Interfacial Polymerization Dynamics: new insights on film formation using in-situ microscopy and particle-tracking

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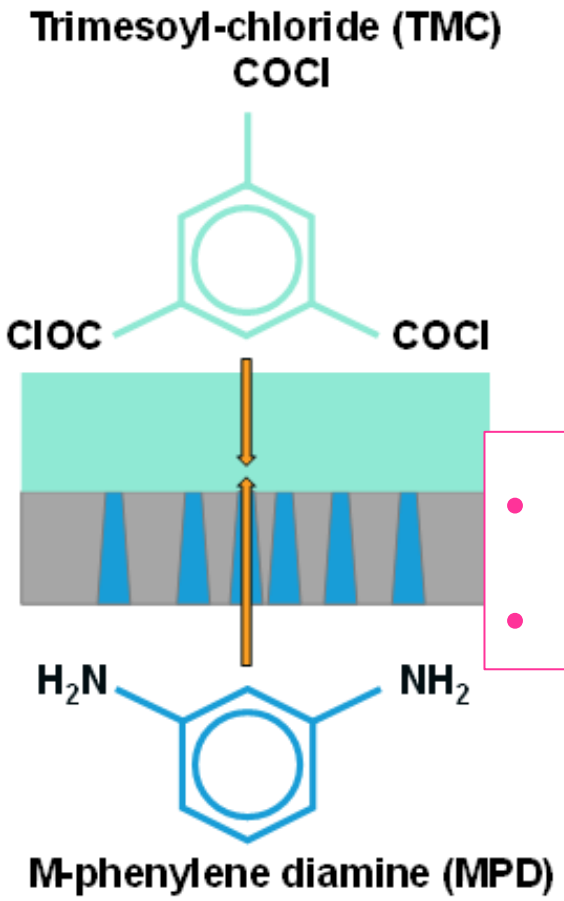
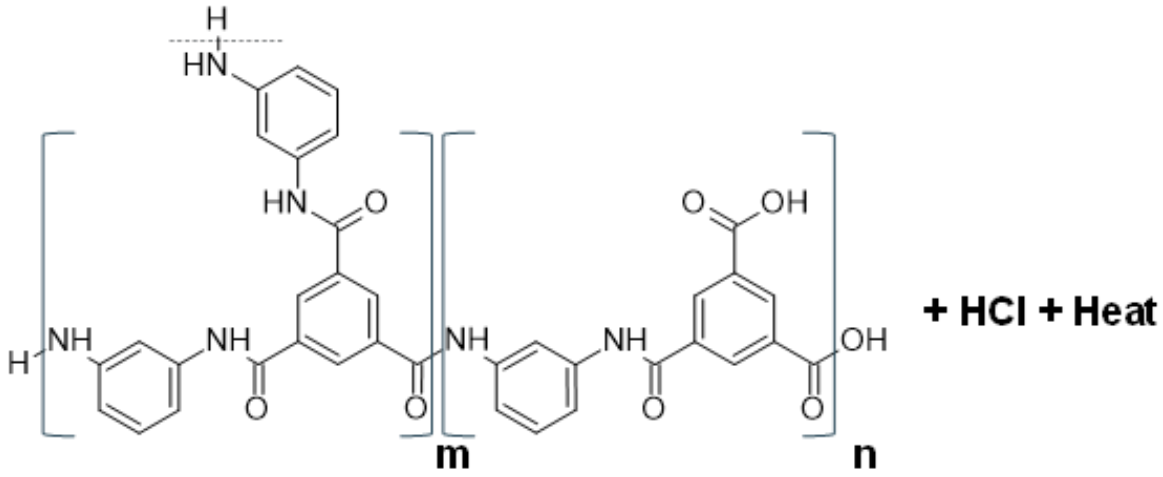
Water & Energy Technologies Laboratory

Interfacial Polymerization (IP)





- A very **fast** reaction <1 sec.
- A **thin** (<250nm) PA selective layer

Nulens and Ben Zvi et al., *JMS* (2022)

Desalination by RO

The product of IP:

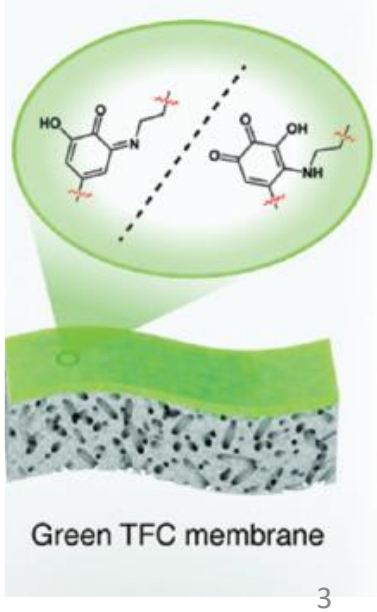
Crumpled polyamide film

Synthesis — ? — Morphology — ? — Performance

Why?

⇩

- ✓ Improve existing membranes
- ✓ Move towards ‘green materials’

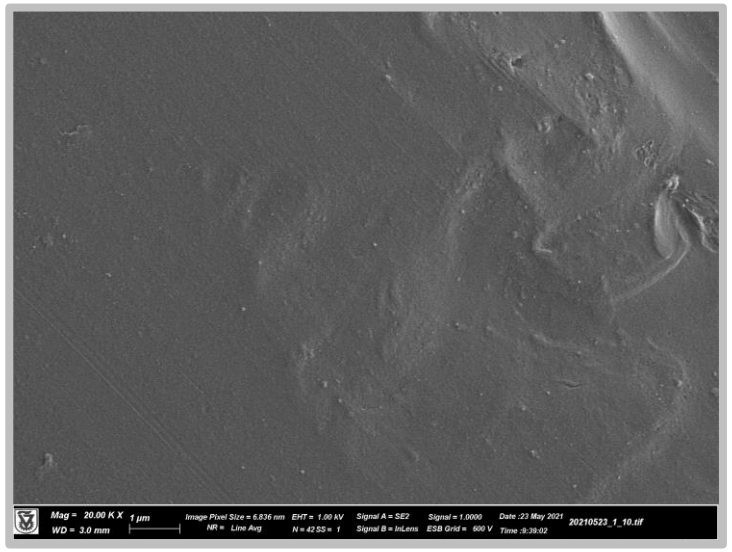


Park et al., Green Chem. 2021

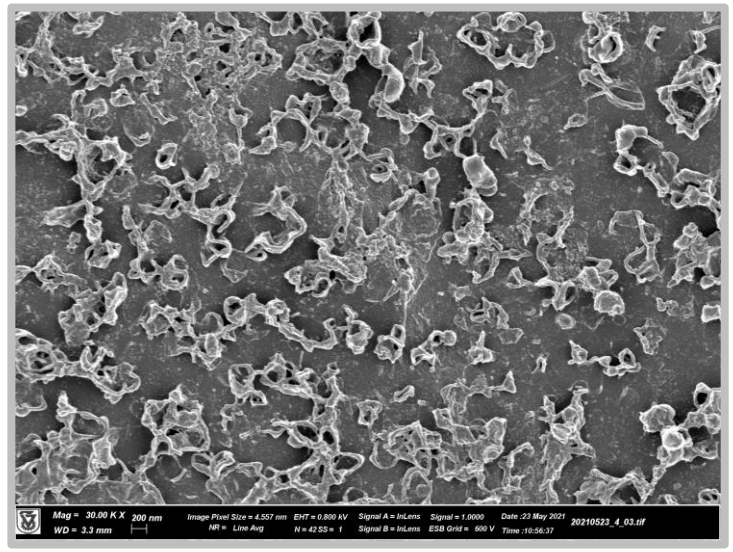
System's stability

Film morphology

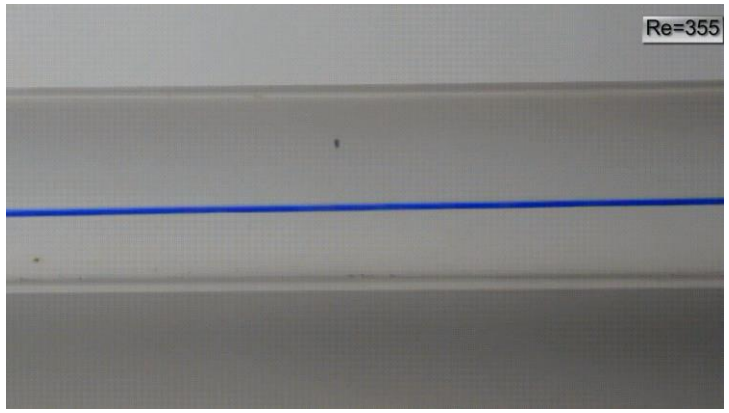
The Concept



Instability mechanisms



Smooth= Stable



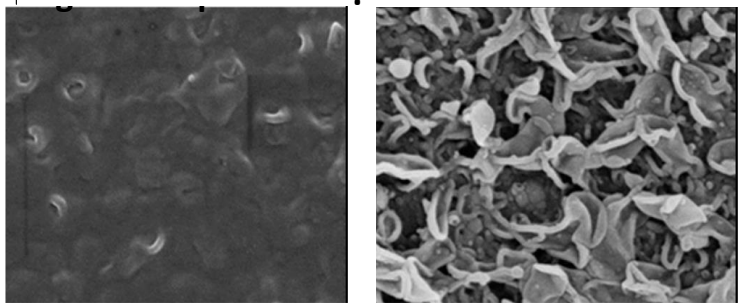
Crumpled= Unstable

https://www.youtube.com/watch?v=y0WRJtXvpSo

Nulens and Ben Zvi et al., *JMS* (2022)

Instability mechanisms

During IP



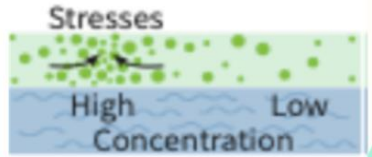
Ma et al., *Environ. Sci. Technol. Lett.* (2018)

Bubble formation

Elastic crumpling

Thermo-capillarity

Soluto-capillarity



Freger and Ramon, *Prog. Polym. Sci.* (2021)

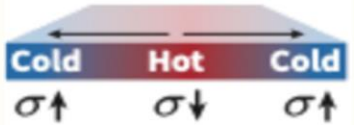
Instability mechanisms

During IP

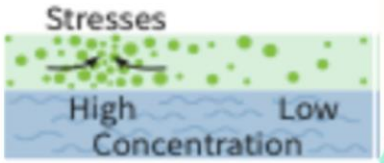
Bubble formation

Elastic crumpling

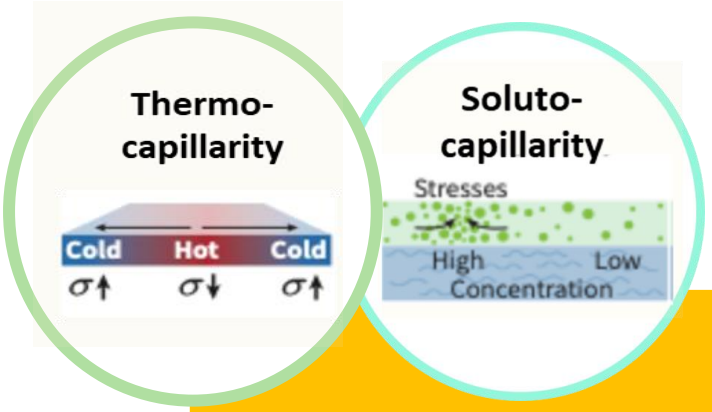
Thermo-capillarity



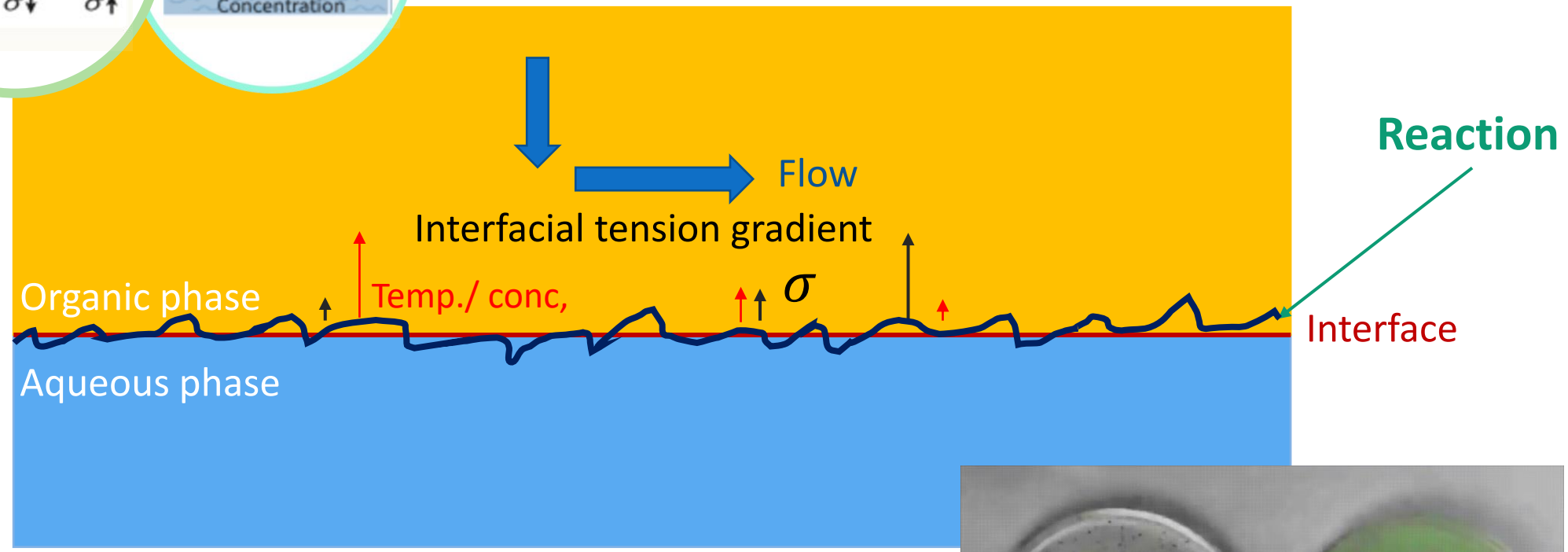
Soluto-capillarity



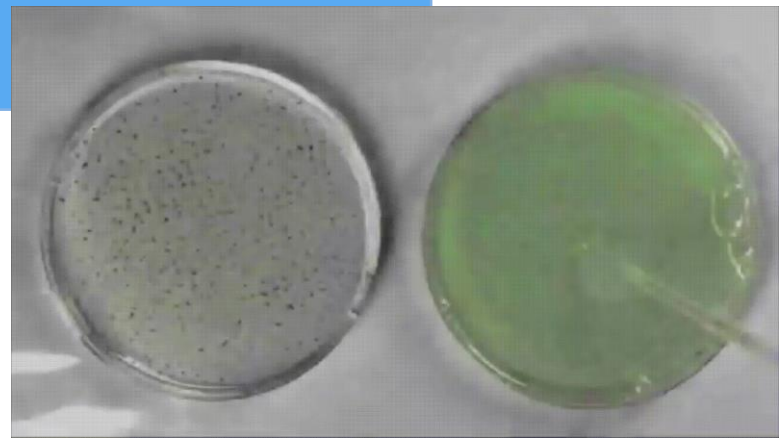
Freger and Ramon, *Prog. Polym. Sci.* (2021)



IP system



Gradients in interfacial tension drive a flow: **Marangoni flow**



https://www.youtube.com/watch?v=y0WRJtXvpSo

Instability mechanisms

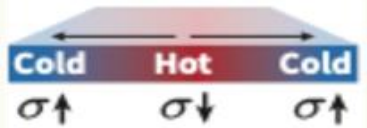
During IP

Hydrodynamic Instability = flow in IP system

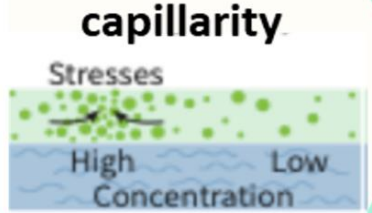
Bubble formation

Elastic crumpling

Thermo-capillarity



Soluto-capillarity



Freger and Ramon, *Prog. Polym. Sci.* (2021)

How can we observe a flow in IP ?

Motivation:

Instability

Synthesis → Morphology → Performance

Methods:

In-situ monitoring – insight of reaction dynamics

Microfluidic device

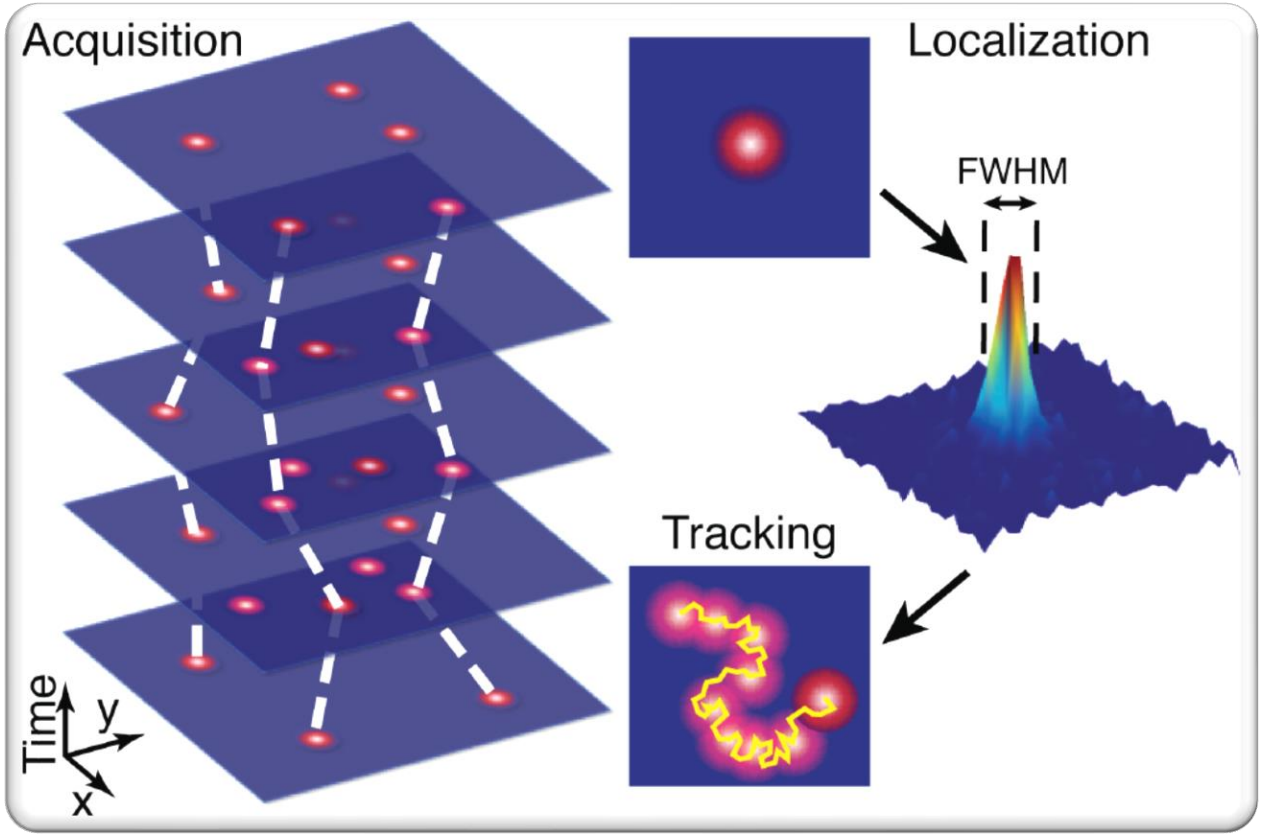
Confocal Microscopy

Videos of 2D image over time
~39 frames/sec

Aqueous phase: fluorescent particles (1µm) + MPD

Organic phase: Isopar-G + TMC

Particle Tracking



Manzo et al., Rep. on Prog. in Phys. (2015)

- Acquisition of the displacement using confocal microscopy
- Tracking particles using TrackMate plugin, Fiji.

What do we expect to see?

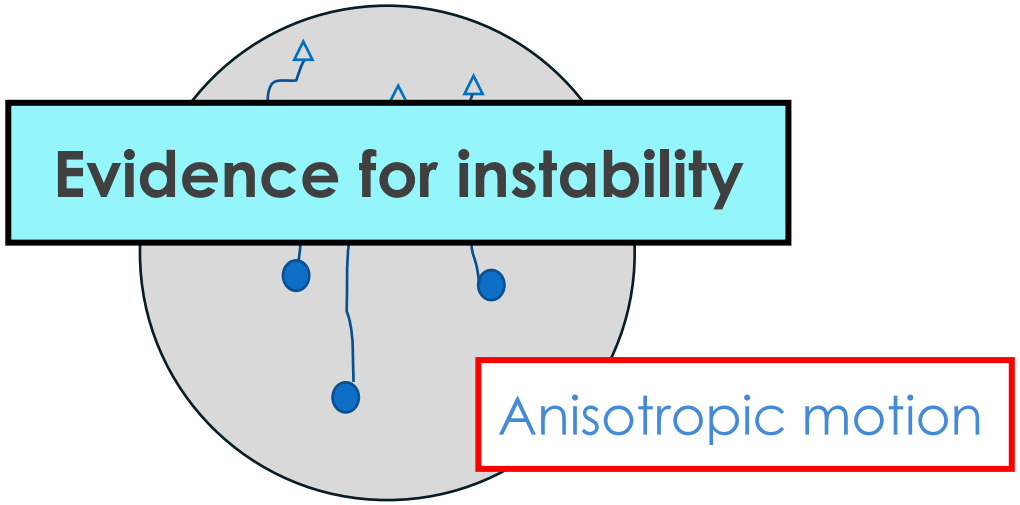
Random motion (Brownian)

Trajectories:

- No bulk flow.
- The motion is thermal-driven.

Directed motion

Trajectories

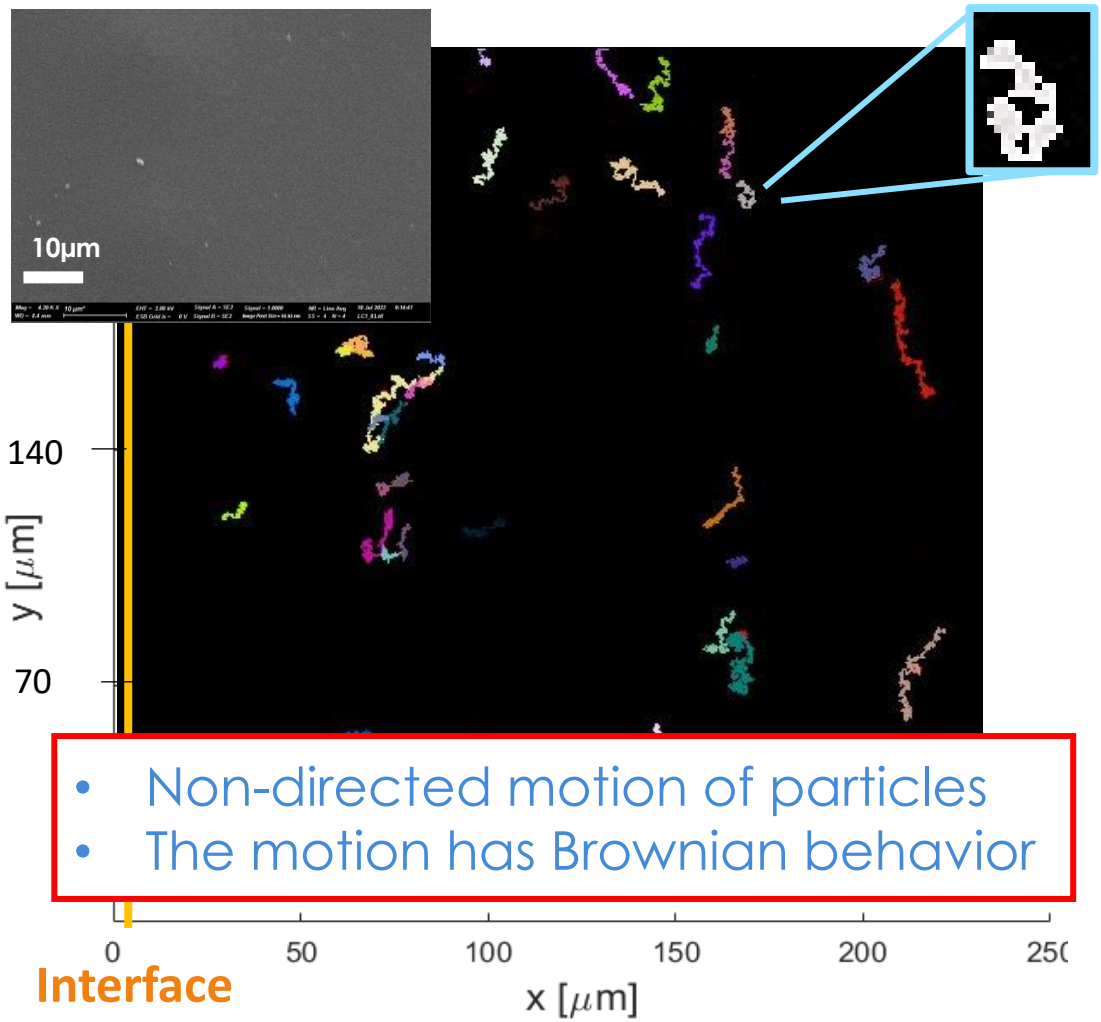


- Particles act as tracers that move with the bulk.
- **Brownian + bulk directed motion**

Observed trajectories

Low concentrations:

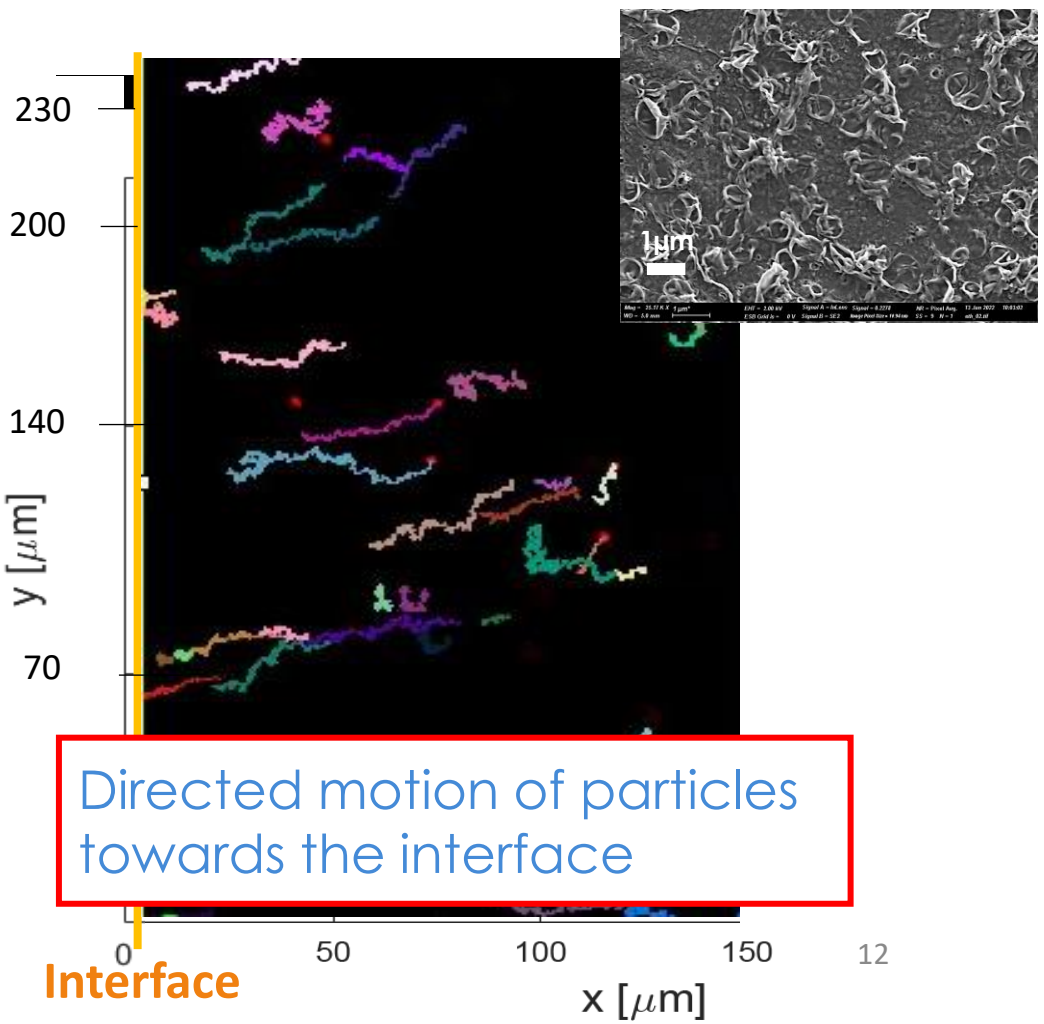
0.02% MPD; 0.001% TMC



- Non-directed motion of particles
- The motion has Brownian behavior

Standard concentrations:

2% MPD; 0.1% TMC



Directed motion of particles towards the interface

MPD diffusion ↑

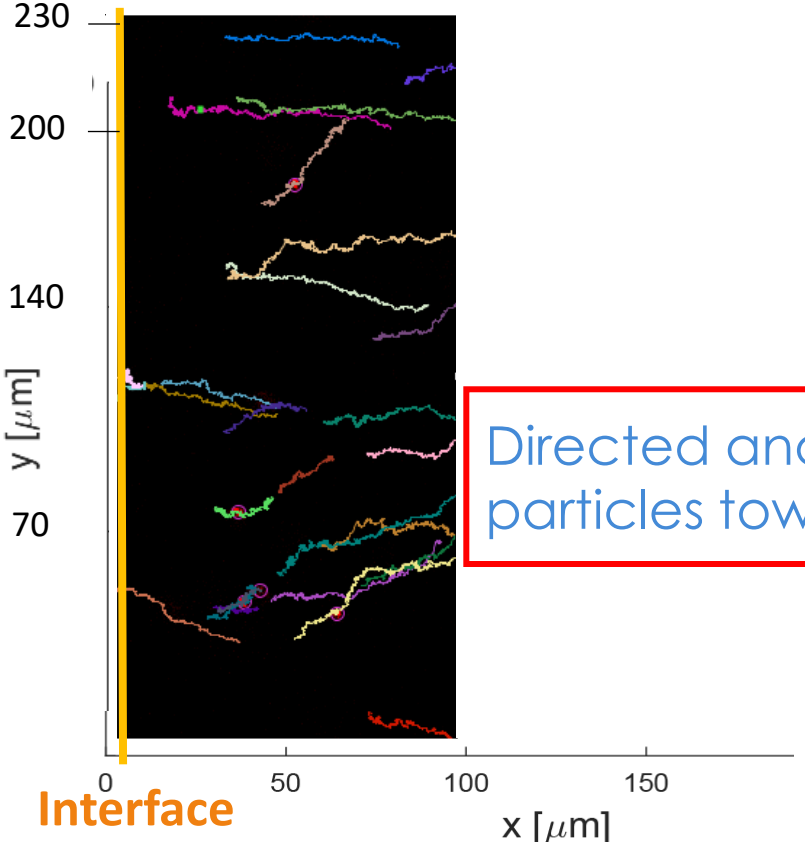
MPD partitioning ↑

Interfacial tension ↓

Observed trajectories

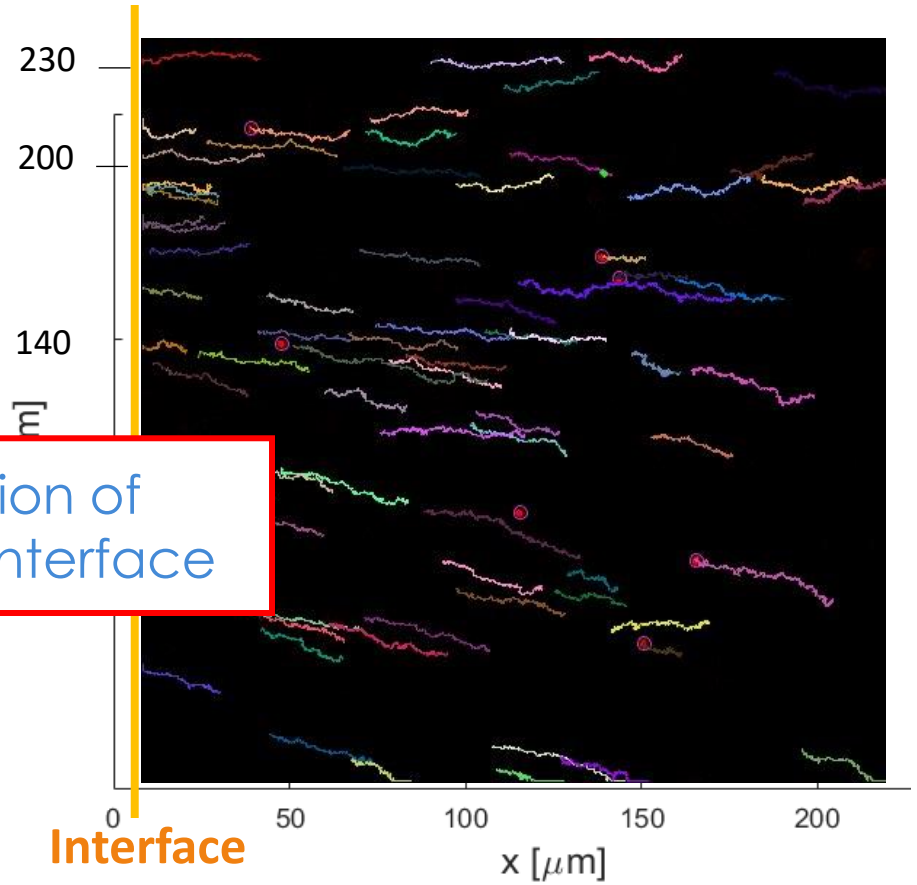
Polymerization ↑

CO-Solvent:
2% MPD; 0.1% TMC +
2% Ethyl acetate



Directed and fast motion of particles towards the interface

High concentrations:
4% MPD; 0.2% TMC



Observed trajectories

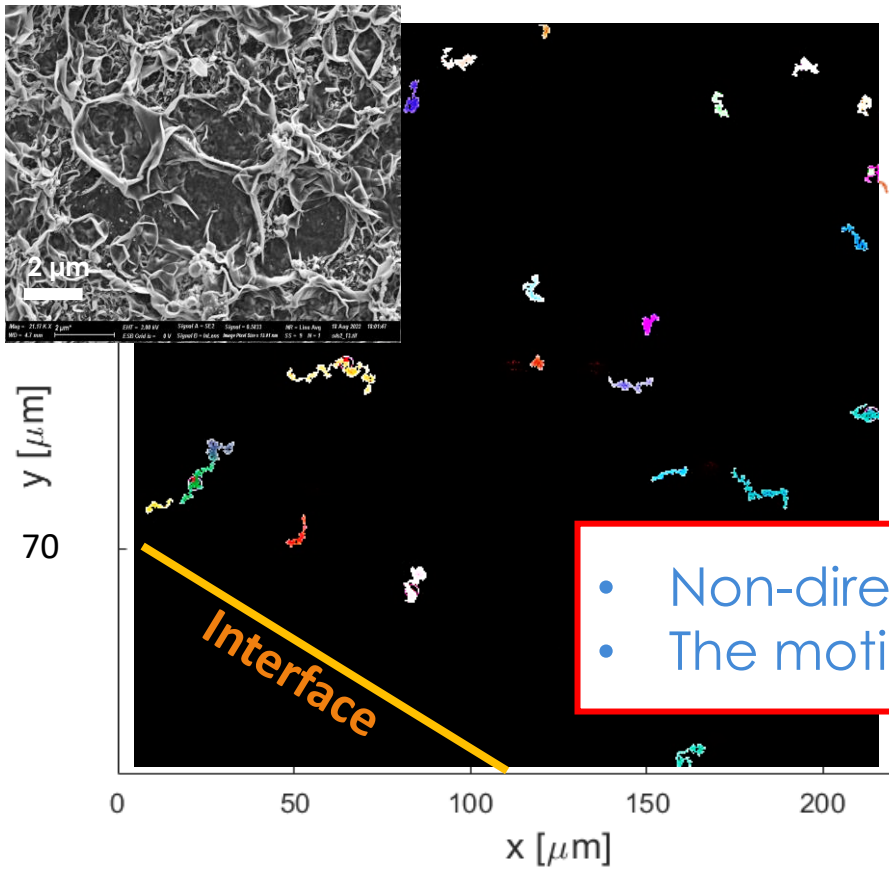
Interfacial tension ↓

Additives in the aqueous phase

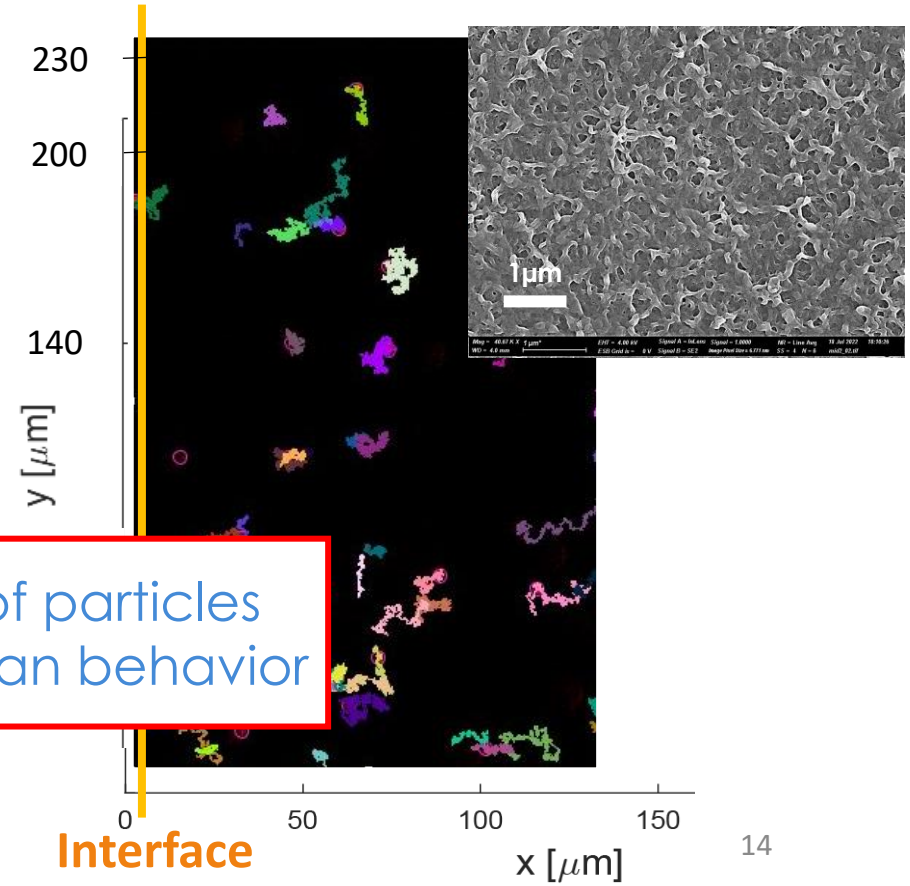
Bubbling ↑

Sustains reaction ↑

SDS:
2% MPD +2% SDS;
0.1% TMC



NaHCO3:
2% MPD +2% NaHCO3;
0.1% TMC



- Non-directed motion of particles
- The motion has Brownian behavior

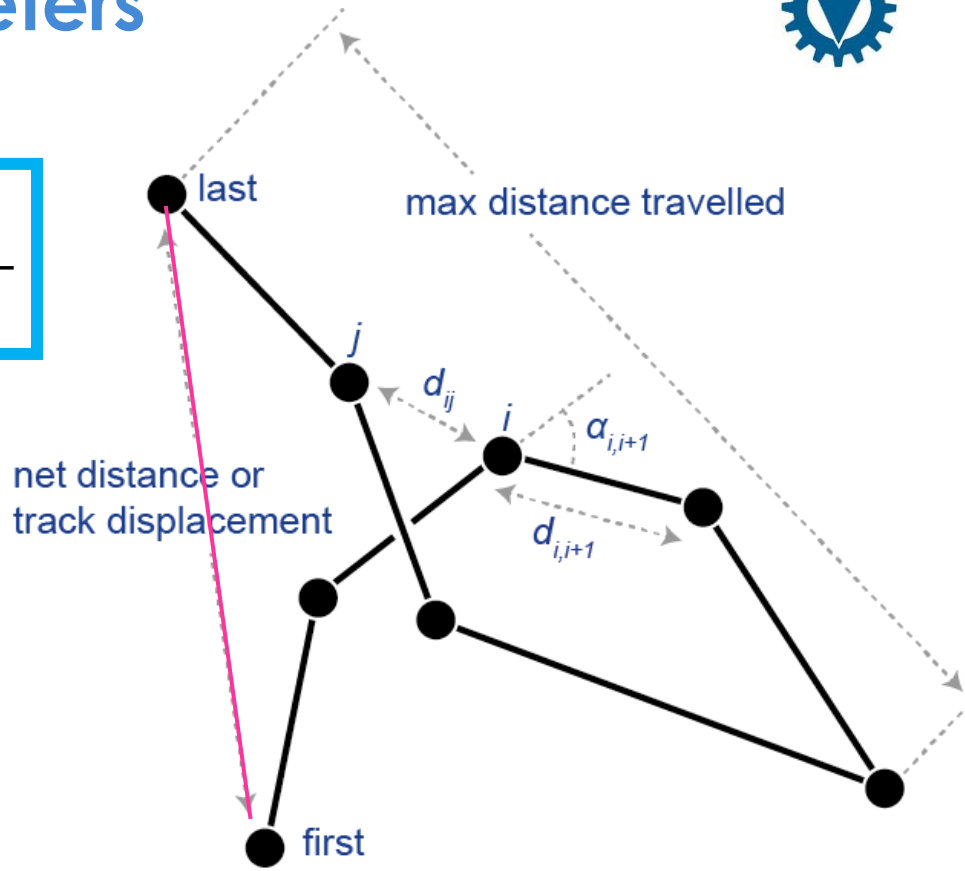
Motion Parameters

1. **Confinement ratio=** $\frac{\text{net distance}}{\text{total distance travelled}}$

$0 < \text{Confinement ratio} < 1$

"Confined" movement~ Brownian motion

Directed motion



total distance travelled = $\sum d_{i,i+1}$

max distance travelled = Max d_{ij}

mean directional change = 1/N $\sum \alpha_{i,i+1}$

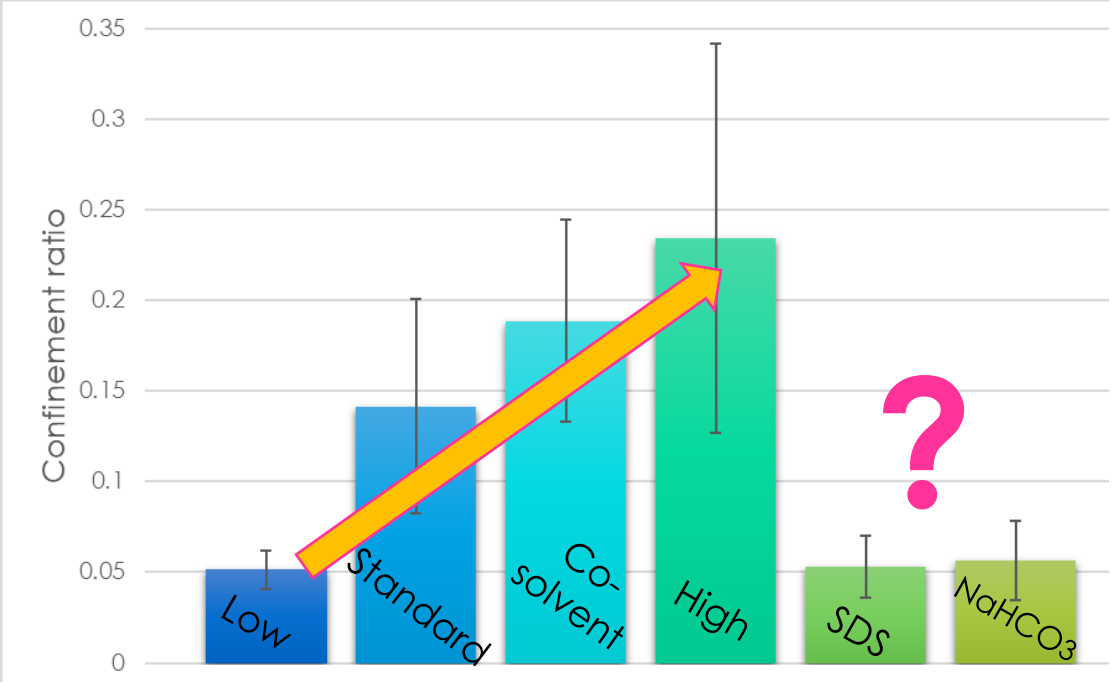
2. **Straight line speed=** $\frac{\text{net distance}}{\text{total track time}}$

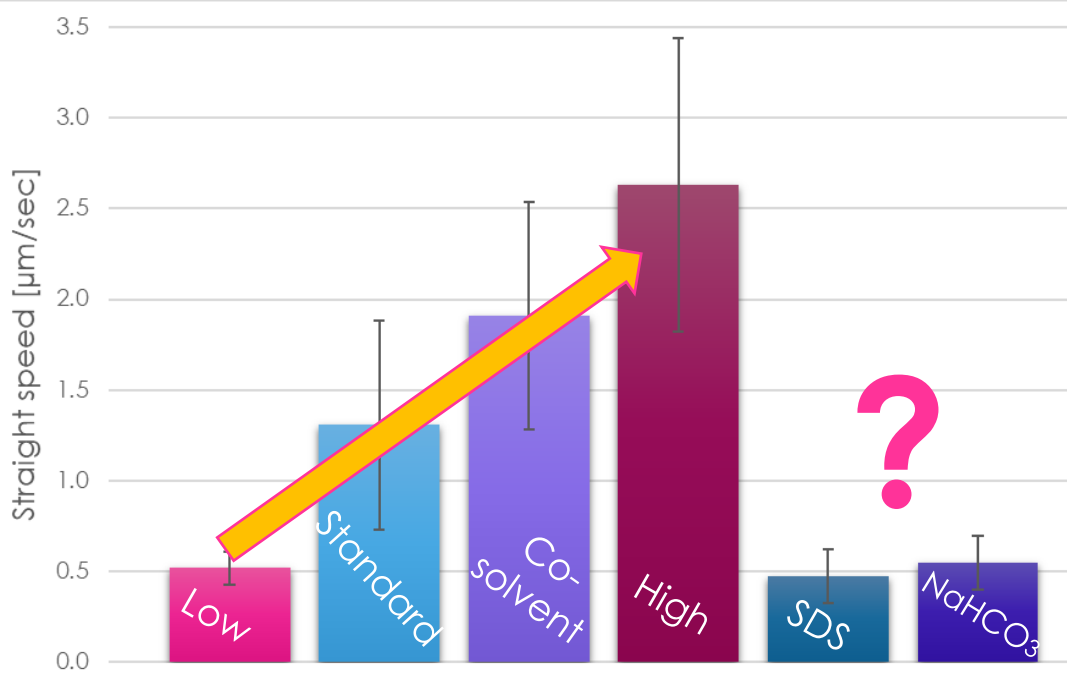
Meijering et al., Meth. Enzymol. (2012)

Motion Parameters

Confinement ratio= $\frac{\text{net distance}}{\text{total distance travelled}}$

Straight line speed= $\frac{\text{net distance}}{\text{total track time}}$

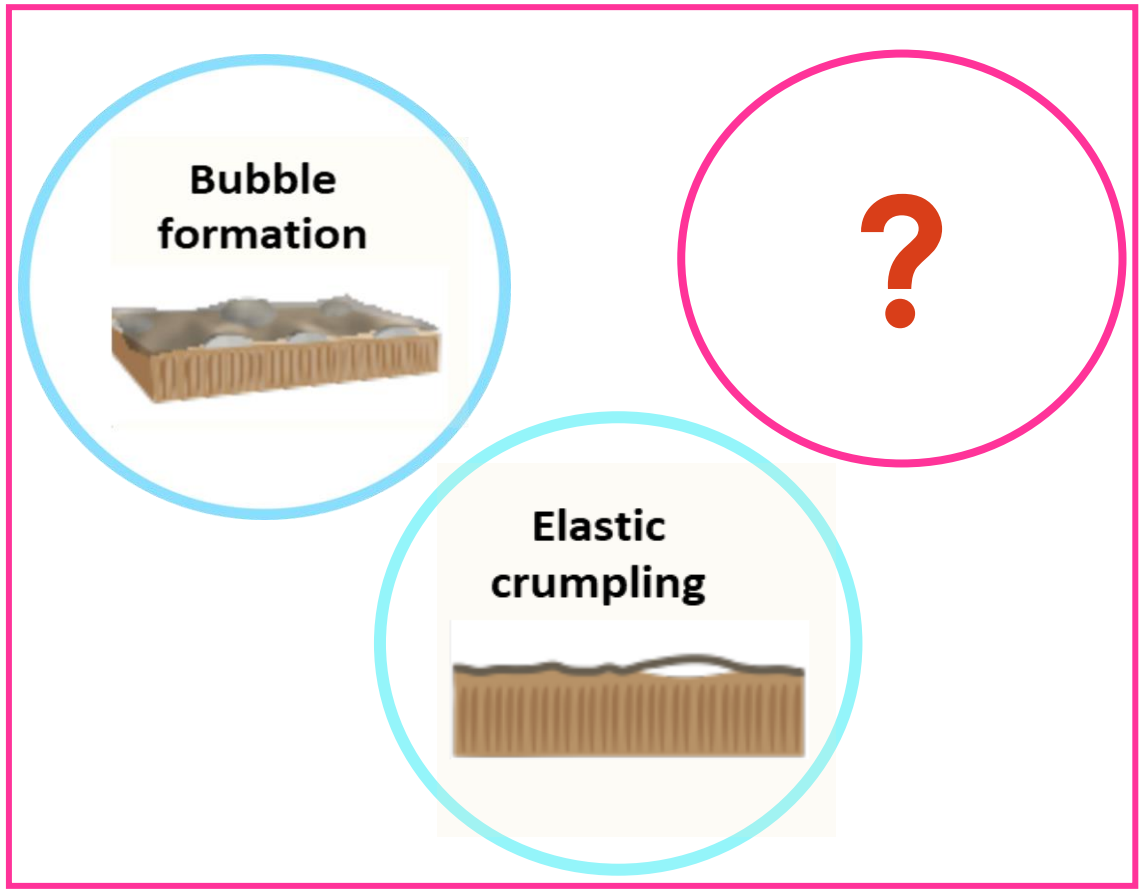


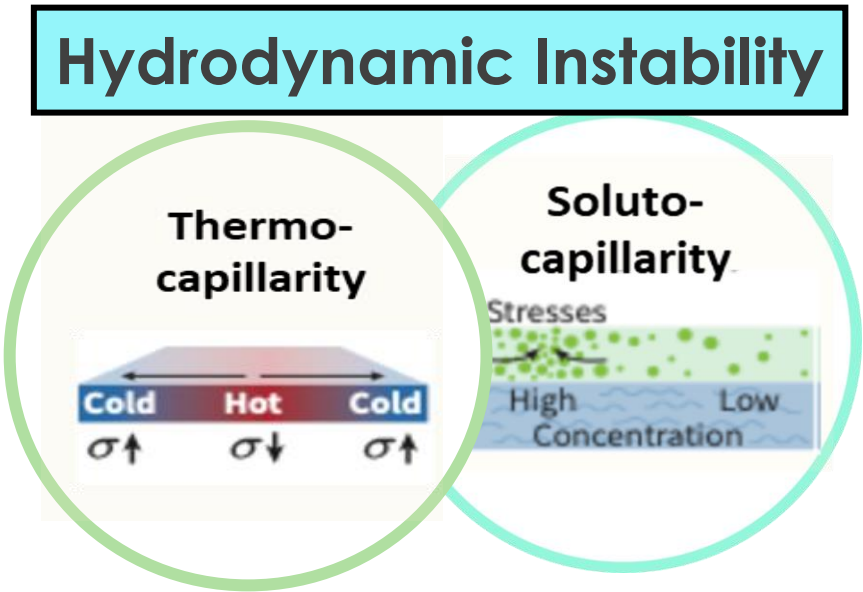


- Motion parameters increase when monomer concentrations increase and with the addition of co-solvent = **more directed flow**
- Motion parameters for the additives are like **Brownian motion**

Instability mechanisms

During IP





Freger and Ramon, *Prog. Polym. Sci.* (2021)

Conclusions

- Different motion behaviors between the tested conditions.
- At higher monomer concentrations and\or with a co-solvent a directed and fast motion towards the interface.
- Addition of SDS or $NaHCO_3$, resulted in Brownian motion.
- Tracking particles provides us with new insights about IP.

Future work:

- Test other kinds of additives.
- Data analysis.

Acknowledgements

Thank you for Listening ☺

קרן קימת לישראל
K K L - J N F

ISRAEL SCIENCE FOUNDATION

RBNI The Russell Berrie Nanotechnology Institute
Technion - Israel Institute of Technology

BSF
United States – Israel
Binational Science Foundation