Dissipative dynamics simulations of star polymer microdroplets

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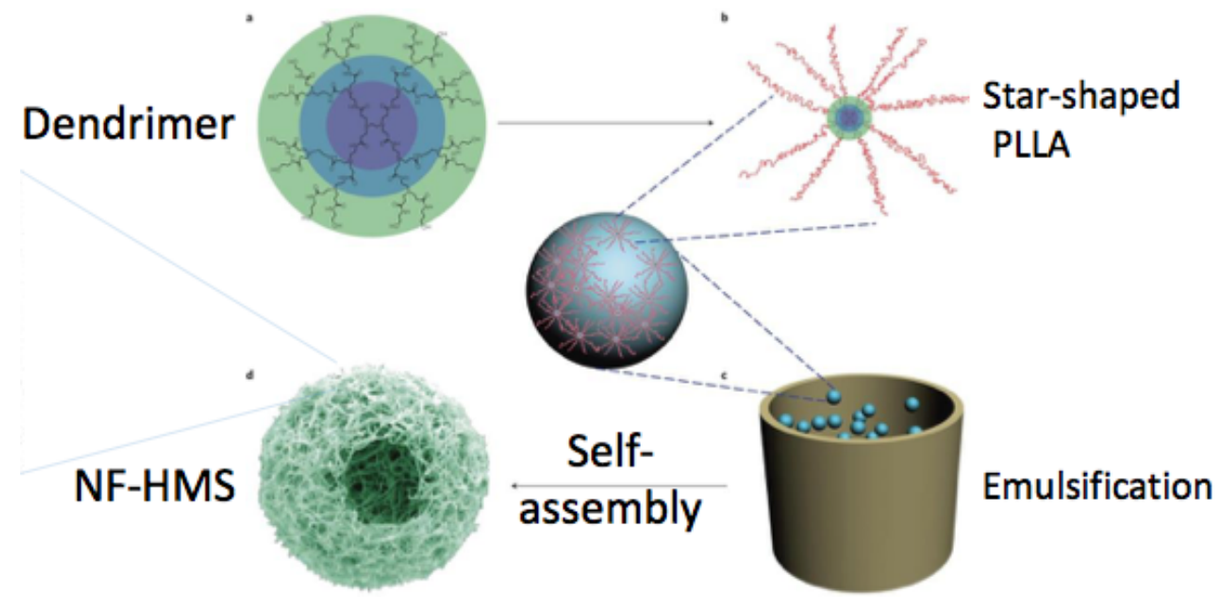
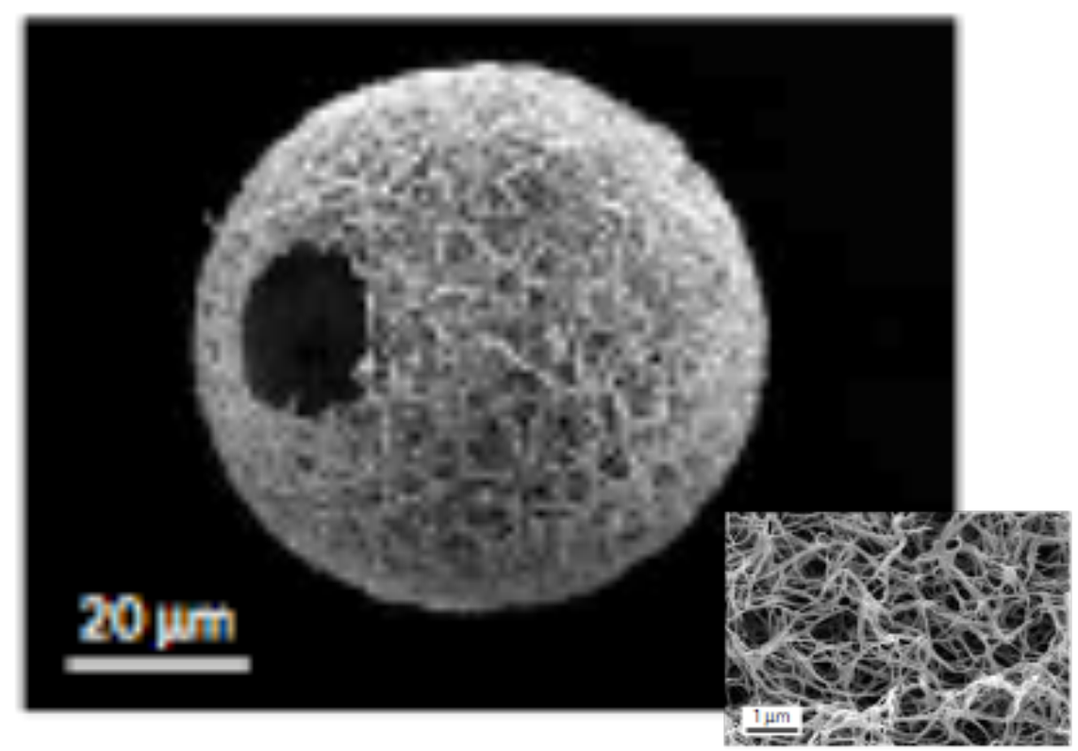
Intro — Hollow microspheres for tissue regeneration

- Droplet morphology convenient for implanting in tissue.
- Initial structure formation was poorly understood. Mechanism for pore formation.
- Combined experimental/ computational study to elucidate formation mechanisms.





Ma et al., *Nature Materials* (2012)

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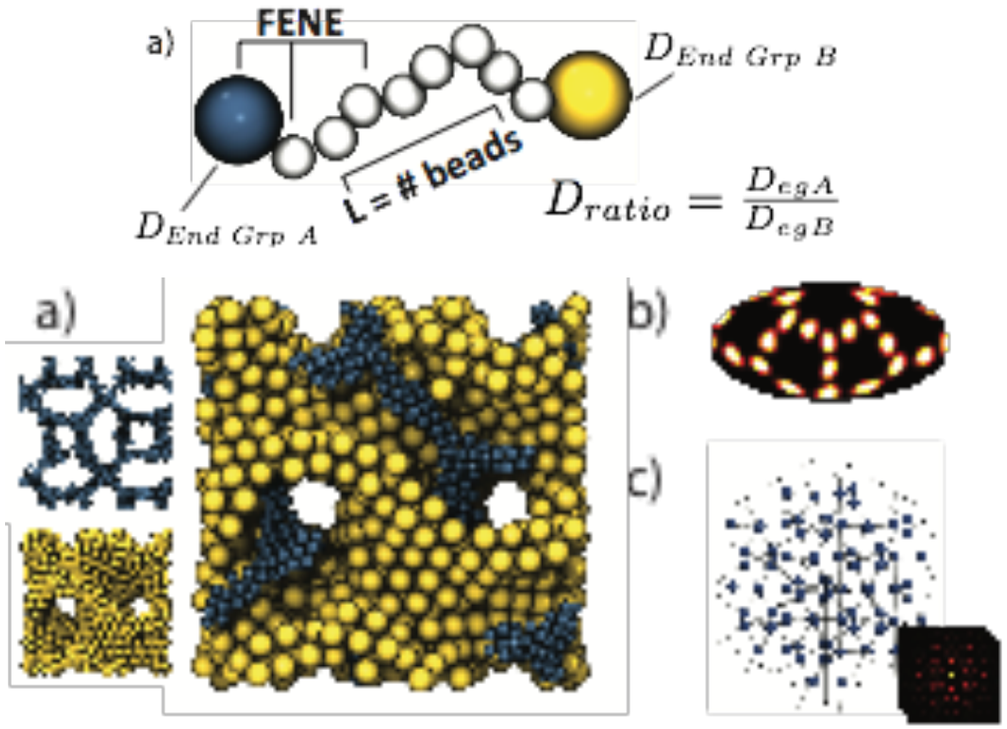
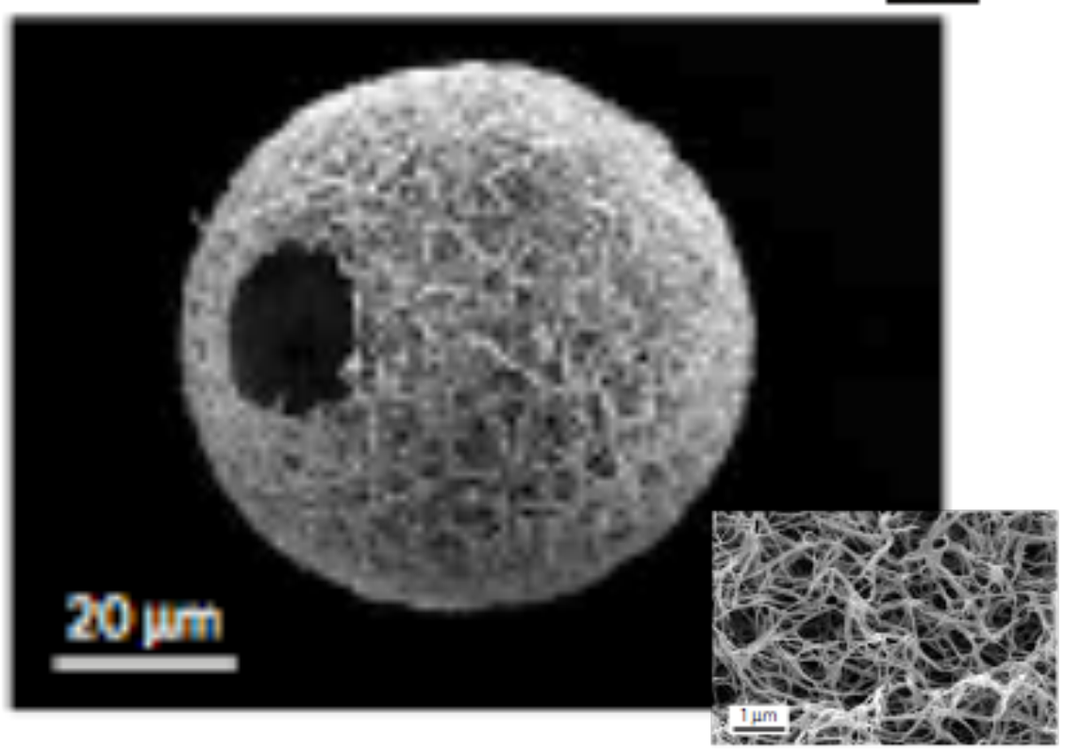
Marson et al., *Nano Letters* (2014)





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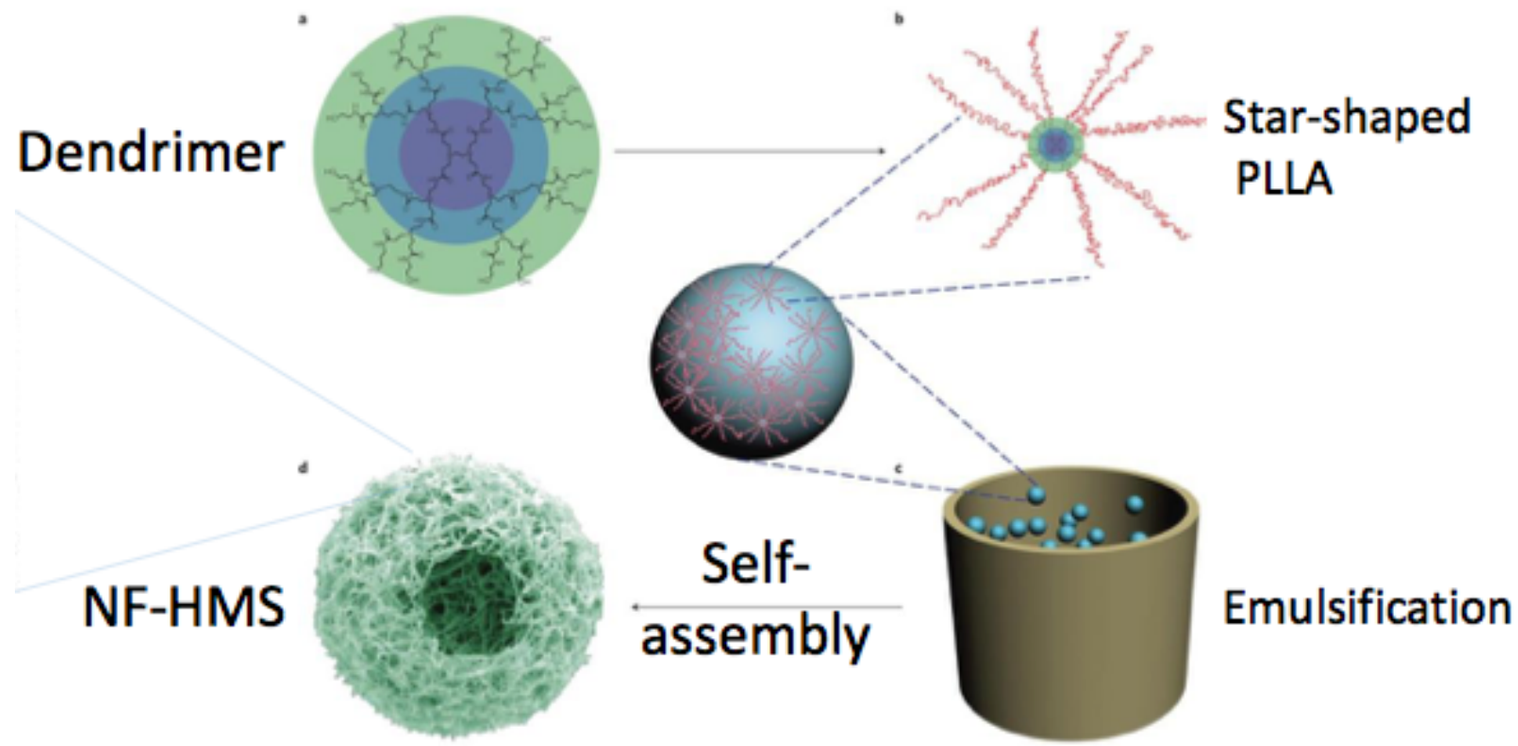
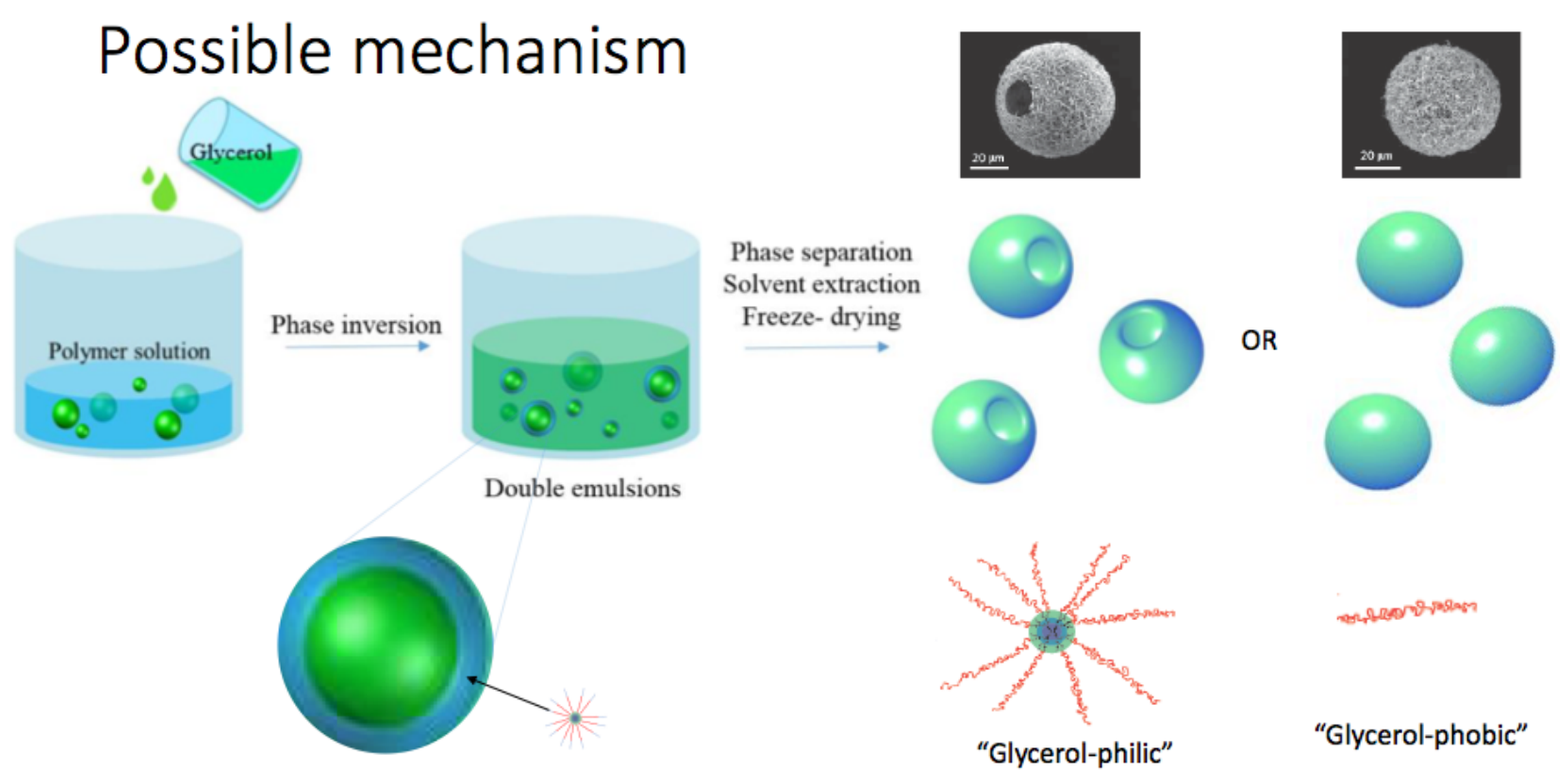
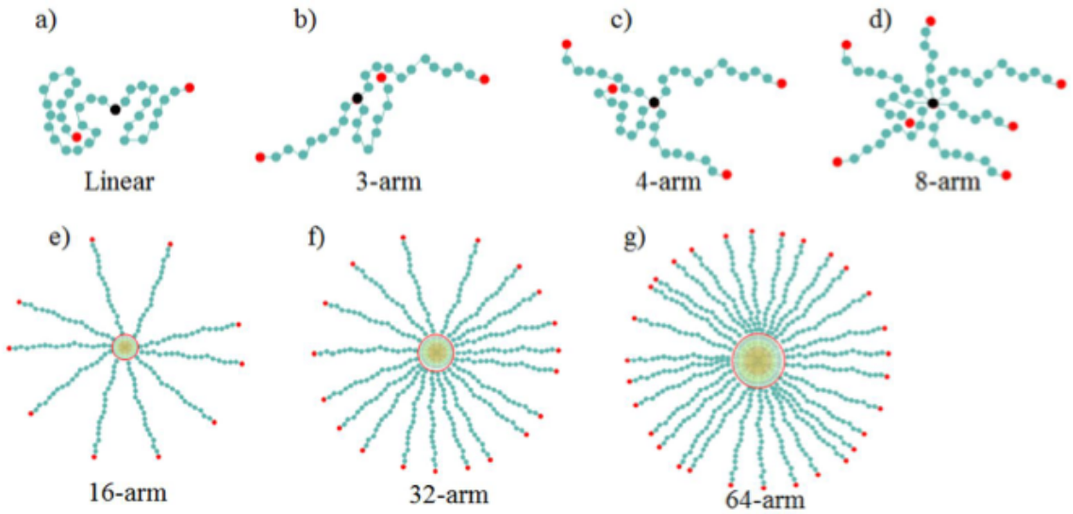
Experiments - Star polymer double emulsion

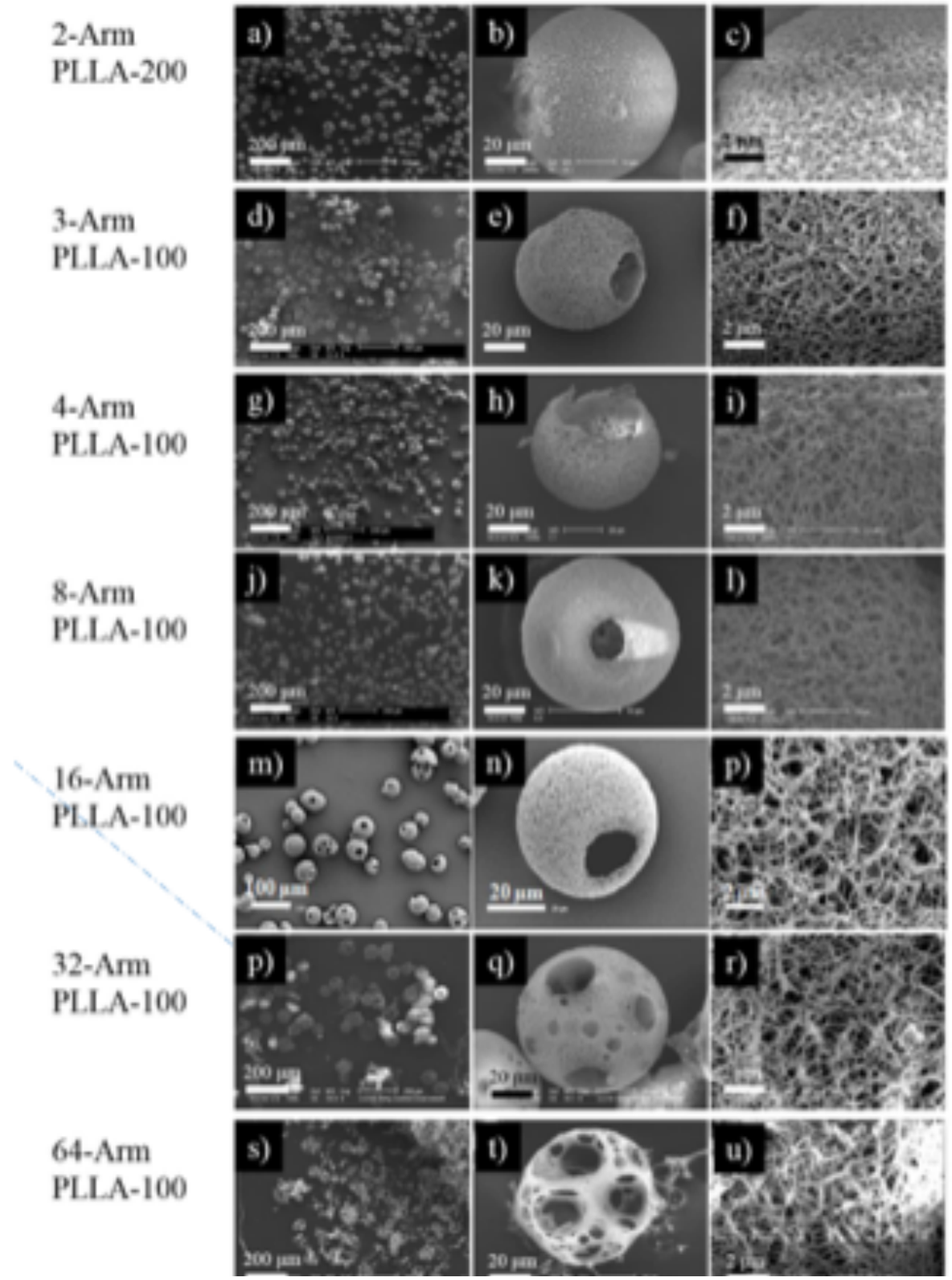
- PLLA star polymer
- Double emulsion leads to a confined assembly at droplet surface
- Immiscible components





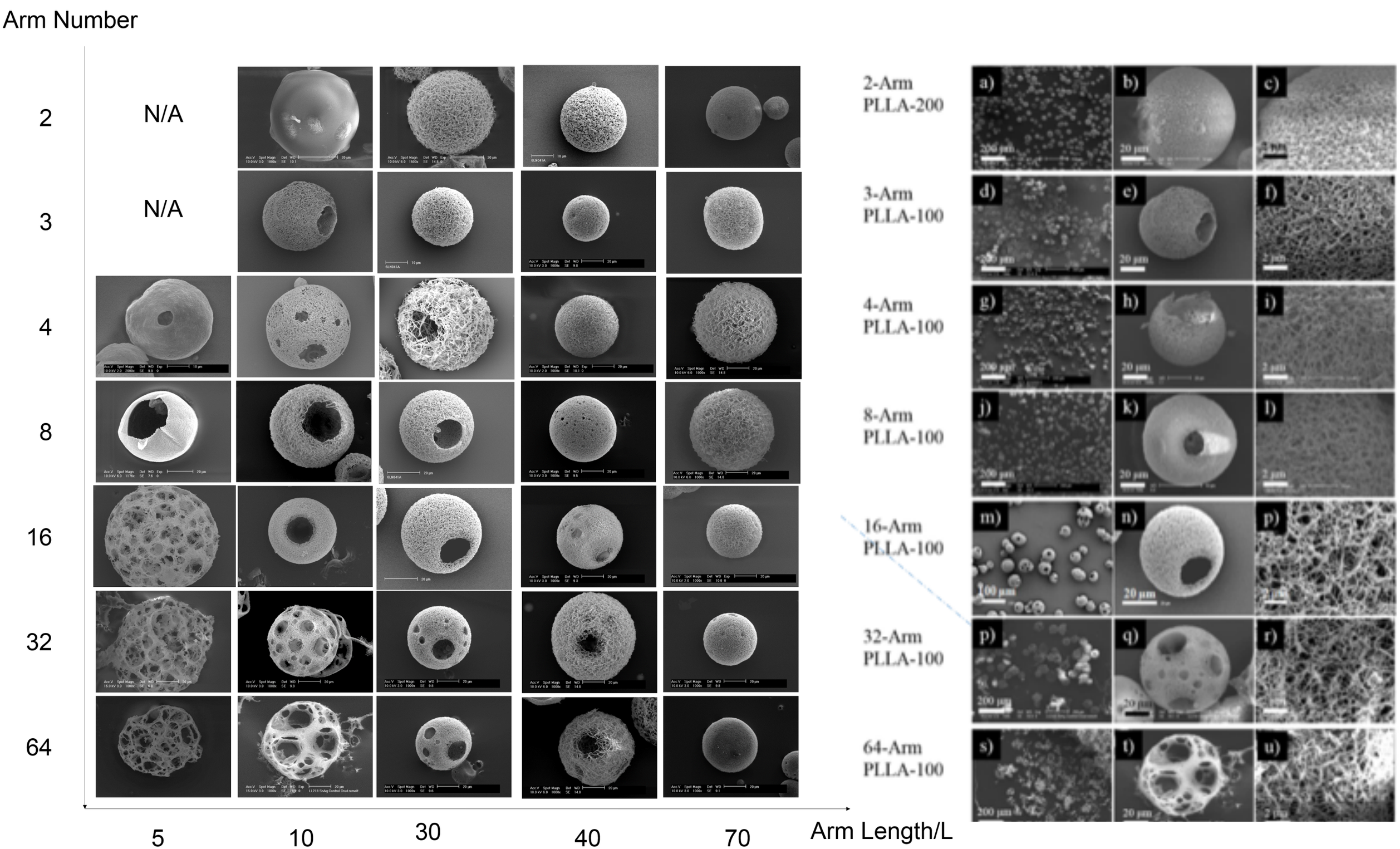
Droplet morphologies - Affect of building blok





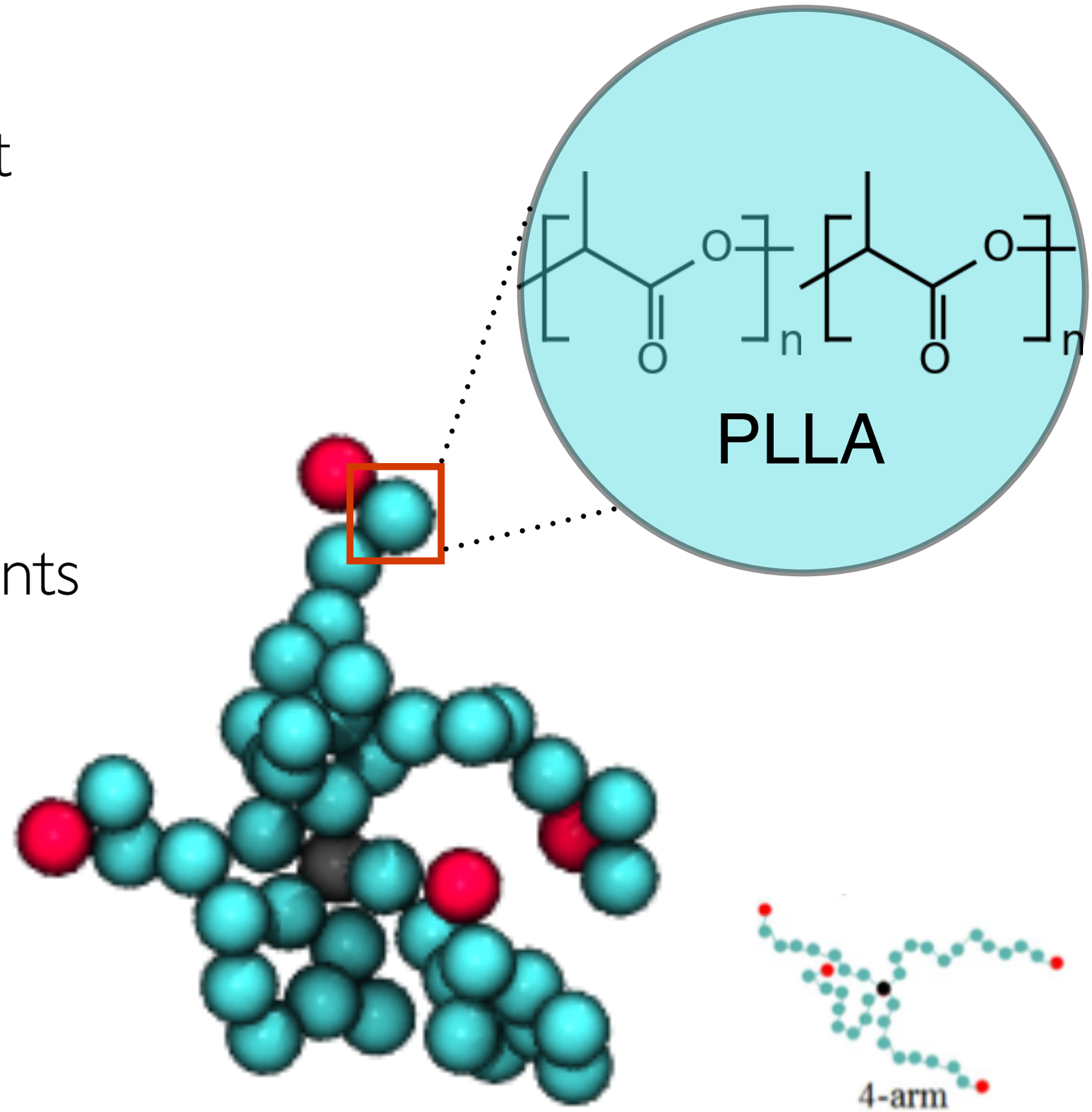
- Varying arm number and length affect the assemblies
- Short arms favor the formation of hollow, porous structures.
- Hydroxyl density plays a very important role

Parameter space

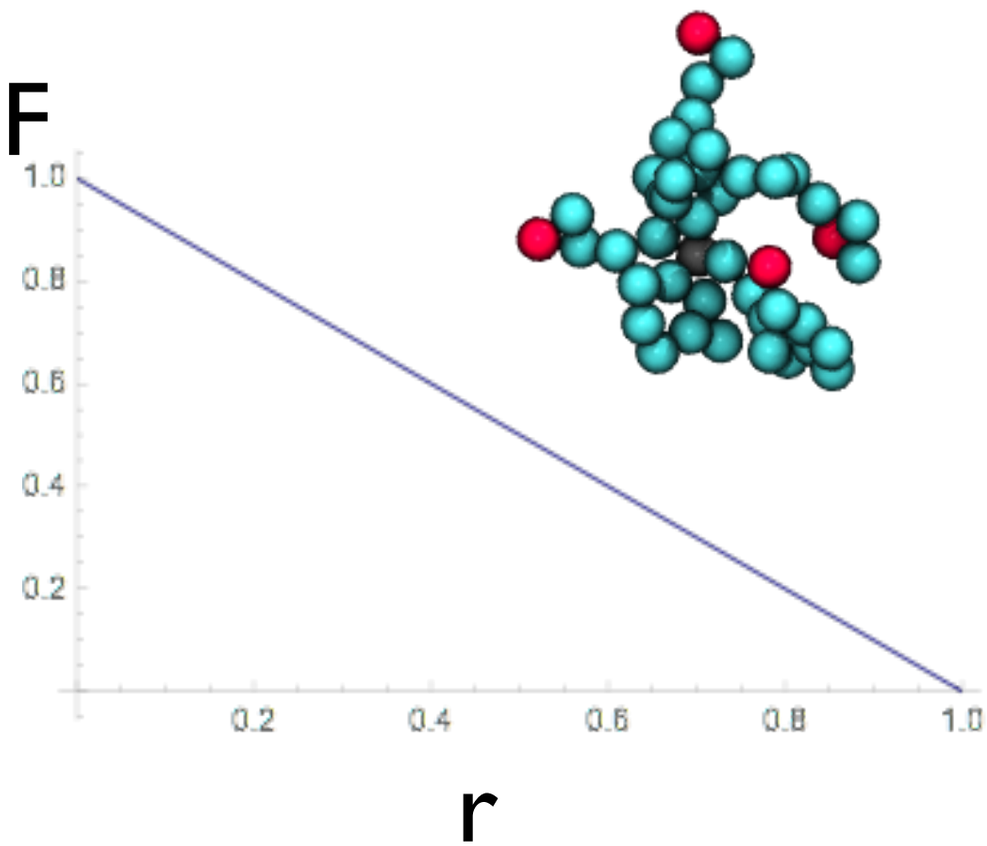


Model - Coarse graining

- Hydroxyl groups are **glycerophilic** - want to contact glycerol solution.
- Polymer is **glycerophobic** - wants to avoid glycerol.
- Central core with unreacted and/or exposed hydroxyl groups



Model - Dissipative Particle Dynamics - HOOMD



$$F = F_{\mathrm{C}}(r) + F_{\mathrm{R,ij}}(r_{ij}) + F_{\mathrm{D,ij}}(v_{ij})$$

Conservative, Random, and Dissipative forces

$$F_{\mathrm{C}}(r) = A \cdot w(r_{ij})$$

$$F_{\mathrm{R,ij}}(r_{ij}) = -\theta_{ij}\sqrt{3}\sqrt{\frac{2k_b\gamma T}{\Delta t}} \cdot w(r_{ij})$$

$$F_{\mathrm{D,ij}}(r_{ij}) = -\gamma w^2(r_{ij})\,(\hat{r}_{ij} \circ v_{ij})$$

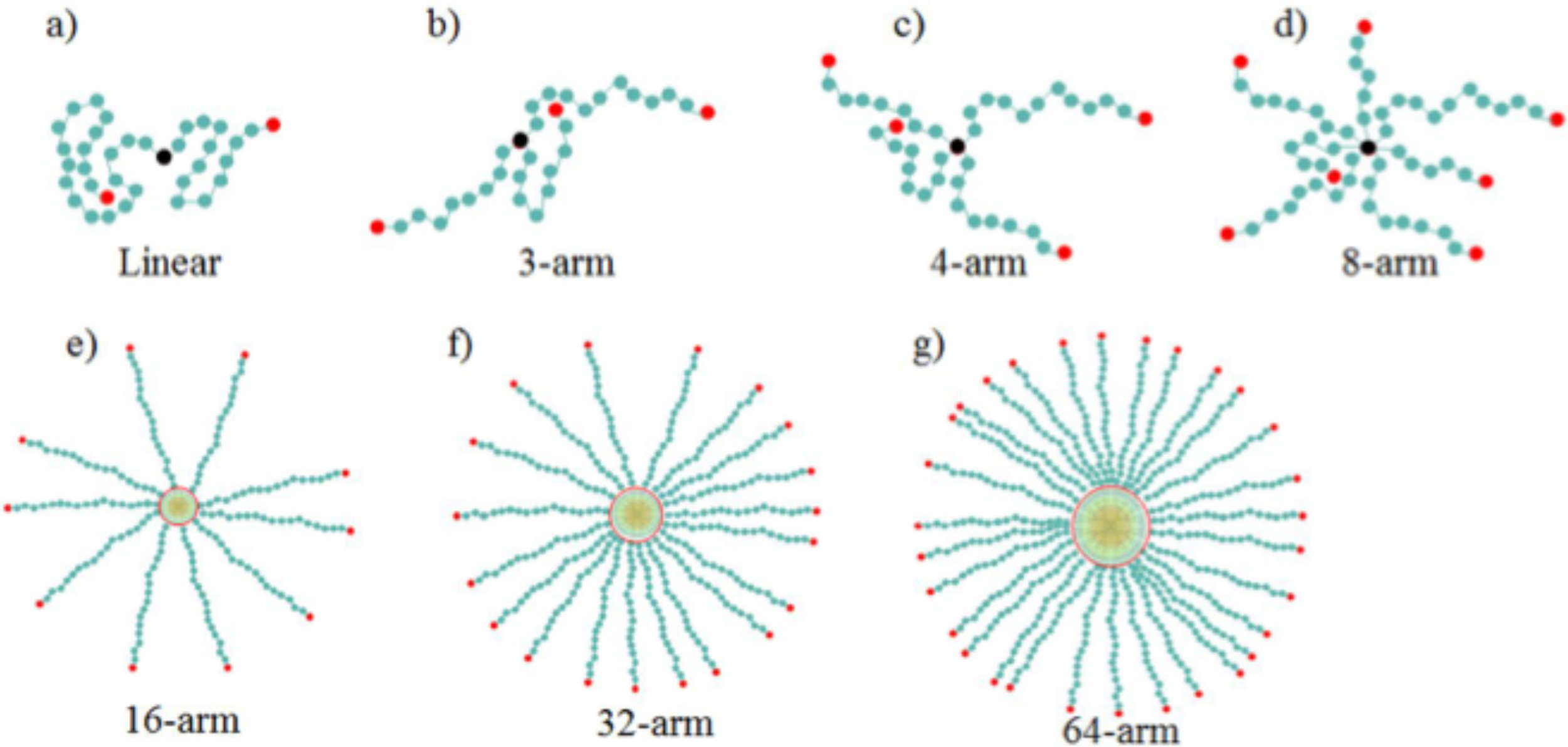
A_{SS}, A_{PP} = 20.0	(neutral)
A_{HP}, A_{SP} = 40.0	(dislikes)
A_{HH},A_{HS} = 10.0	(likes)

$$w(r_{ij}) = (1 - r/r_{\mathrm{cut}}) \quad r < r_{\mathrm{cut}}$$
$$= 0 \quad r \geq r_{\mathrm{cut}}$$

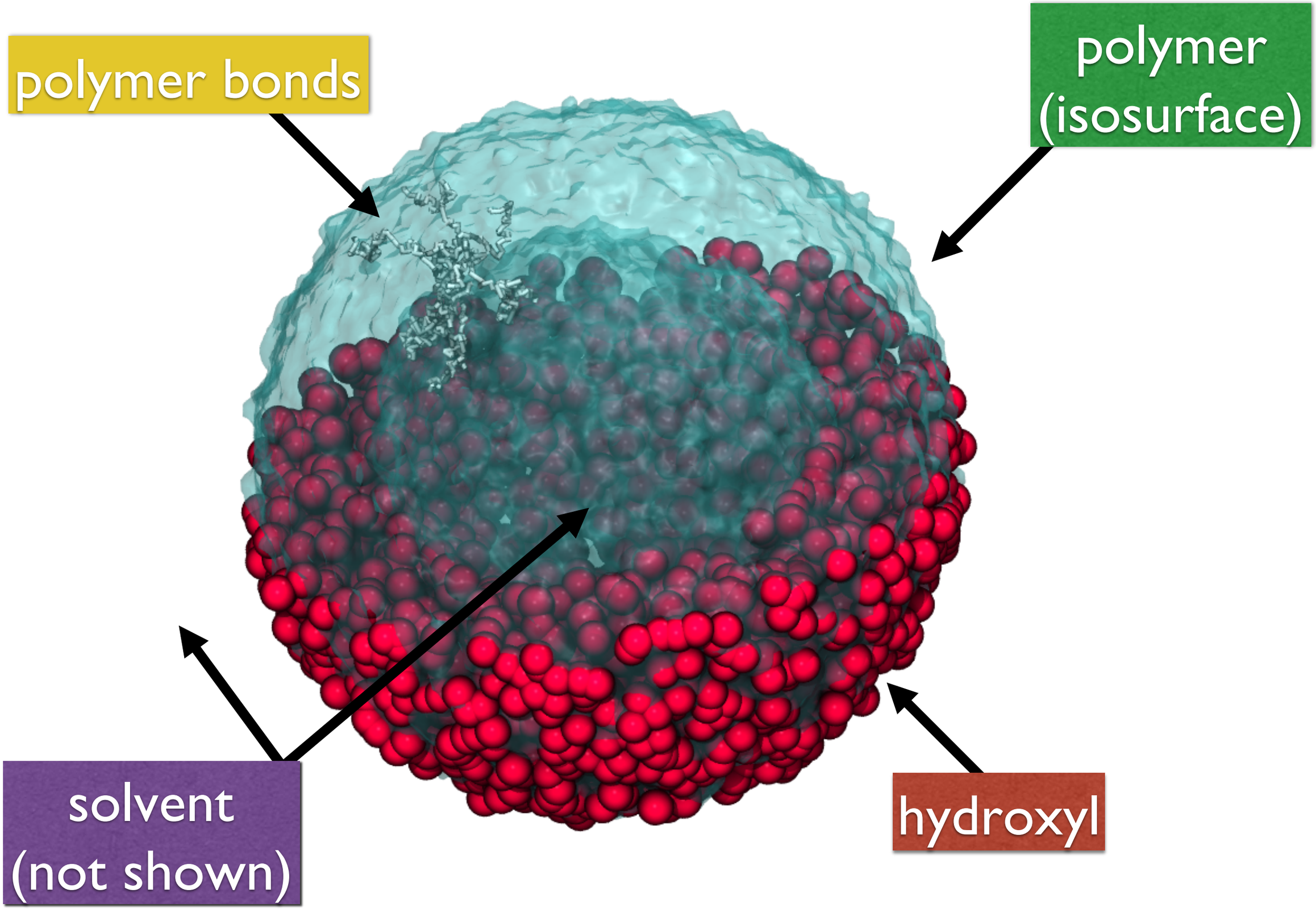
(1) AlSunaidi, a; Den Otter, W. K.; Clarke, J. H. R. Philosophical transactions. Series A, Mathematical, physical, and engineering sciences 2004, 362, 1773–1781.

(2) glotzerlab.engin.umich.edu/hoomd-blue

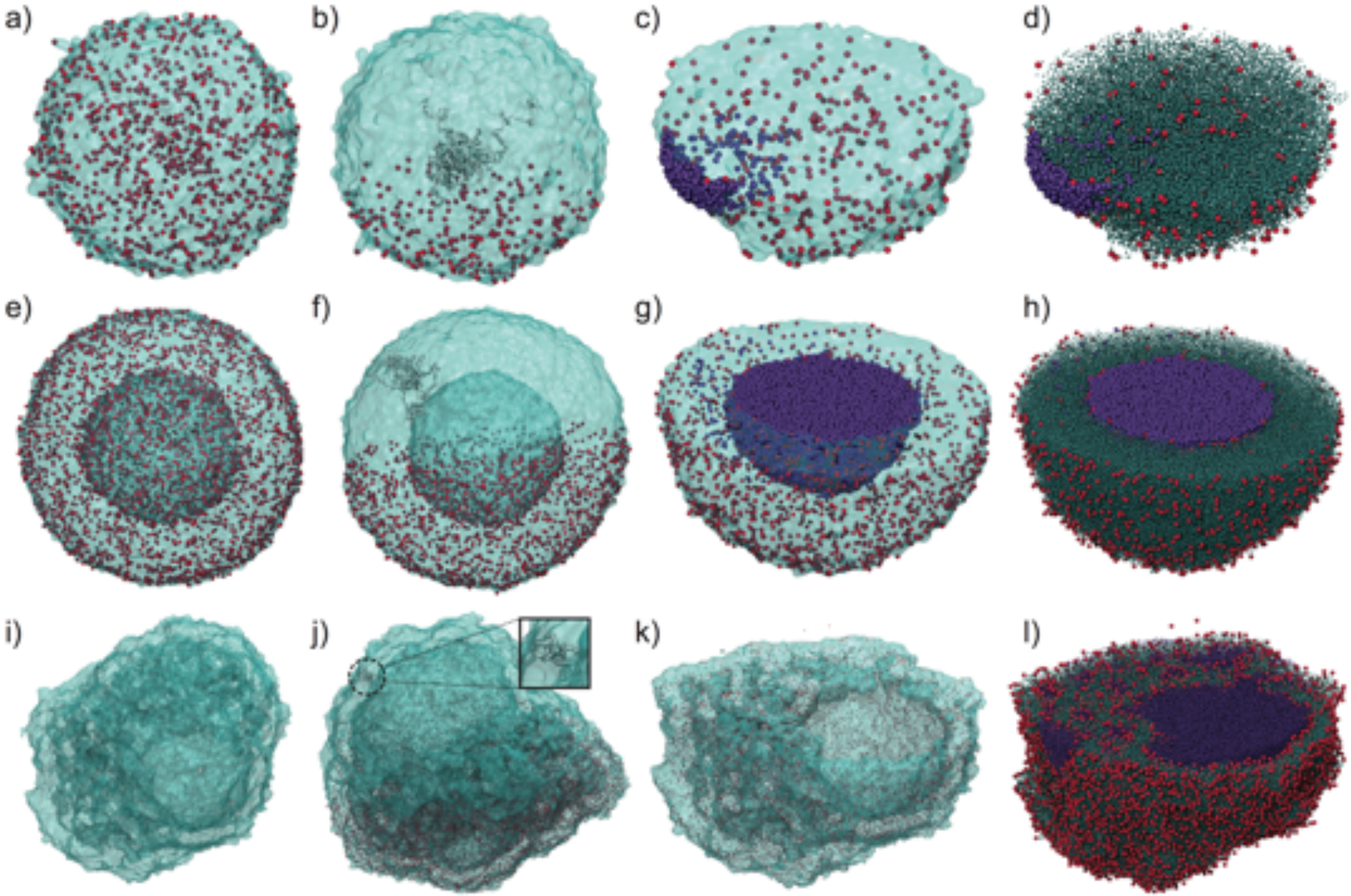
Model - Experimental arm numbers



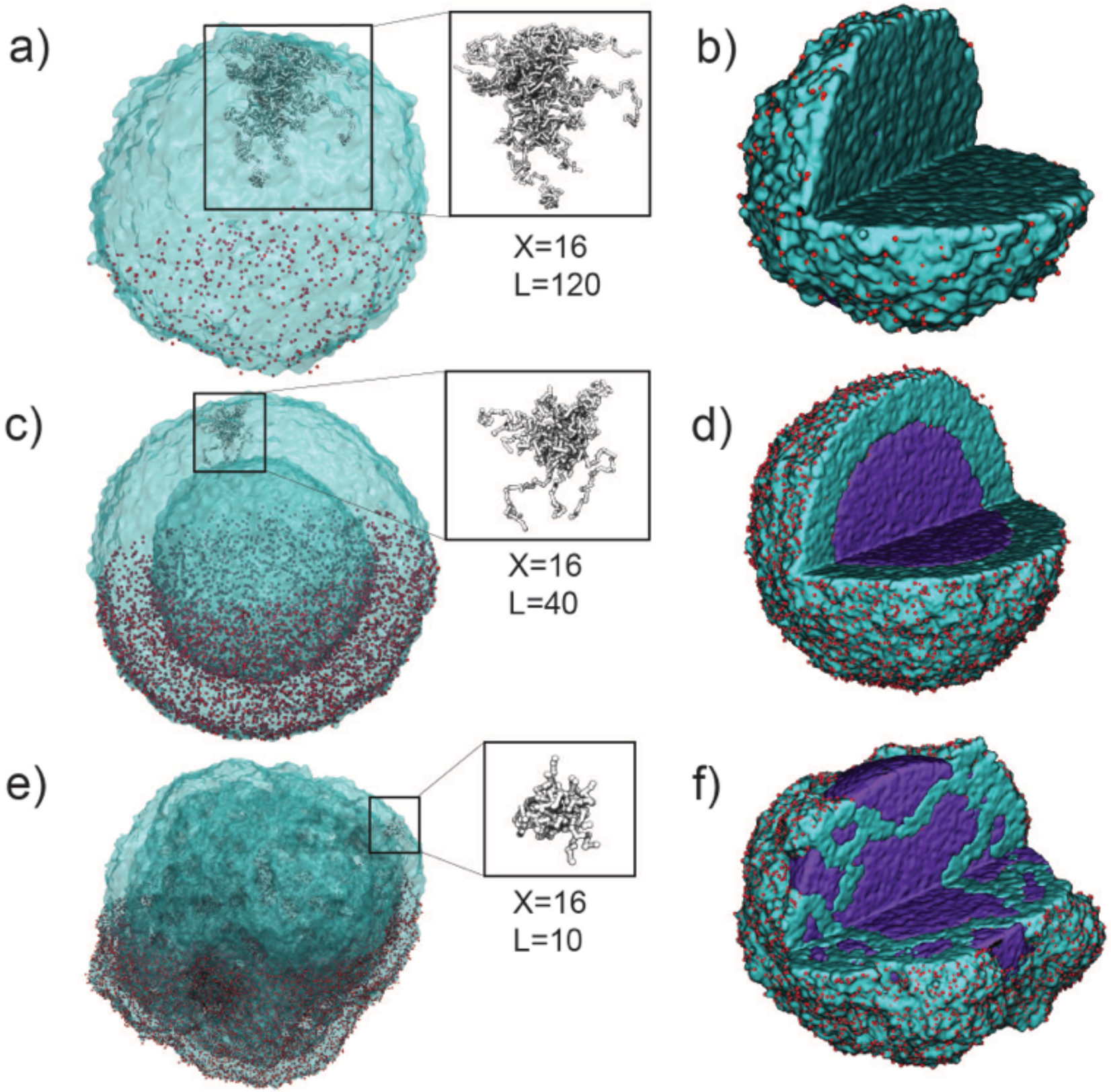
DPD - Constructed droplet assembly



Droplets - hollow, non-hollow, and porous (4 and 8 arm)



Droplets - Transitions based on arm length (16 arm)

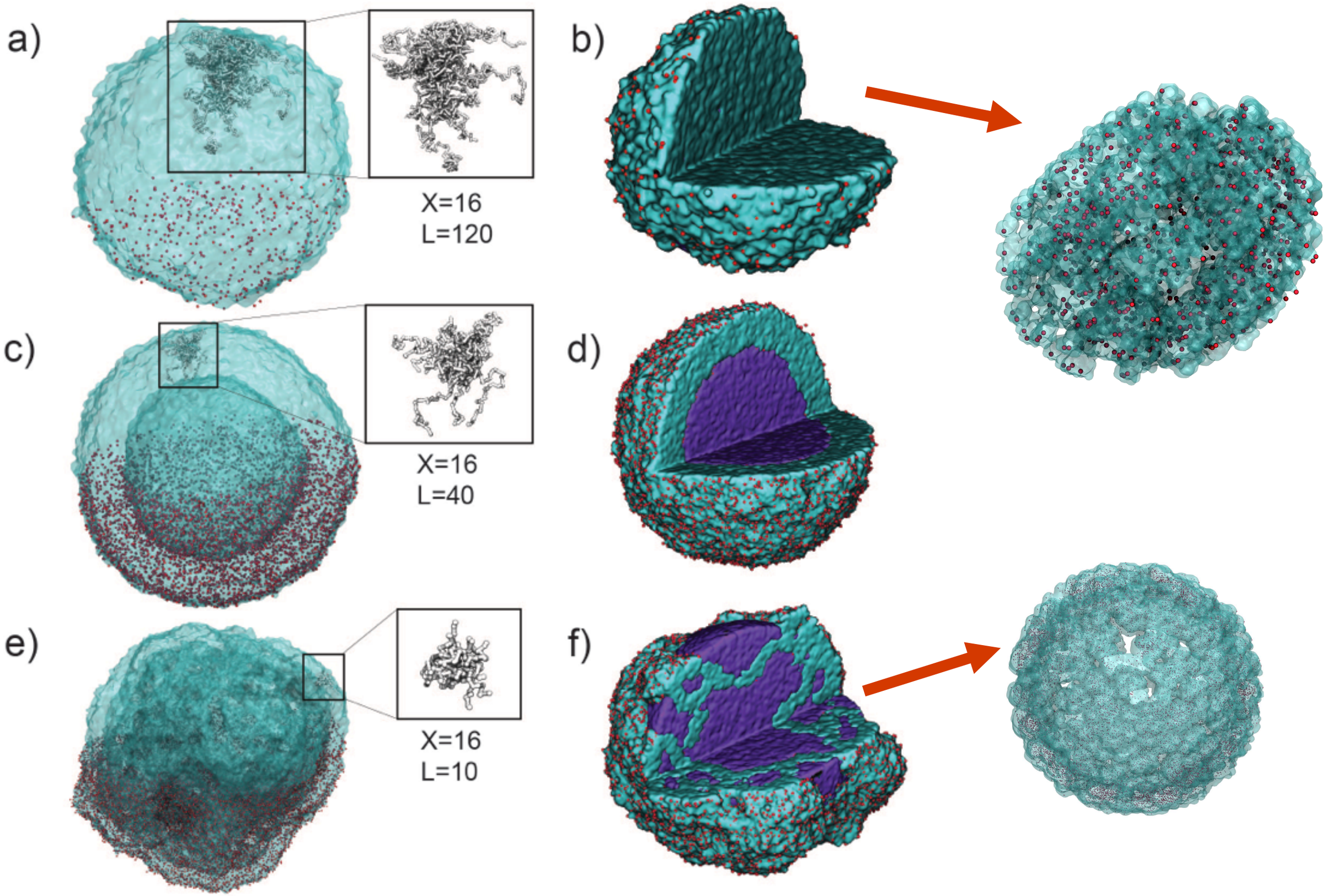


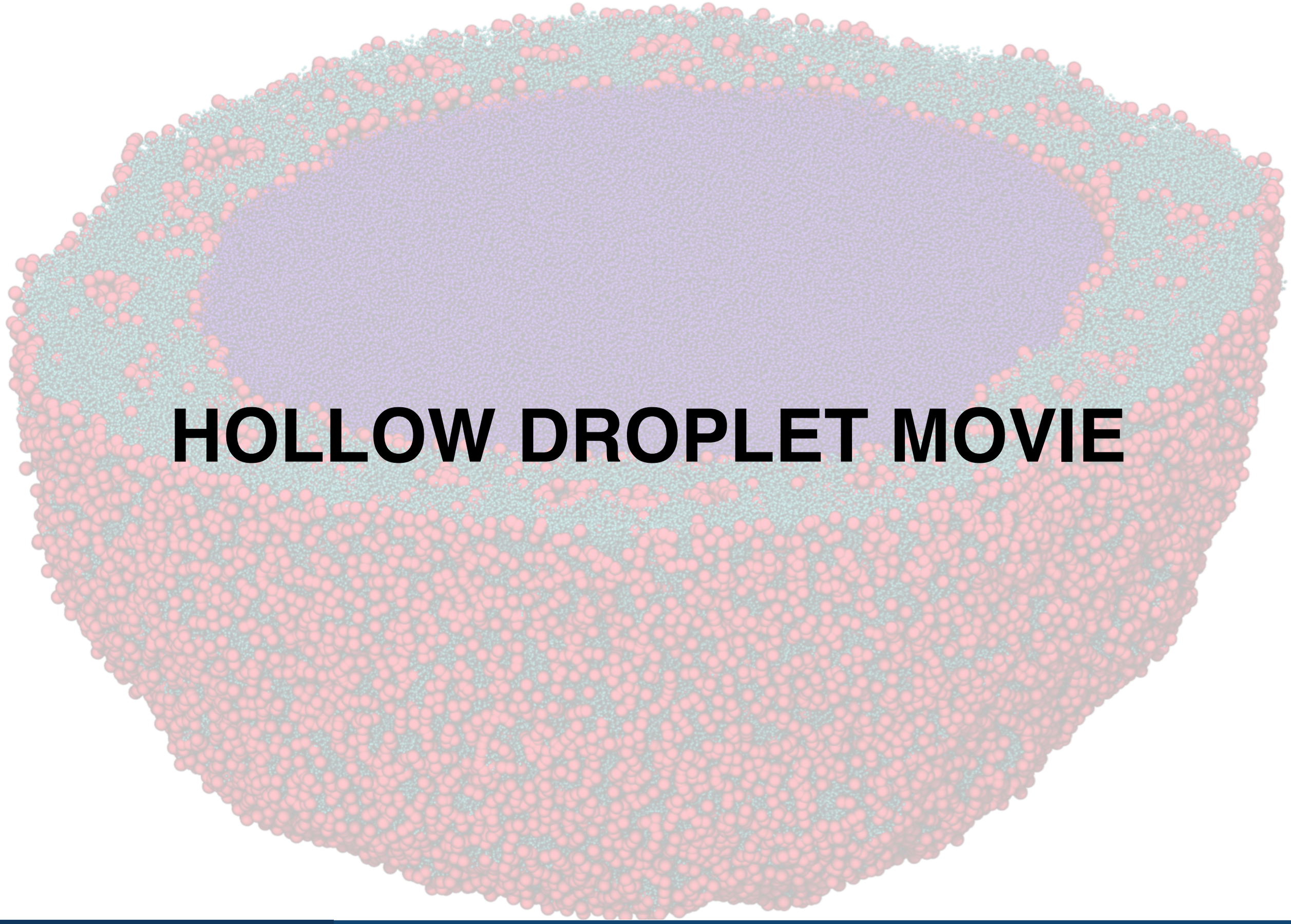
Examples from a 16-arm star poly.

As arm length decreases, hydroxyl density increases.

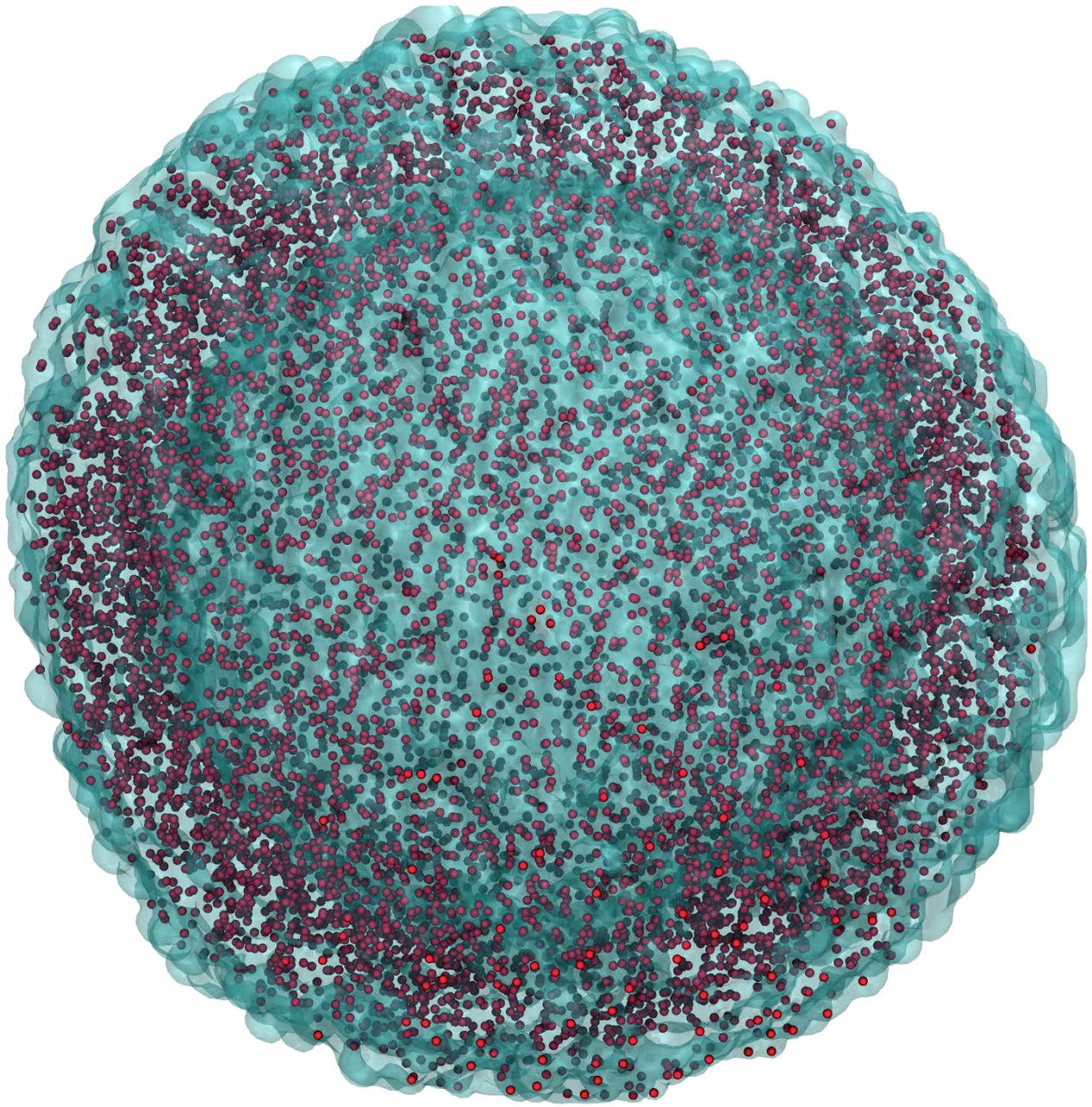
Eventually, the hydroxyl density is high enough to stabilize the interface.

Droplets - 50 million DPD timesteps



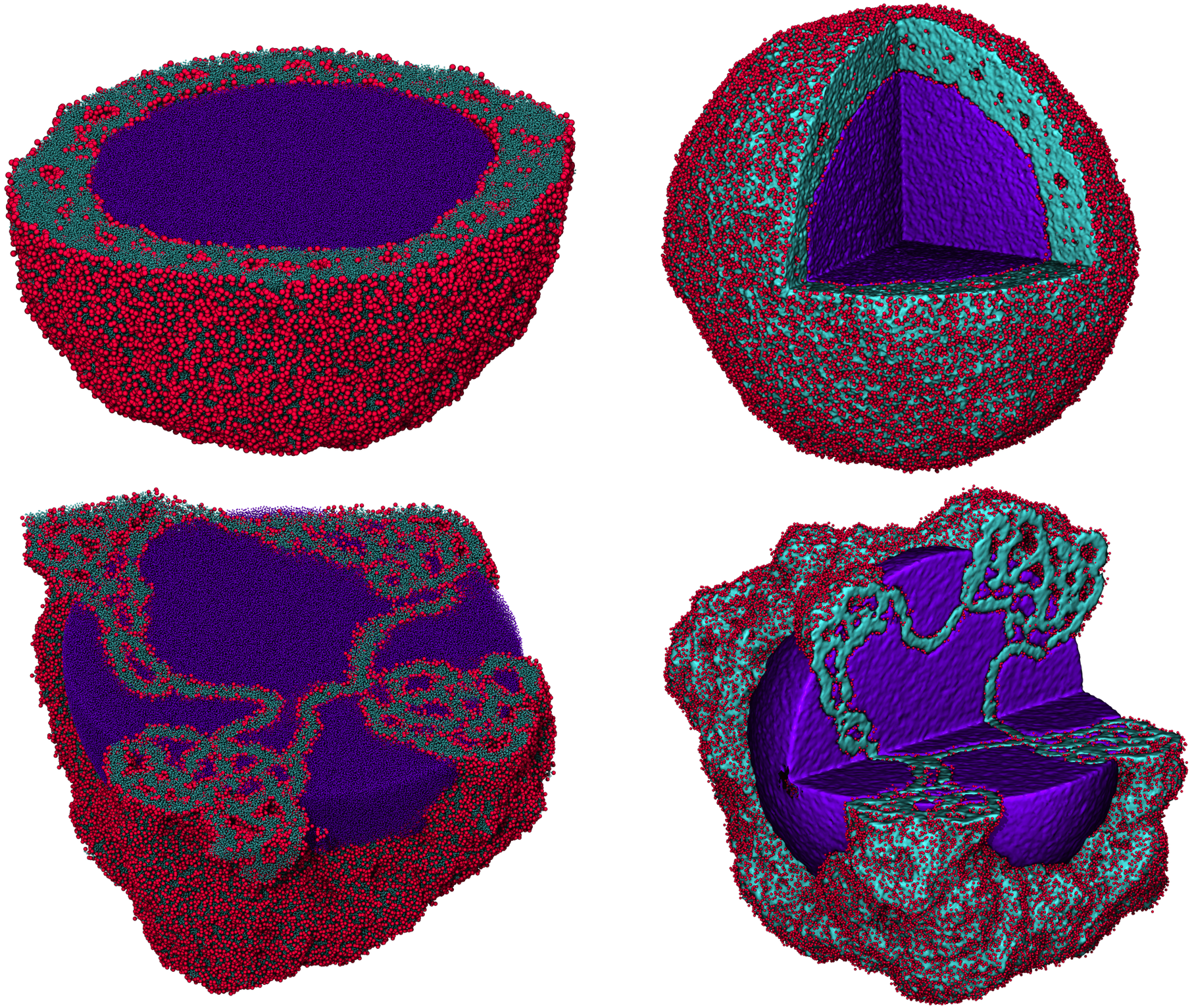


HOLLOW DROPLET MOVIE

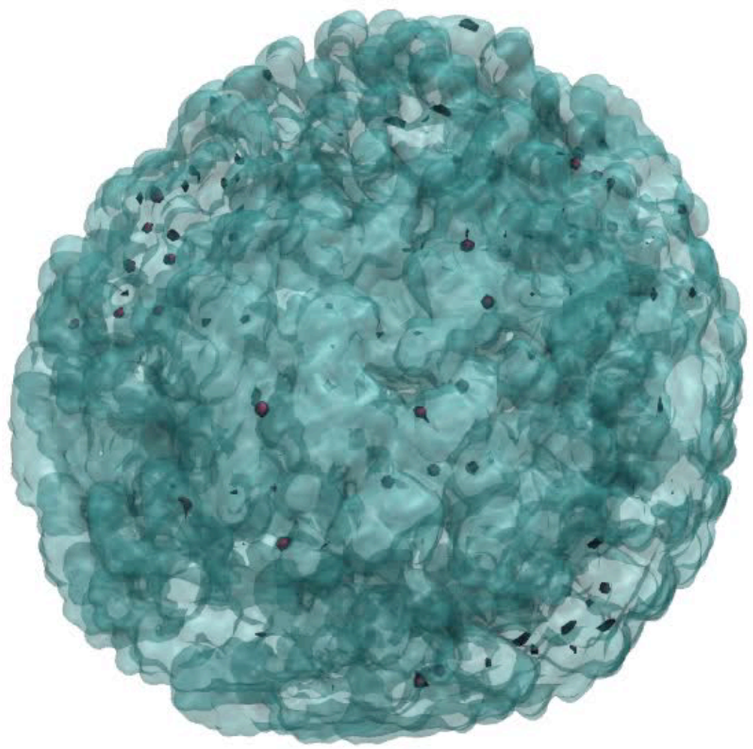


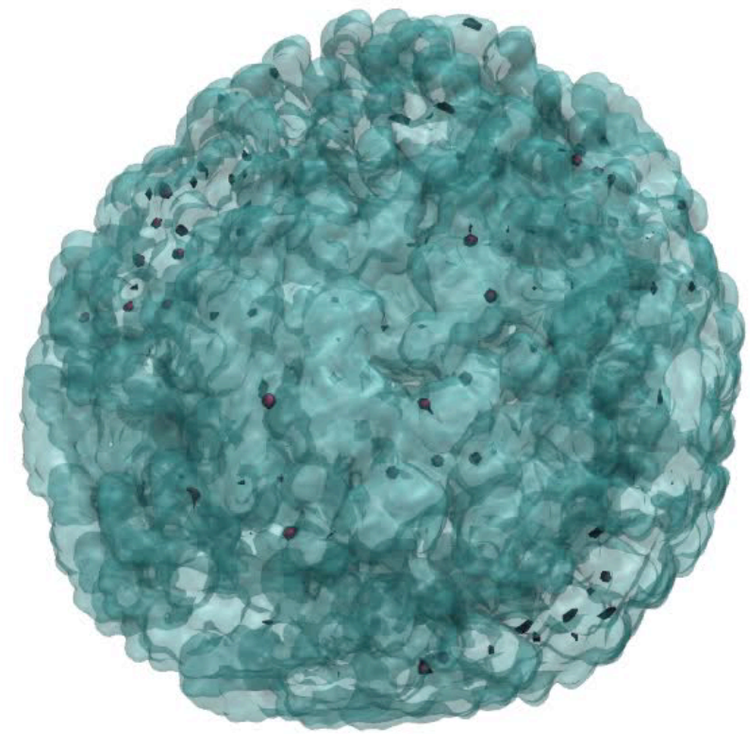
11 million+ particle simulations

- 128 GPUs



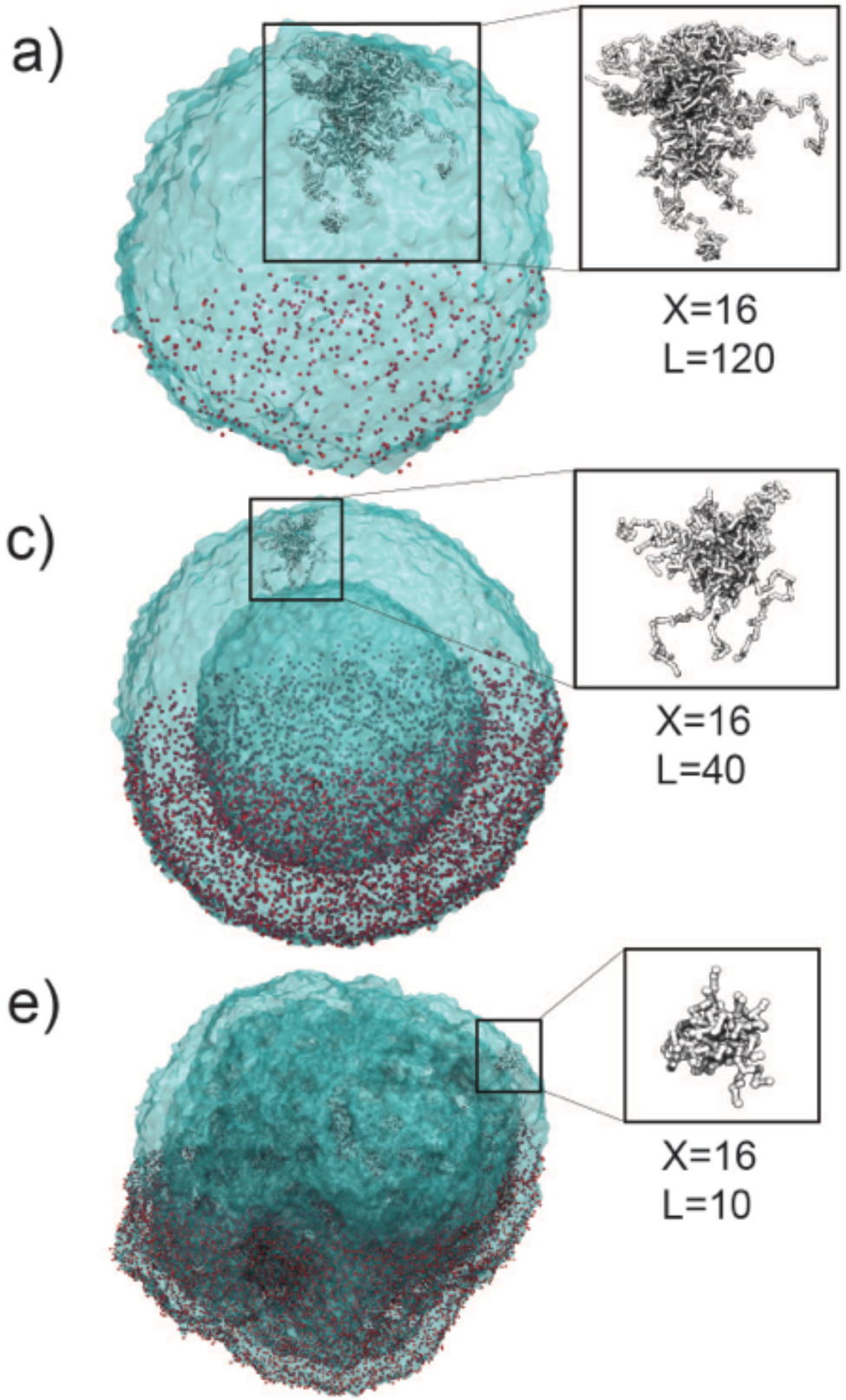
Hydroxyl Hypothesis - Final Conformation

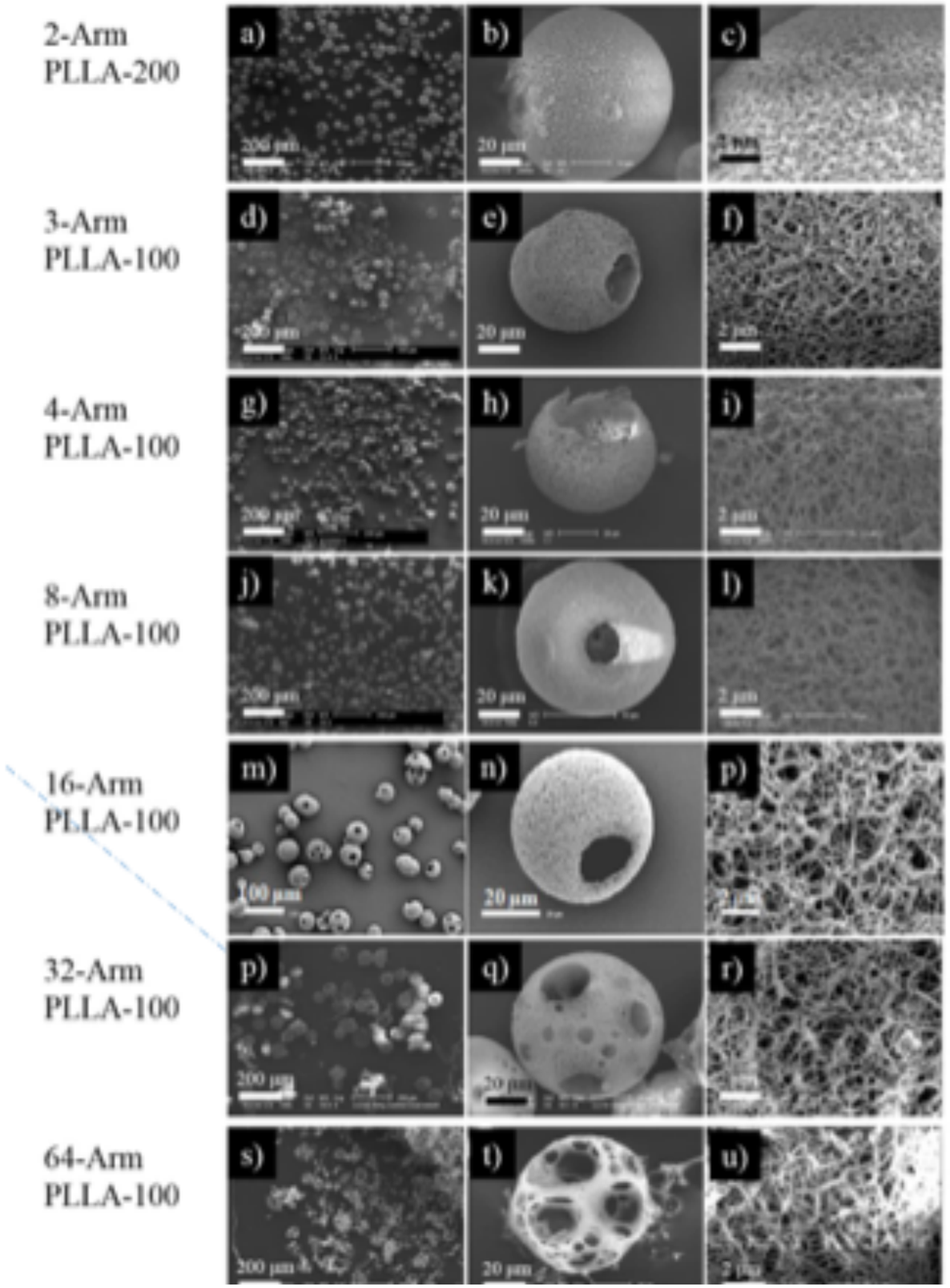




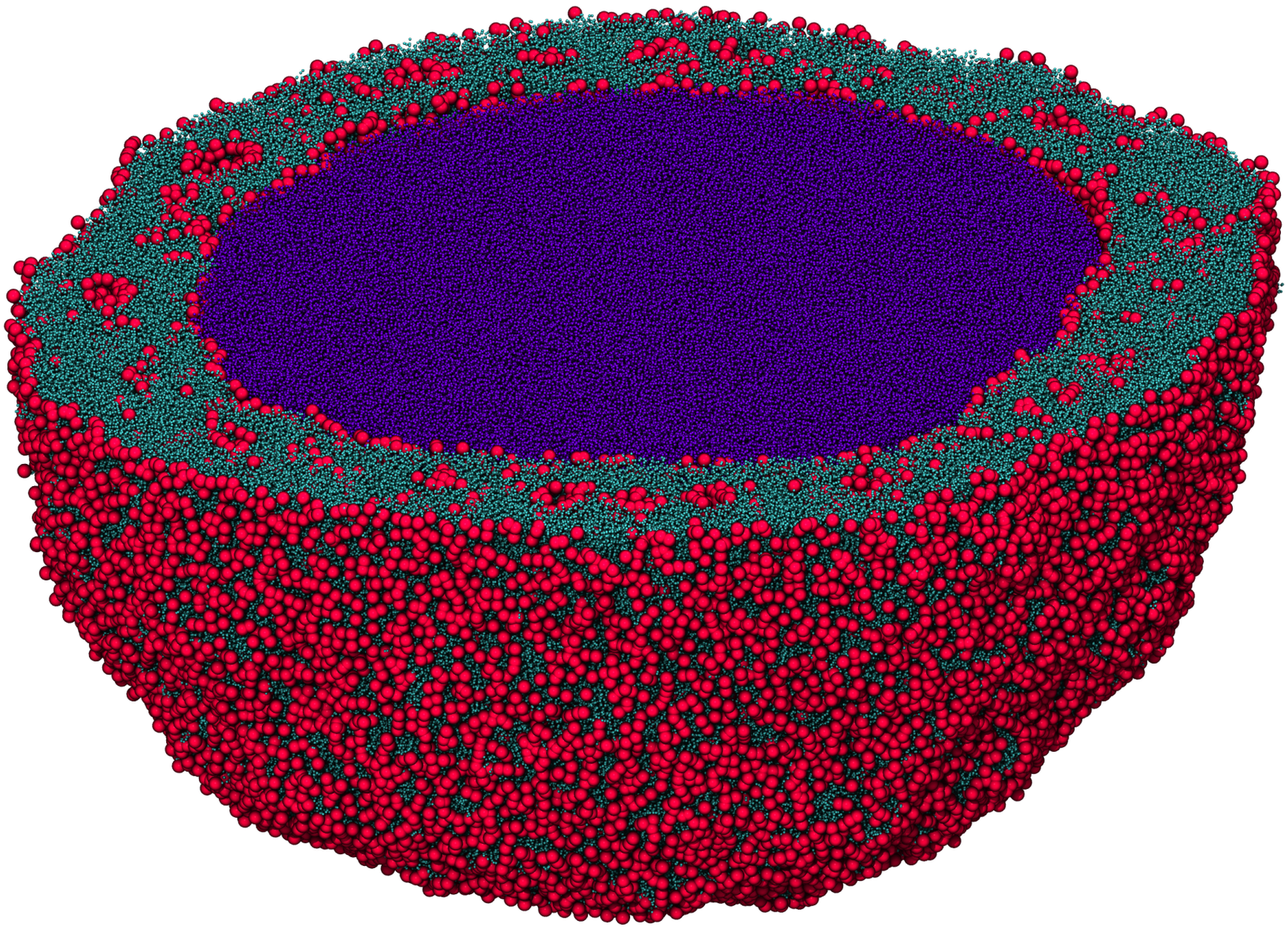
- Doubling Hydroxyl repulsion stabilizes hollow structure

Parameter space - trends corroborate experiments

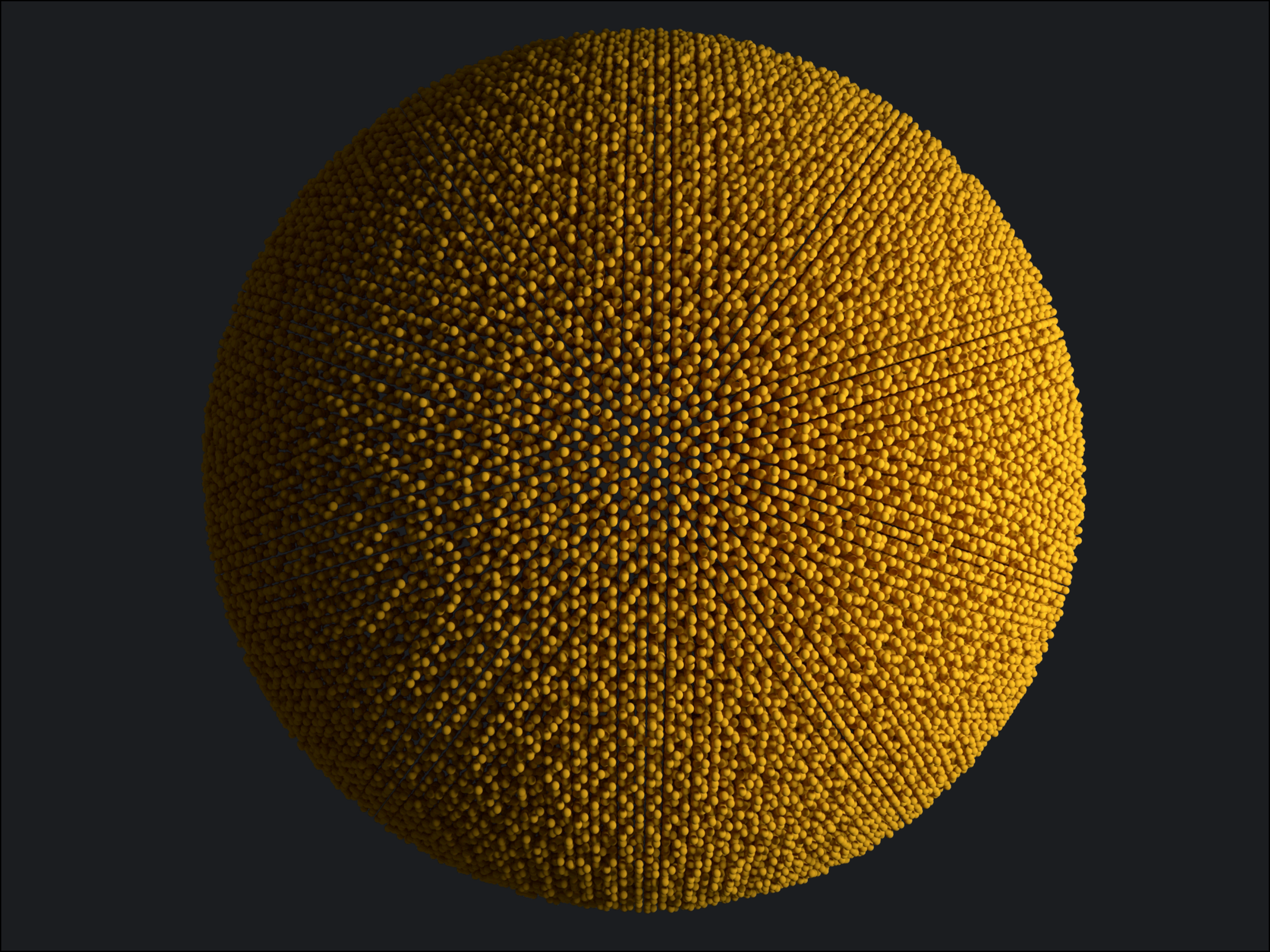


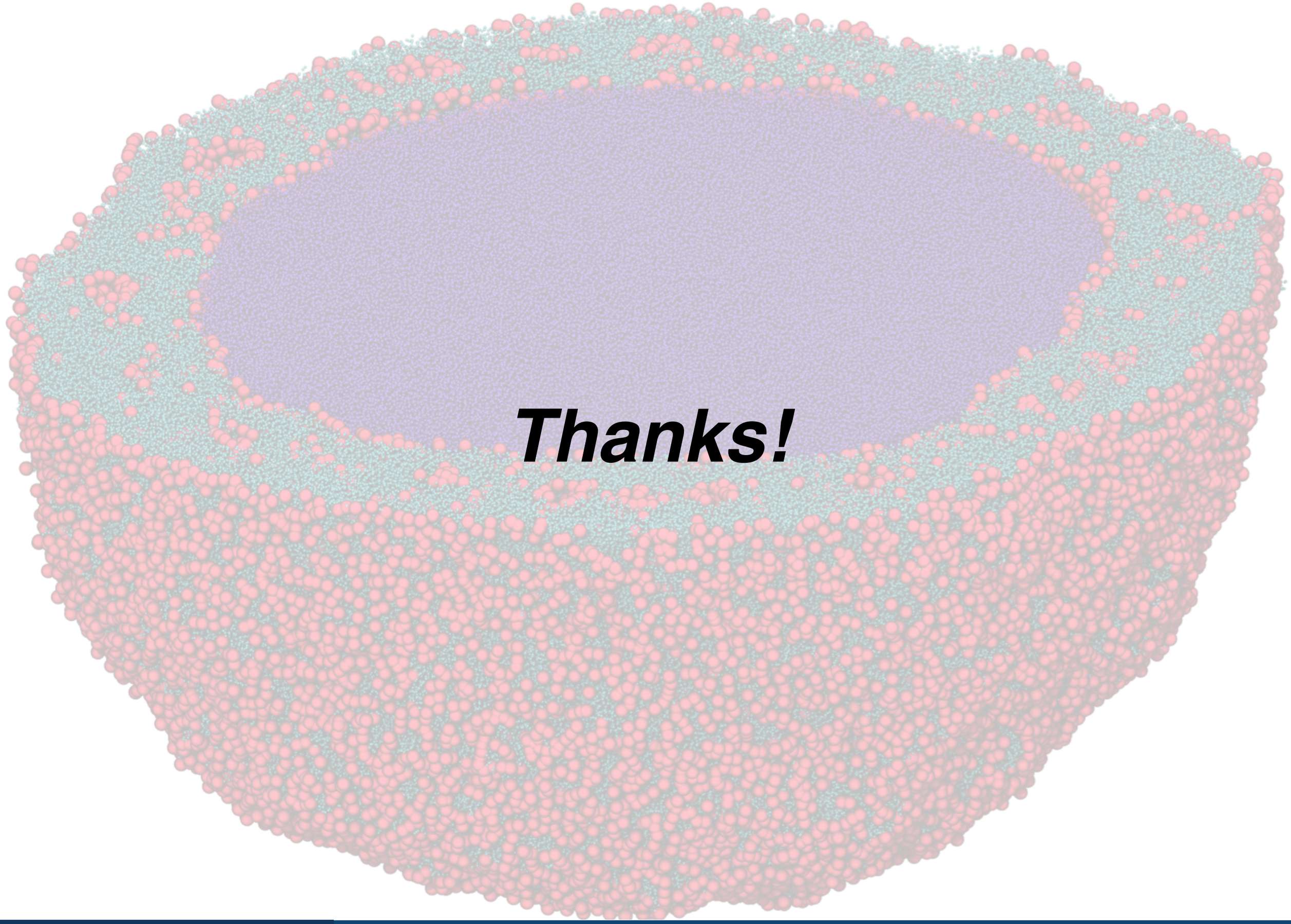


Droplet Study - Conclusions



- Versatile assembly platform
- Fine scale control of micro and nano-scale.
- Interesting regions that could lead to more complex structures.





Thanks!