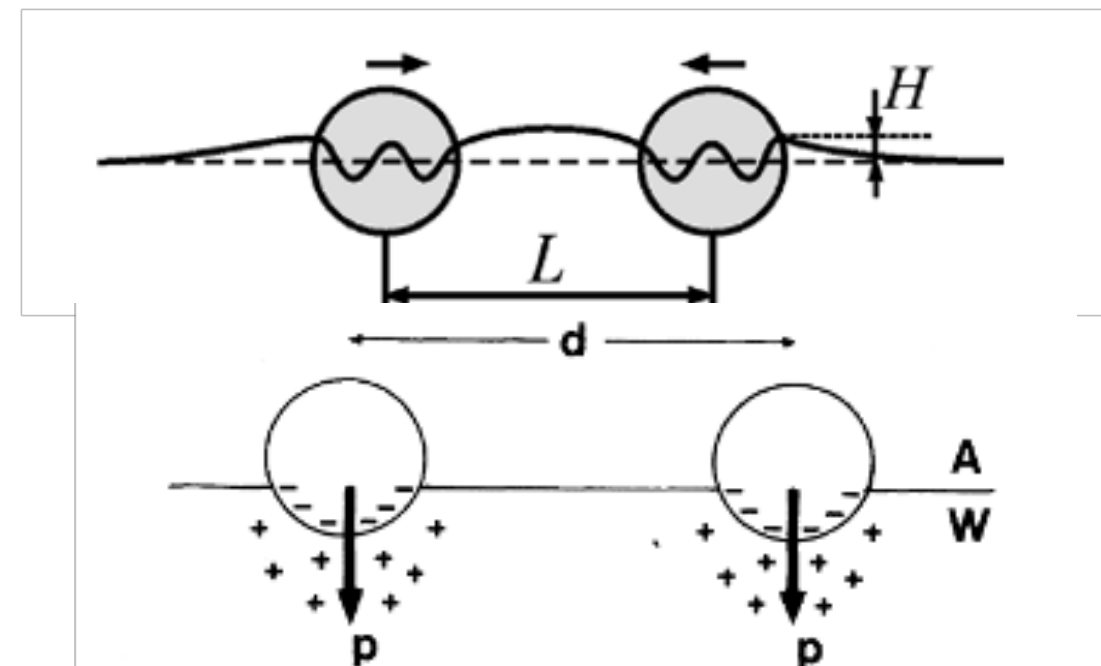
Steric repulsion from compression of coronas is described by the 2D Hertzian potential:



$$U_{steric} = S\sigma_{eff}^2 \left(1 - \frac{r}{\sigma_{eff}}\right)^2 \Theta(\sigma_{eff} - r)$$

$$U_{capillary} = \frac{-B\sigma_c}{r^4 + 1}$$

Capillary interaction (assuming capillary quadrupole):



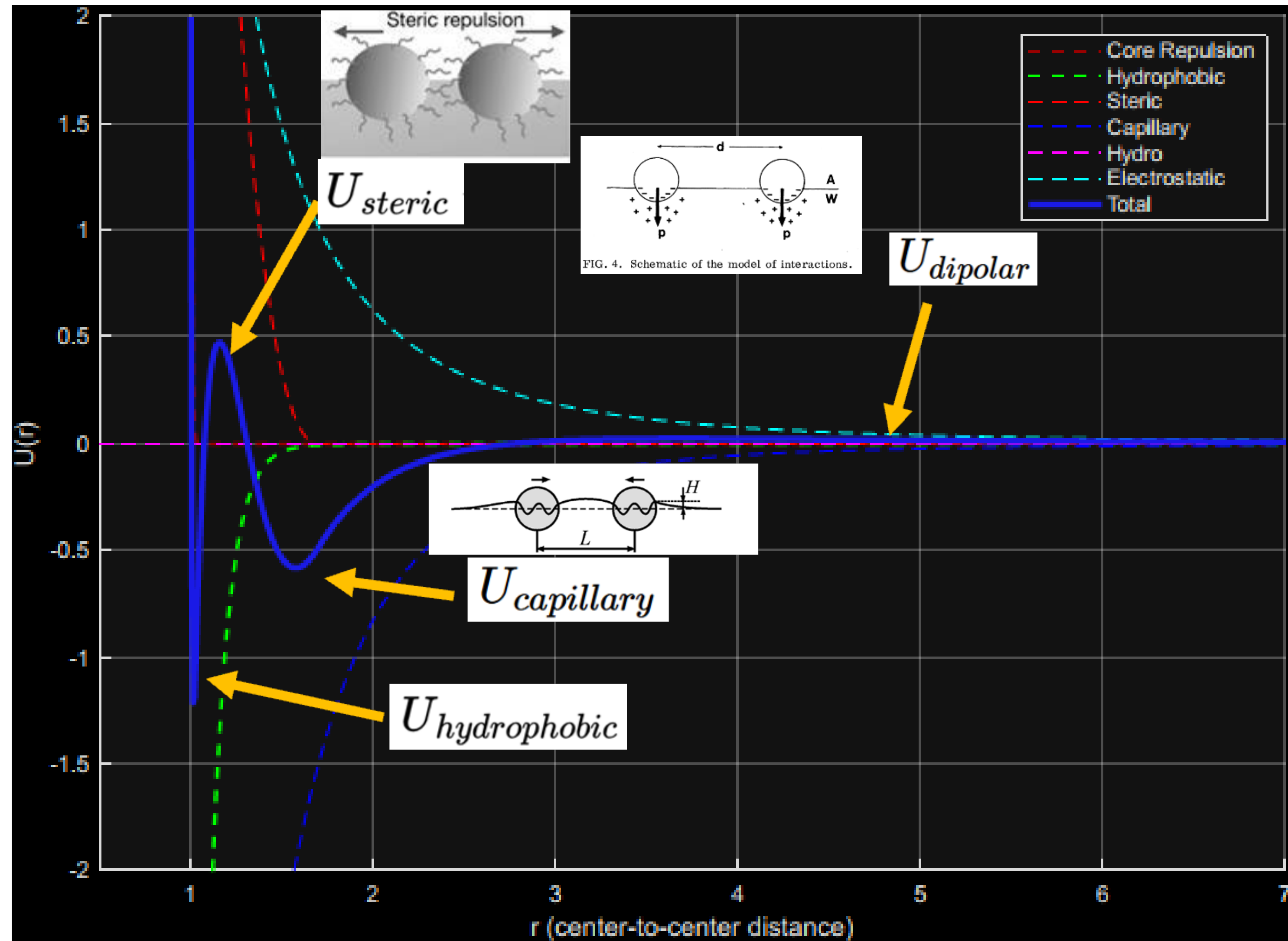
An additional dipolar contribution:

$$U_{electrostatic} = \frac{E}{r^3}$$

FIG. 4. Schematic of the model of interactions.

Visualising the inter-microgel potential

LAMMPS, NVT, Langevin Thermostat



Insights from MD Simulations

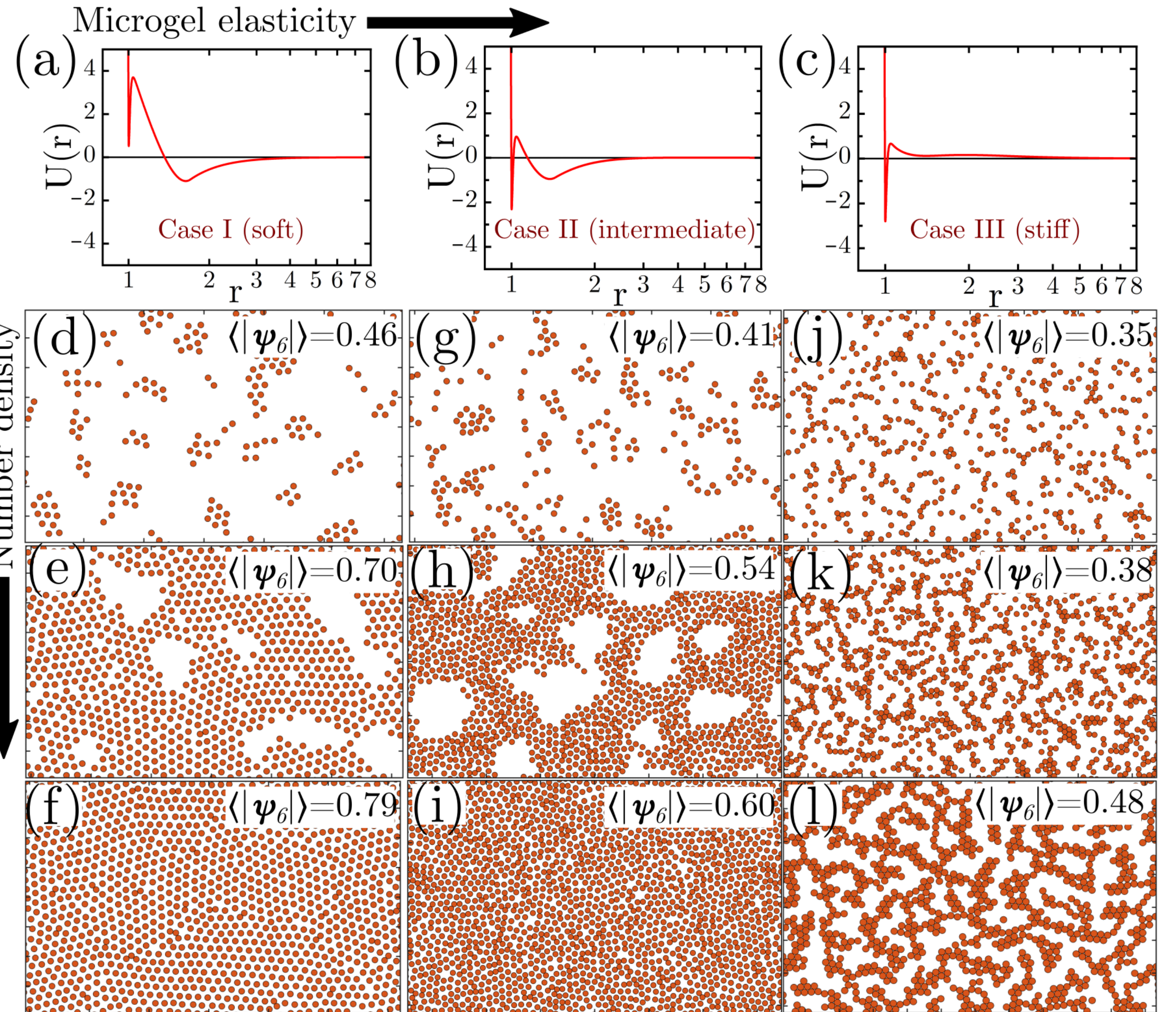
Soft microgels → more deformable,
larger corona → more effective steric
stabilization → trapped in secondary
minimum → form circular clusters,
foam, hexagonal structure.

Stiff microgels → less deformable,
harder cores → overcome steric barriers
→ fall into primary minimum
→ aggregate and gel-like structures.

Intermediate stiffness
→ Both minima are present
→ Frustrated phase between order
and disorder
→ glassy dynamics

Table 1: Simulation parameters for different microgel types.

Case (Microgel Type)	Corona thickness d	Dipolar strength p
I (Soft)	0.35	0.2
II (Intermediate)	0.22	3.0
III (Stiff)	0.05	6.0



$$\sigma_c = 1.0, W_c = 8, \lambda_c = 0.01, B = 10, S = 19$$

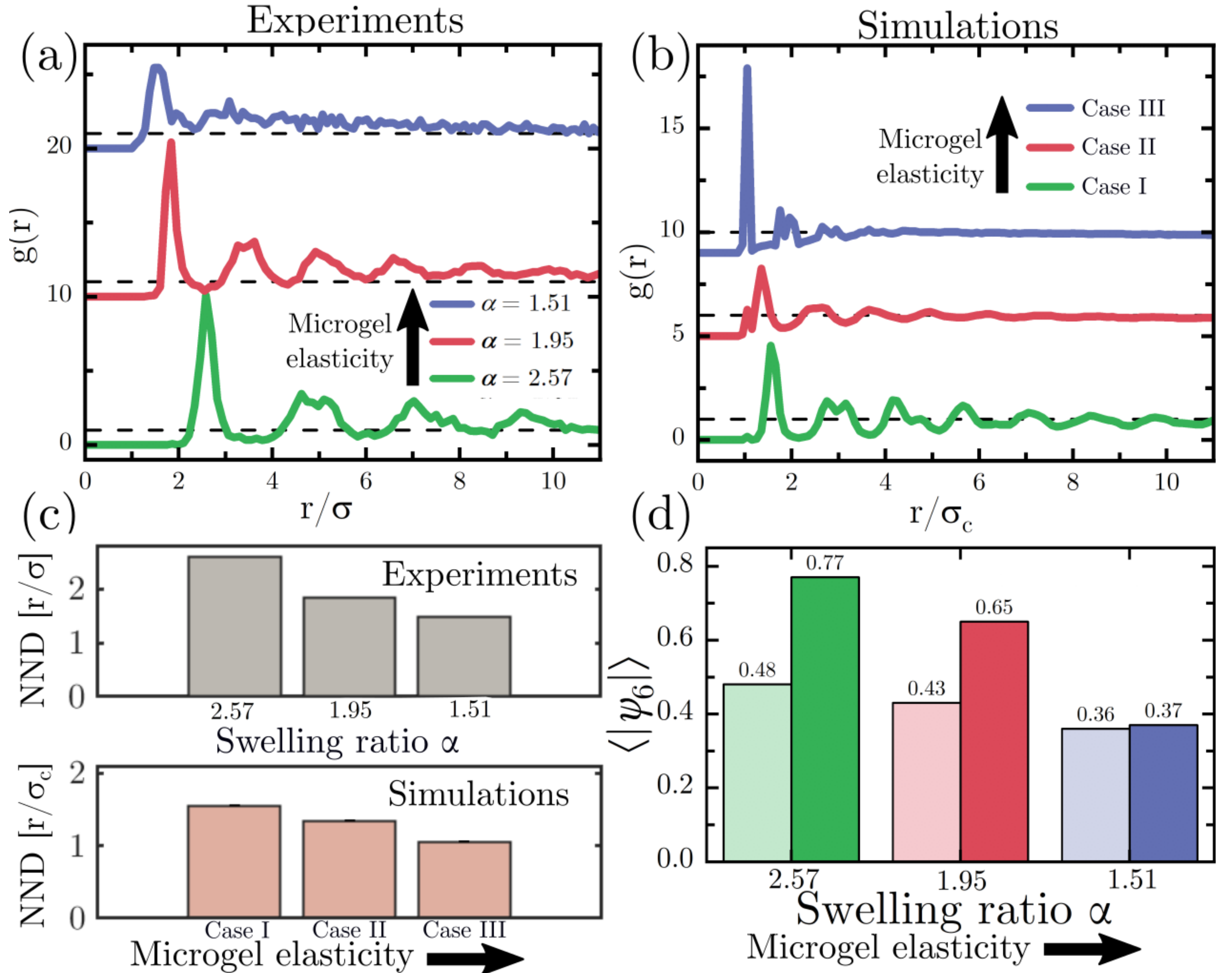
Data analysis

Global bond orientation order parameter:

$$\langle |\psi_{6,j}| \rangle = \left\langle \left| \frac{1}{N_j} \sum_{k=1}^{N_j} e^{i6\theta_{jk}} \right| \right\rangle_j$$

Radial distribution function:

$$g(r) = \frac{A}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(r - |\mathbf{r}_i - \mathbf{r}_j|) \right\rangle$$

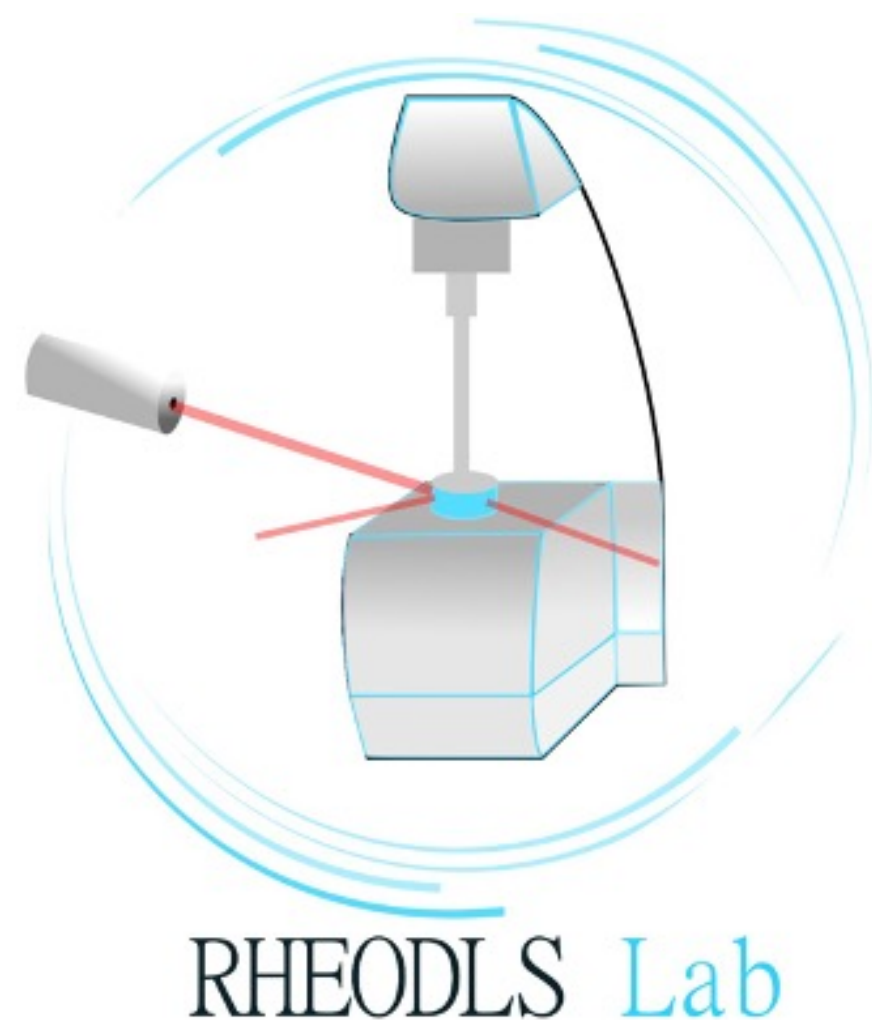


Conclusions

Microgel morphologies at air-water interface very sensitive to particle stiffness

MD simulations with minimal effective double-well potential capture all morphologies

Reentrant ordering with an intervening glassy phase (**glass physics in mono disperse systems**)



Thank you for your attention!