



**UNIVERSITY OF ROME “LA SAPIENZA”
NANOTECHNOLOGIES ENGINEERING**

**MEMBRANE APPLICATIONS IN
NANOTECHNOLOGY:
MEMBRANE APPLICATIONS**

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Possible applications of nanotechnology and membranes

- **Production of standard membranes**
- **Separation of nanoparticles**
- **Production of membranes as nanoproduct**
- **Production of crystals by membranes**
- **Production of nanoparticles by membranes**
 - **By direct reaction**
 - **By micro- and nanoencapsulation**
- **Functionalization of membranes by nanoparticles**
 - **By surface modification**
 - **By inclusion**

HOW TO CAST A MEMBRANE

- **MEMBRANE MATERIALS – GENERAL OVERVIEW**

POLYMERIC MEMBRANES

INORGANIC MEMBRANES

HYBRID MEMBRANES

BIPOLAR MEMBRANES

LIQUID MEMBRANES

HOW TO CAST A MEMBRANE

- **MEMBRANE MATERIALS – GENERAL OVERVIEW**

POLYMERIC MEMBRANES

Widely used due to cheapness and ease of production, may not tolerate aggressive chemicals during operation and washing procedures.

Do not allow use of high temperatures.

The membrane surface is flexible and thus qualified to be used in advanced membrane module production.

The surface exhibits strong pore size and pore density heterogeneity.

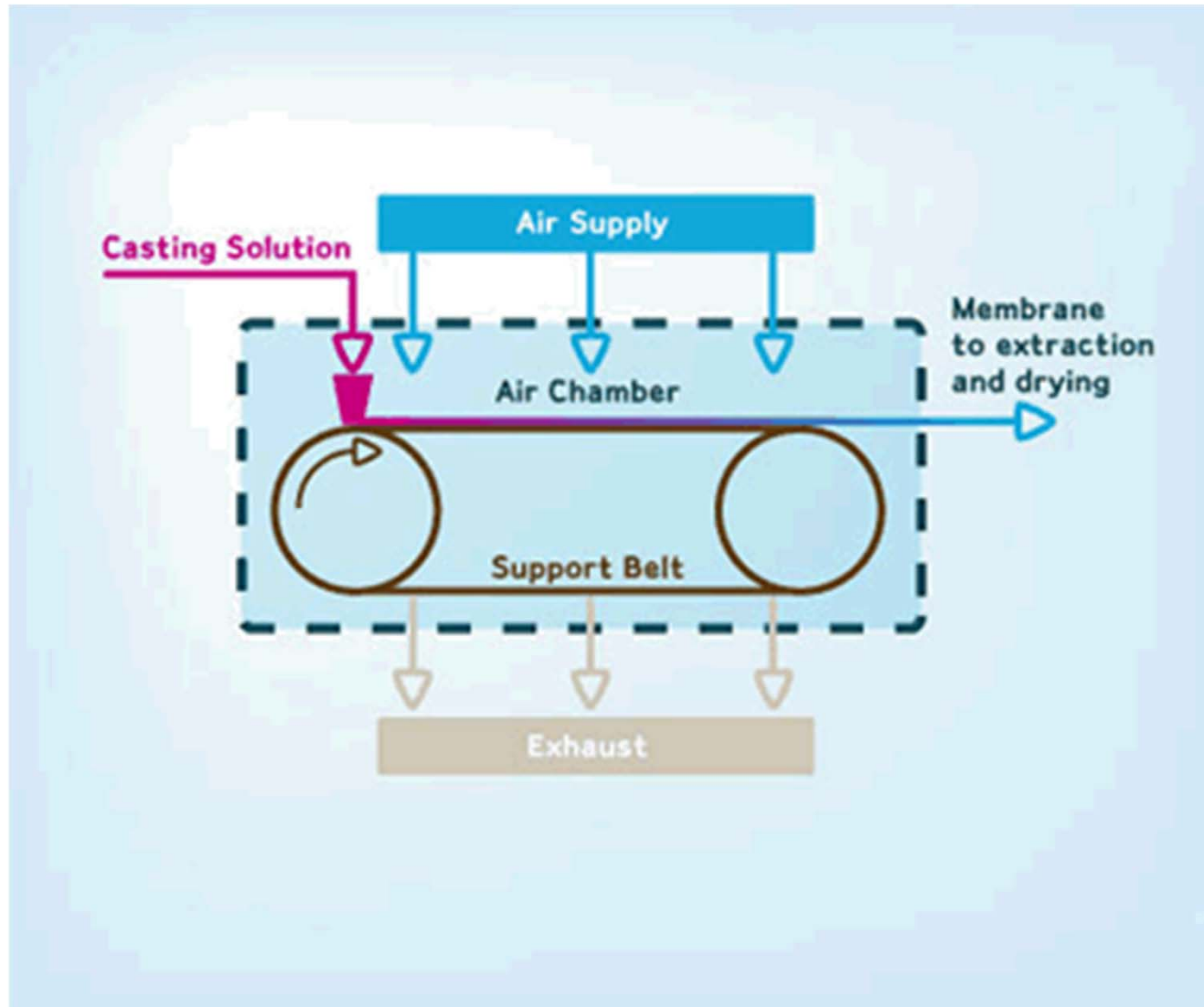
HOW TO CAST A MEMBRANE

- MEMBRANE MATERIALS – GENERAL OVERVIEW

Material	Application					
	MF	UF	NF/RO	GS	PV	MD
Cellulose acetate	X	X	X	X	X	
Cellulose esters	X					
Cellulose nitrate	X					
Poly (vinyl alcohol)	X					
Polyacrylonitrile		X			X	
Poly (vinyl chloride)	X					
PVC copolymer	X	X				
Aromatic polyamide	X	X	X			
Aliphatic polyamide	X	X				
Polyimide	X	X	X	X		
Polysulfone	X	X				
Polyetheretherketone (PEEK)	X	X		X		
Polycarbonate	X					
Polyester	X					
Polypropylene	X				X	X
Polyethylene	X				X	X
Polytetrafluoroethylene (PTFE)	X	X			X	
Poly (vinylidene difluoride) (PVDF)	X	X			X	X
Polydimethylsiloxane (PDMS)				X	X	

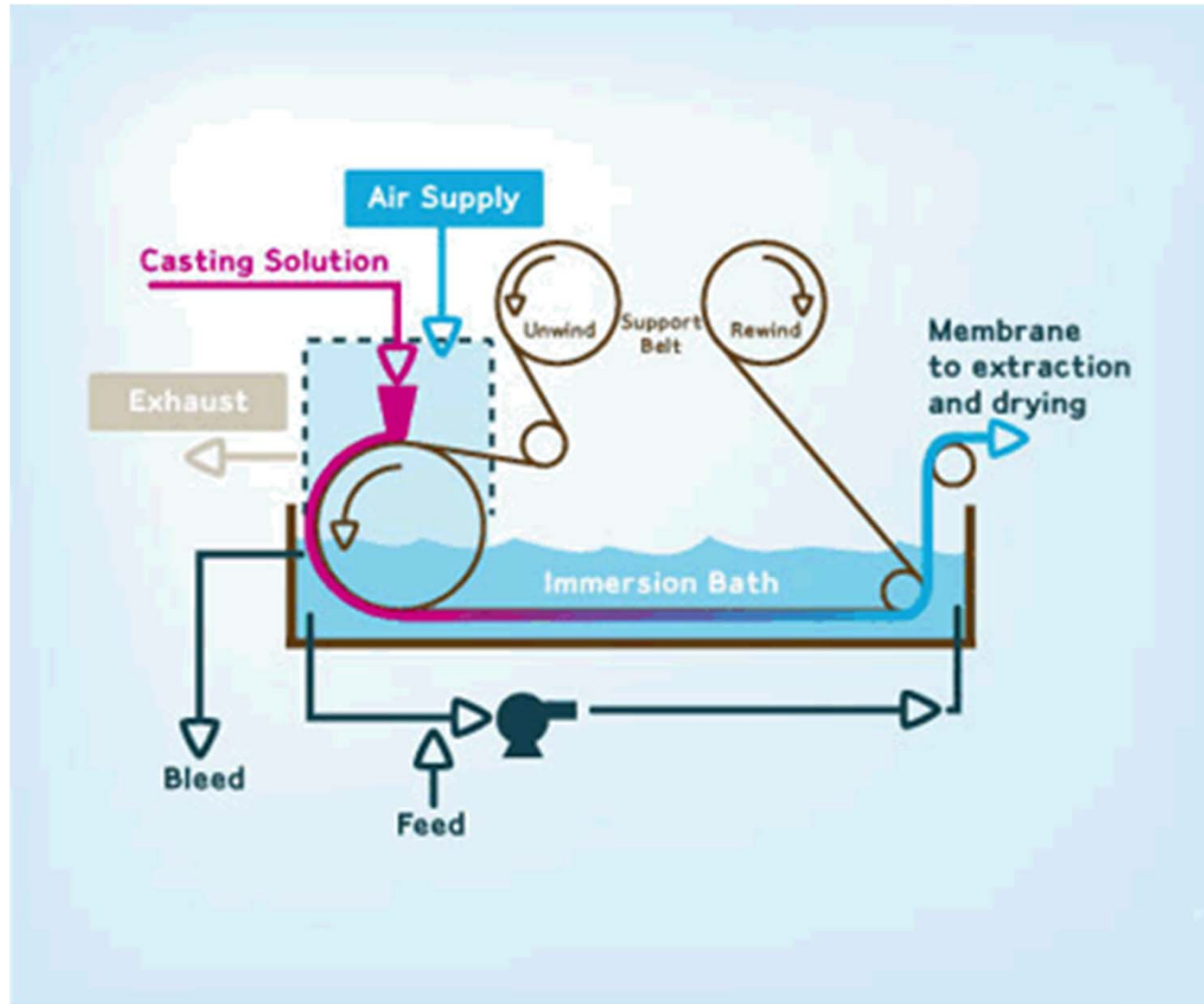
HOW TO CAST A MEMBRANE

- AIR CASTING



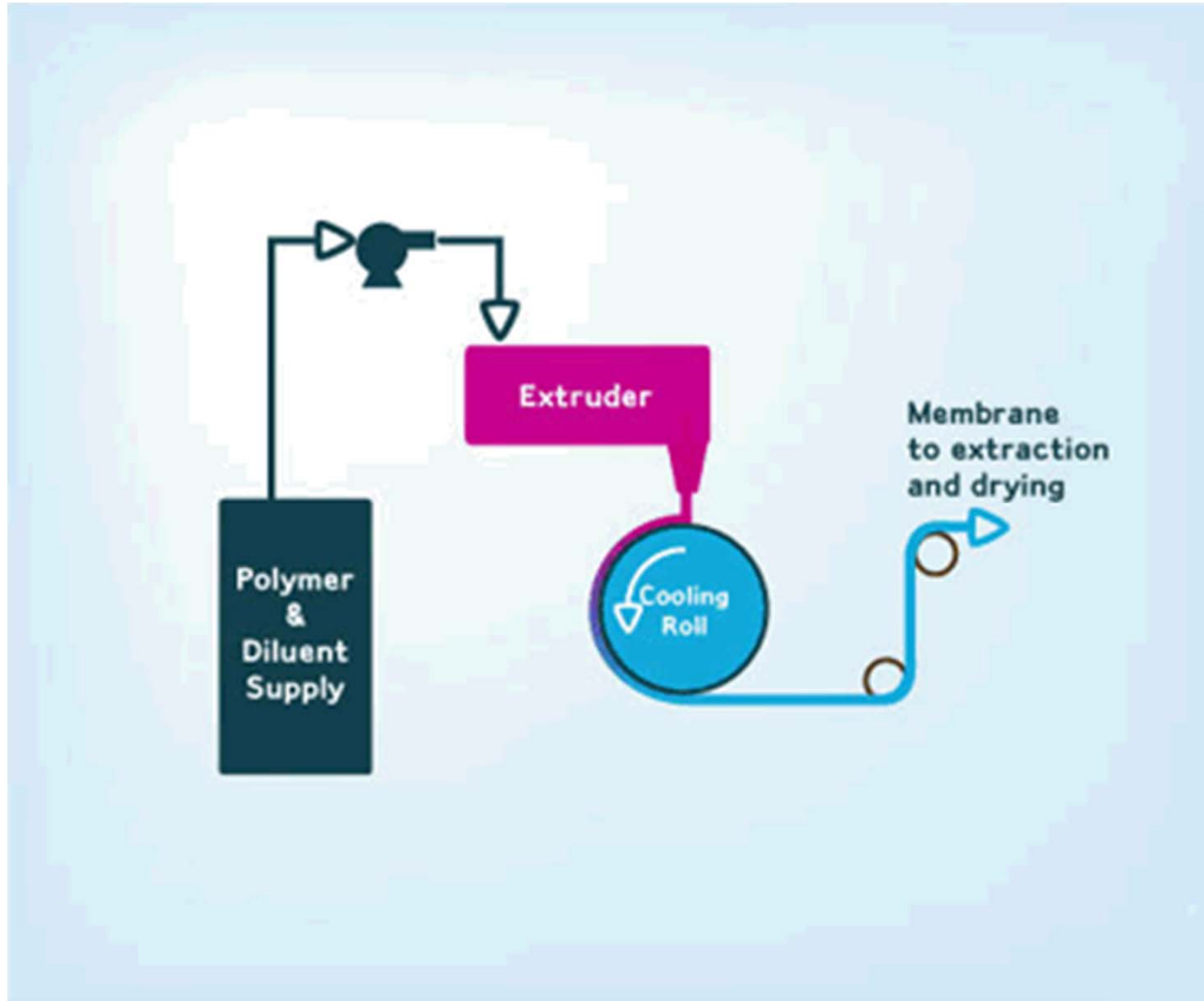
HOW TO CAST A MEMBRANE

- SOLVENT CASTING



HOW TO CAST A MEMBRANE

- THERMAL CASTING



HOW TO CAST A MEMBRANE

- **MEMBRANE MATERIALS – GENERAL OVERVIEW**

INORGANIC MEMBRANES

Inorganic membranes may be metallic or ceramic, with new developments in carbon and zeolite membranes. Difficult to produce, they exhibit rigid membrane surface that resist aggressive chemical contact. Moreover:

Arguments For Inorganic Membranes	Arguments Against Inorganic Membranes
Long-term stability at high temperatures	High capital costs
Resistance to harsh environments	Brittleness
Resistance to high pressure drops	Low membrane surface per module volume
Inertness to microbiological degradation	Difficulty in achieving high selectivities in large scale microporous membranes
Easy cleanability after fouling	Generally low permeability of the highly selective (dense) membranes at medium temperatures
Easy catalytic activation	Difficult membrane-to-module sealing at high temperatures

HOW TO CAST A MEMBRANE

- **MEMBRANE MATERIALS – GENERAL OVERVIEW**

INORGANIC MEMBRANES

Materials for ceramic membranes includes:

- *Silica*
- *Titania*

Materials for metallic membranes includes:

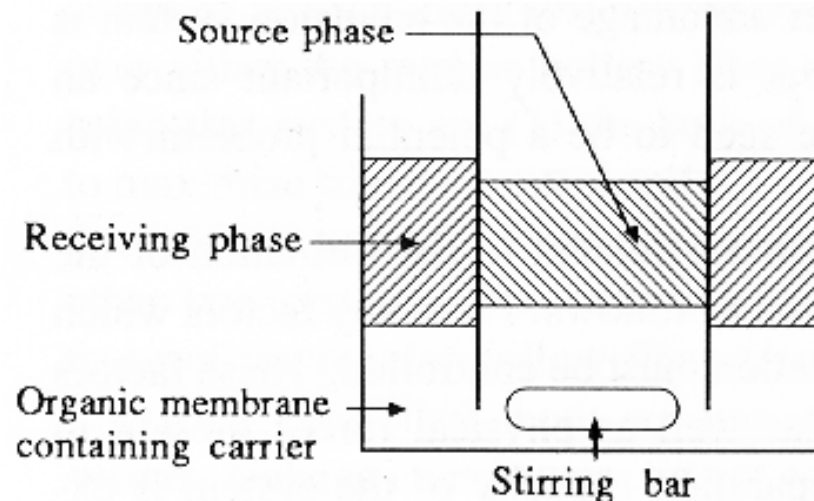
- *Palladium (and alloys with Platinum and/or Tungsten)*
 - *Ferrum*
 - *Nickel*

HOW TO CAST A MEMBRANE

- **MEMBRANE MATERIALS – GENERAL OVERVIEW**

LIQUID MEMBRANES

Liquid membranes exhibit very high selectivity, but low permeate fluxes. It exhibits no pores, thus works by diffusion. May be used for special applications (biotechnology). The difficulty is to have increased membrane area without disturbing and/or destroying the membrane phase.



HOW TO CAST A MEMBRANE

- **MEMBRANE MATERIALS – GENERAL OVERVIEW**

WE NEED LARGE PORES TO HAVE HIGH FLUXES

BUT:

**HIGH FLUXES LEADS TO FOULING WHICH NEED TO BE INHIBITED
PORES REDUCES SELECTIVITY WHICH MUST GUARANTEE TARGET VALUES**

→ PORE SIZE AND PORE DENSITY MUST BE CONTROLLED

BUT:

**THIS IS NOT CHEAP, SINCE POLYMERIC MEMBRANES SUFFERS
HETEROGENEITY AND ARE THUS UNSUITABLE.**



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**MEMBRANE APPLICATIONS IN
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MEMBRANES AS NANOPRODUCT**

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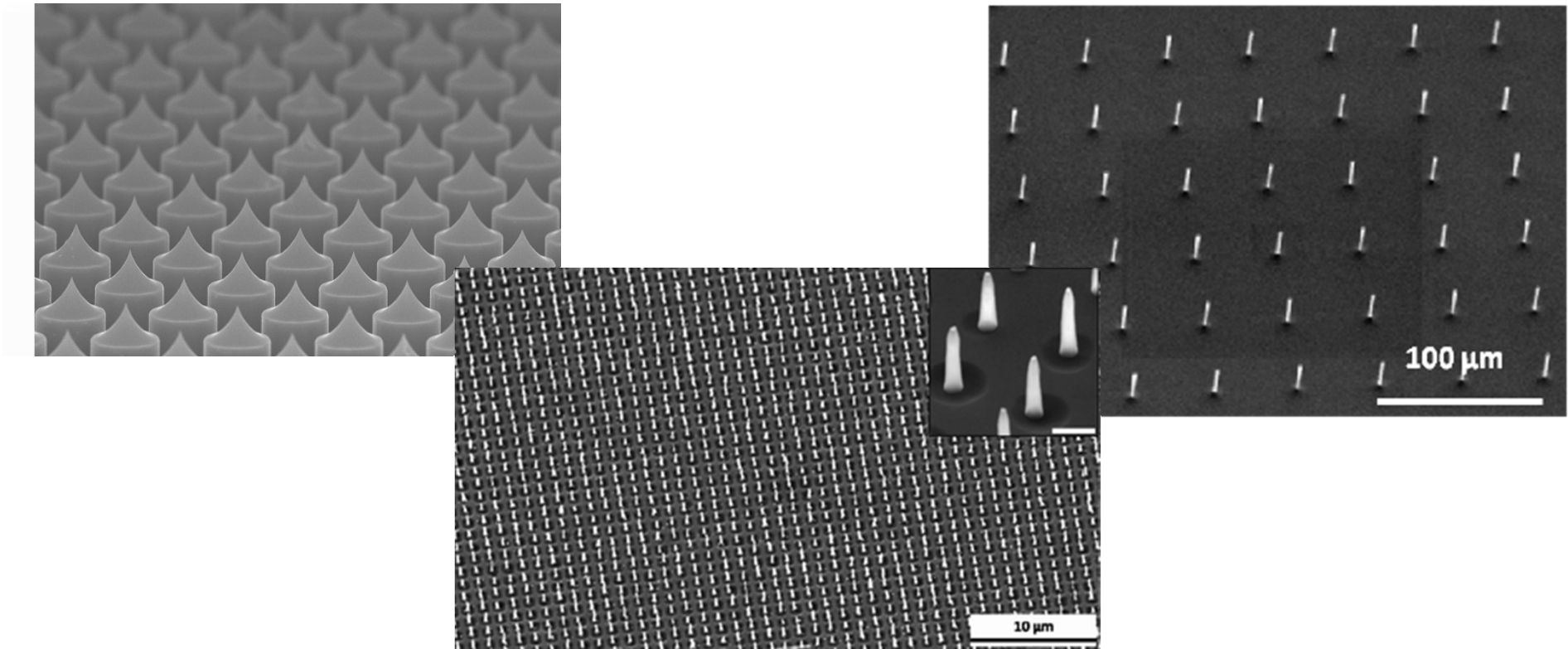
MEMBRANES AS NANOTECH

PRODUCT

- All the seen methods are valid to produce standard asymmetric membranes, but in case of polymers pore size is only “statistically” controlled by the process, the casting solutions and the operating conditions.
- May nanotechnology help us out? Yes, by producing “microsieves” and “nanosieves”.

MEMBRANES AS NANOTECH PRODUCT

- Production by micro needles

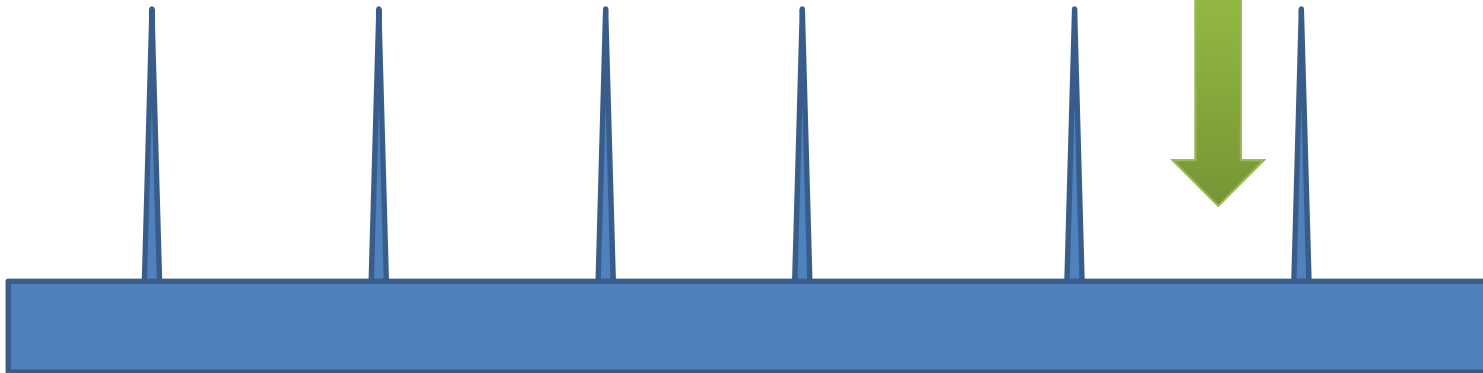


- Are produced by photolithography, chemical treatment, self-assembly and imprinting techniques.

MEMBRANES AS NANOTECH PRODUCT

- Production by micro needles

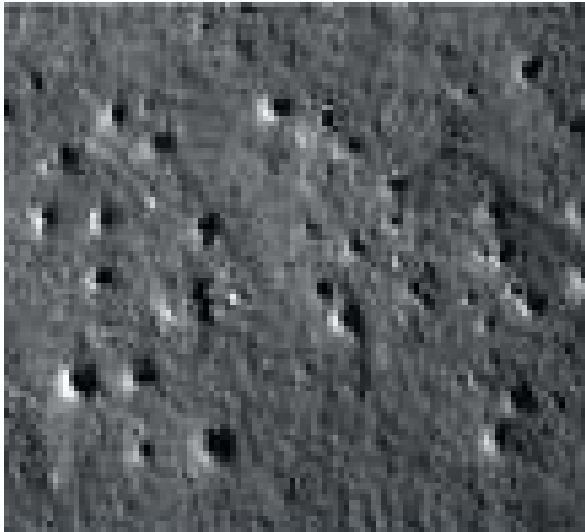
Dense membrane is punctured by the nanoneedles



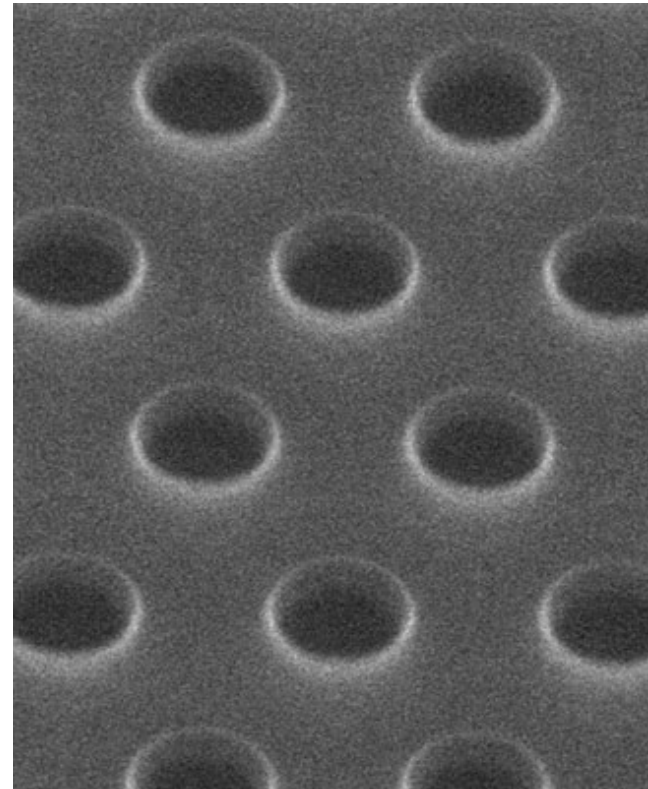
Advantage: this technique can be used on polymeric materials.

MEMBRANES AS NANOTECH PRODUCT

- Production by micro needles

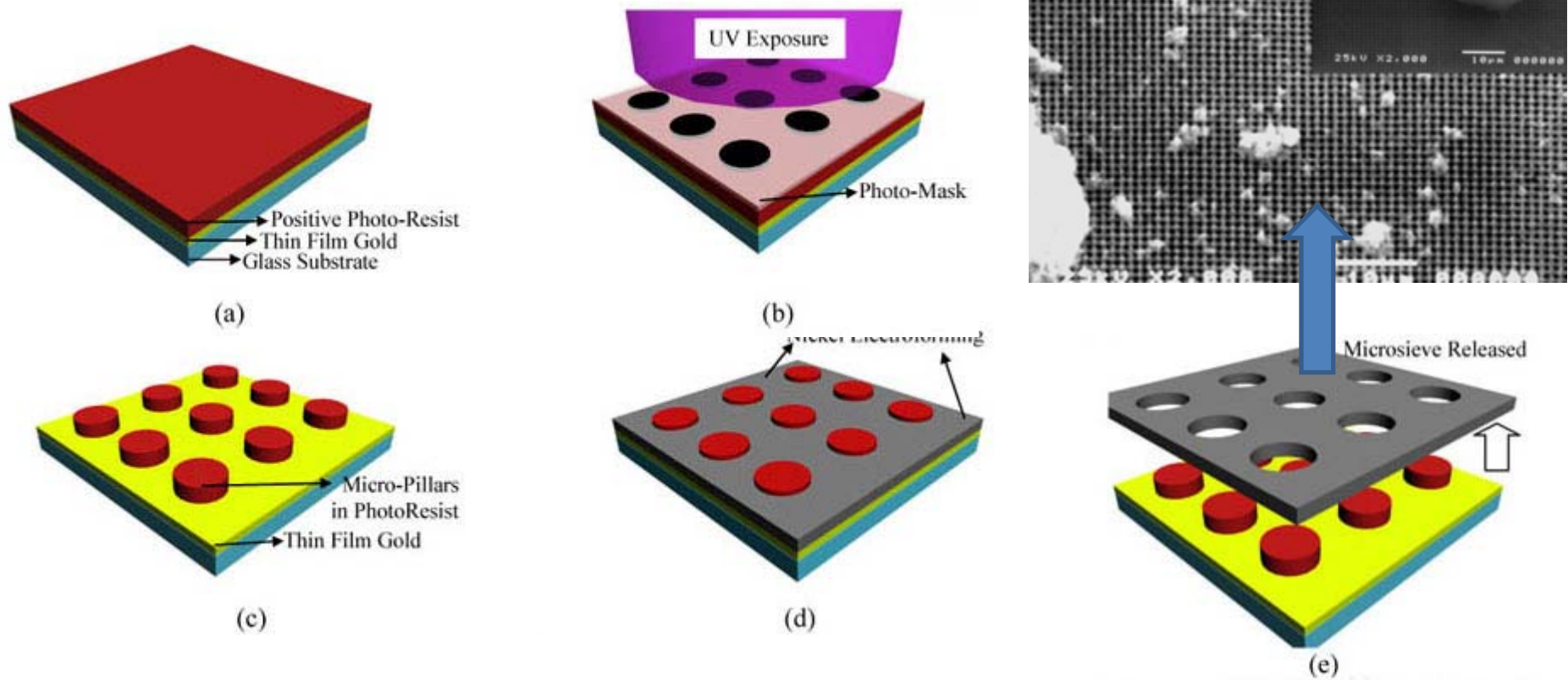


VS



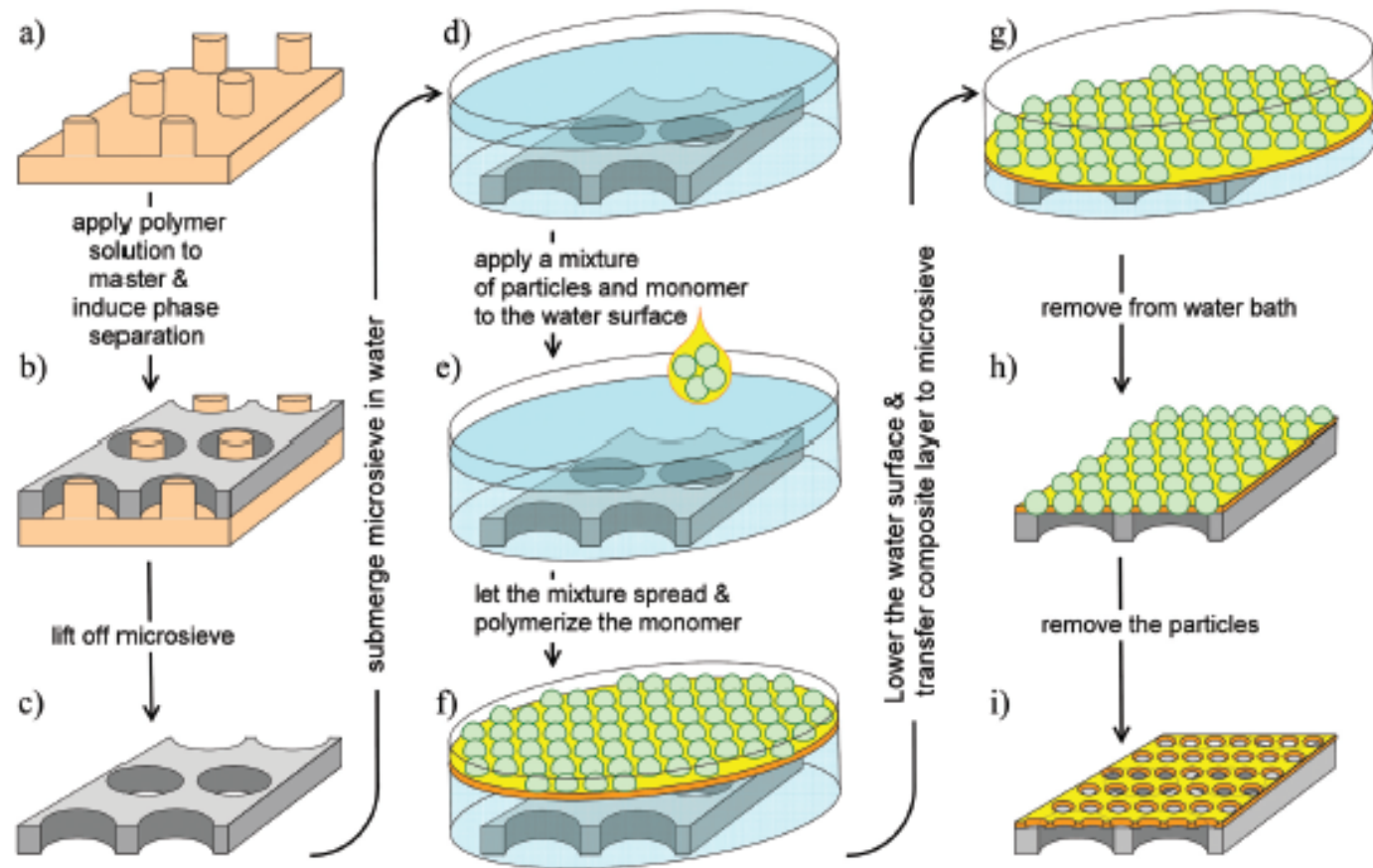
MEMBRANES AS NANOTECH PRODUCT

- Production by Lithography



MEMBRANES AS NANOTECH PRODUCT

- Polymeric nanosieve



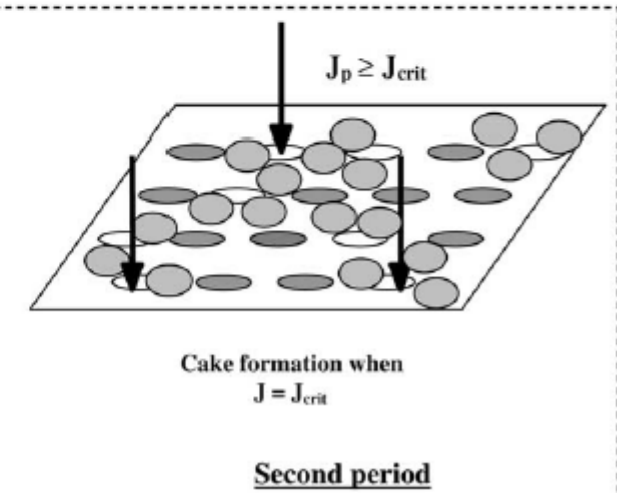
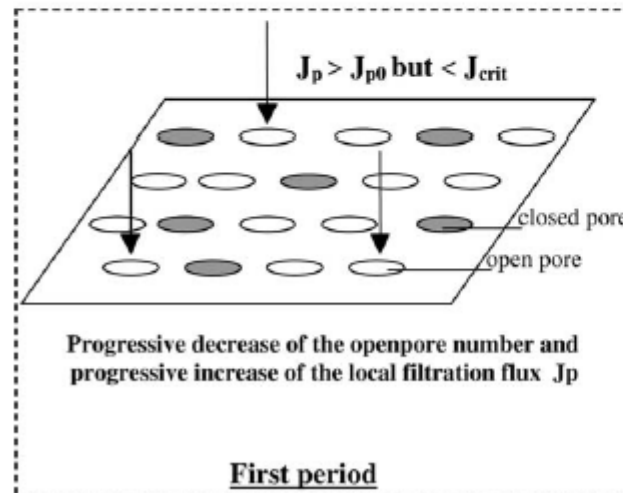
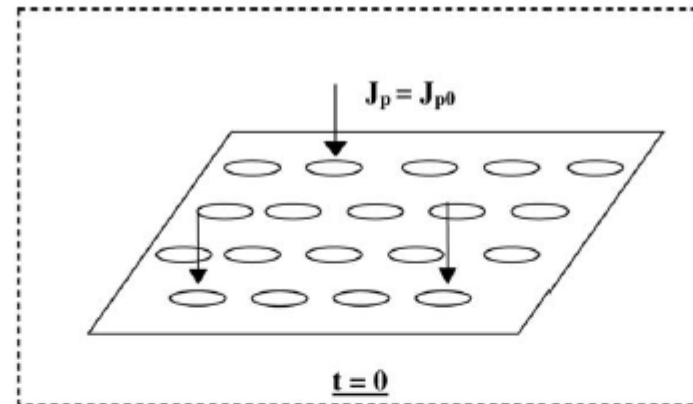
MEMBRANES AS NANOTECH

PRODUCT

- The advantage of having same pore size is to have controlled selectivity and maximum pore density, but experience using these membranes give rise to unexpected fouling issues.
- A heterogeneity in pore size and pore density protect the membrane from fouling, since smaller pores are sacrificed to maintain integrity of bigger ones (theory of the local critical flux).
- Membrane as nanotech product may apply only specific purposes (not affected by fouling issues).

MEMBRANES AS NANOTECH PRODUCT

- Theory of the local critical flux





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**MEMBRANE APPLICATIONS IN
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CRYSTALLIZATION BY MEMBRANES**

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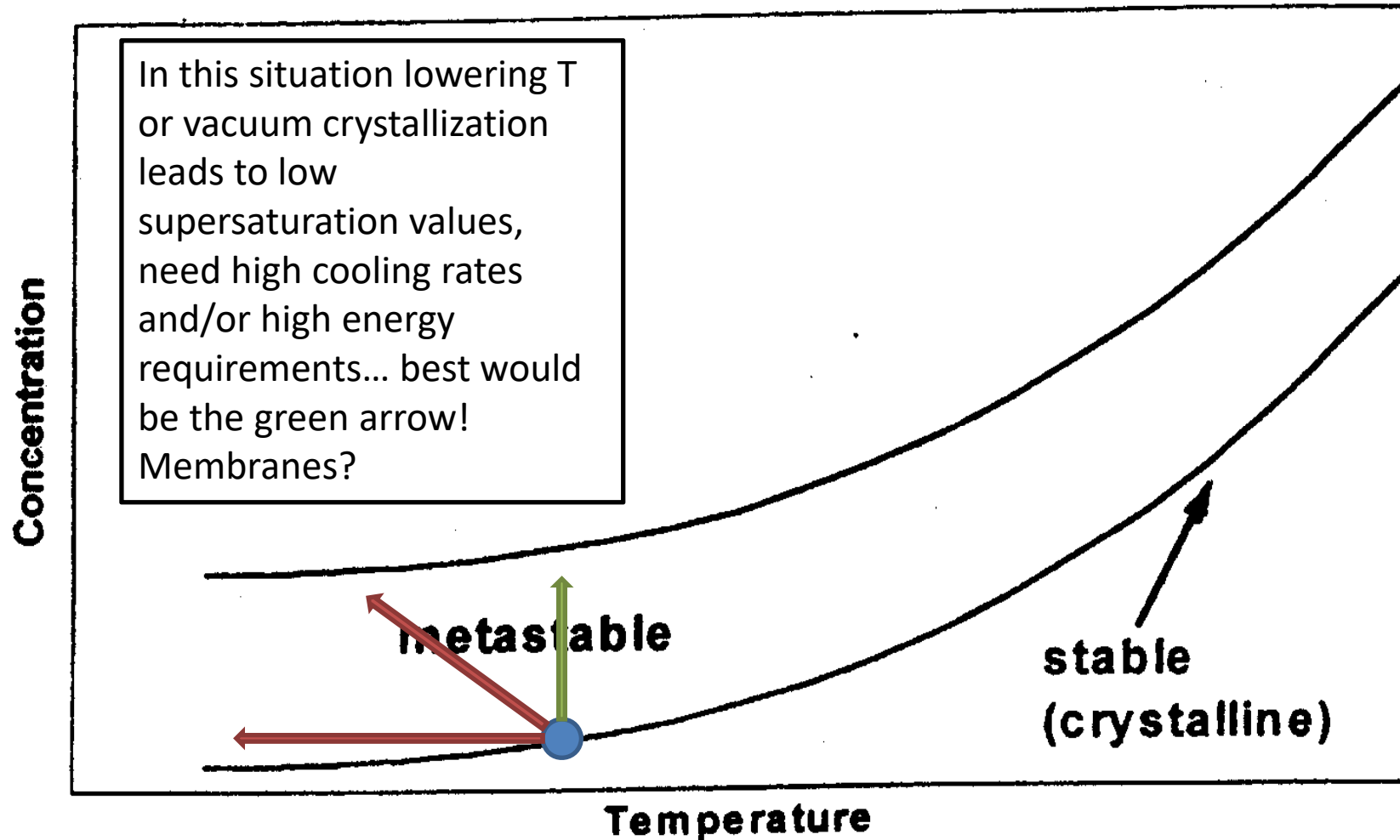
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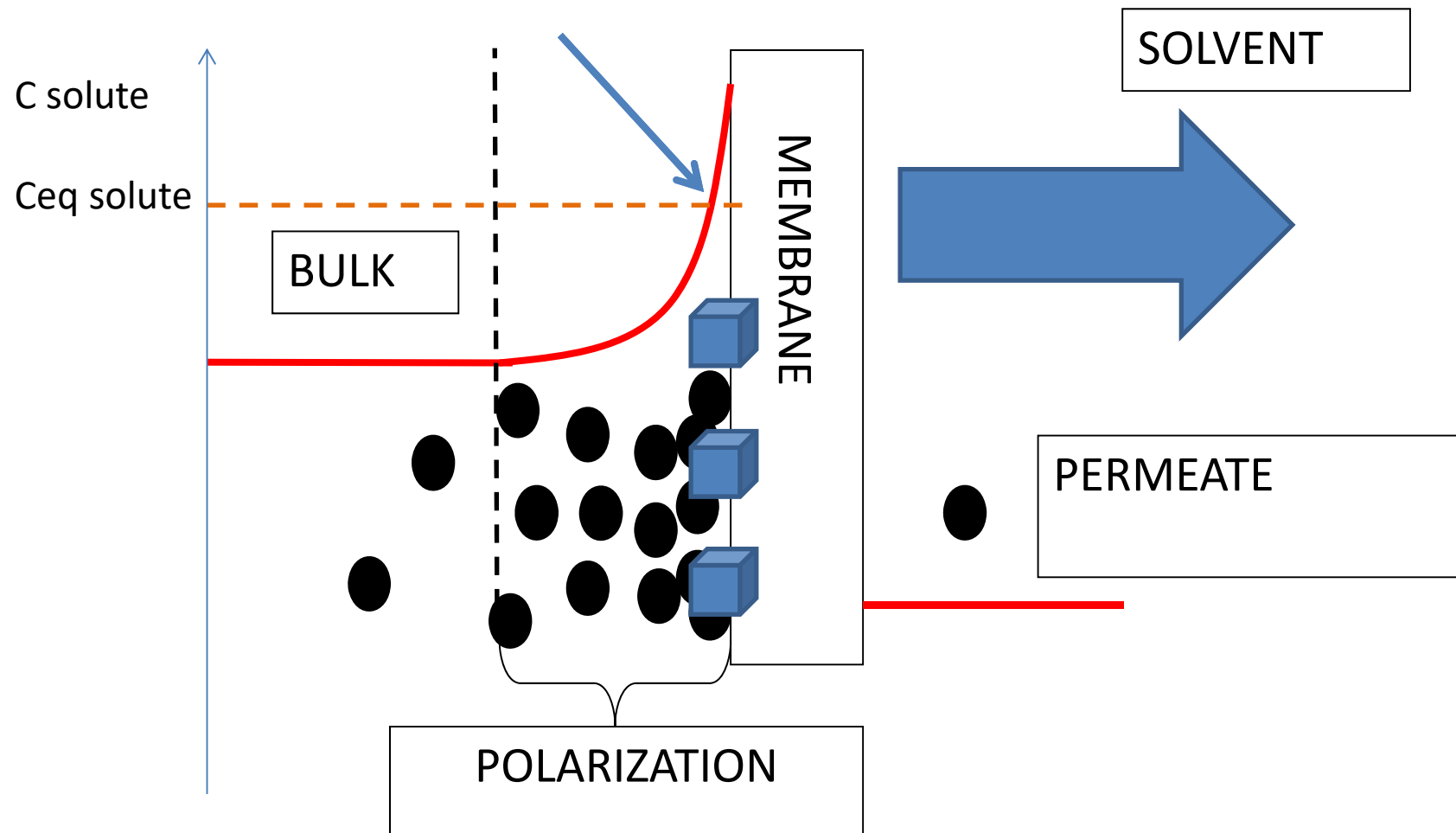
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Back to crystallization fundamentals

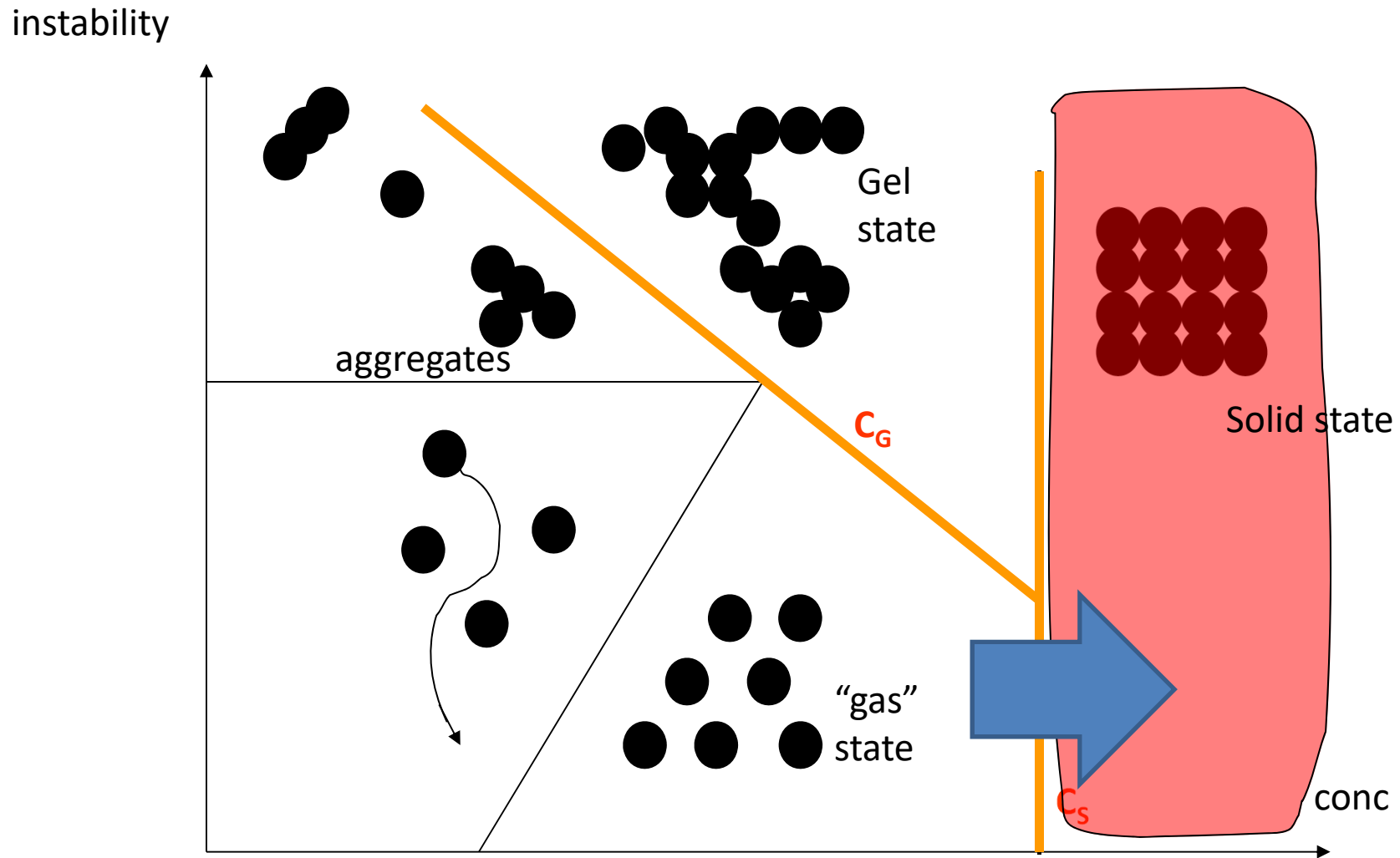


Take advantage of polarization

Membranes remove solvent thus concentrating solutes. Moreover, equilibrium values are reached by polarization!



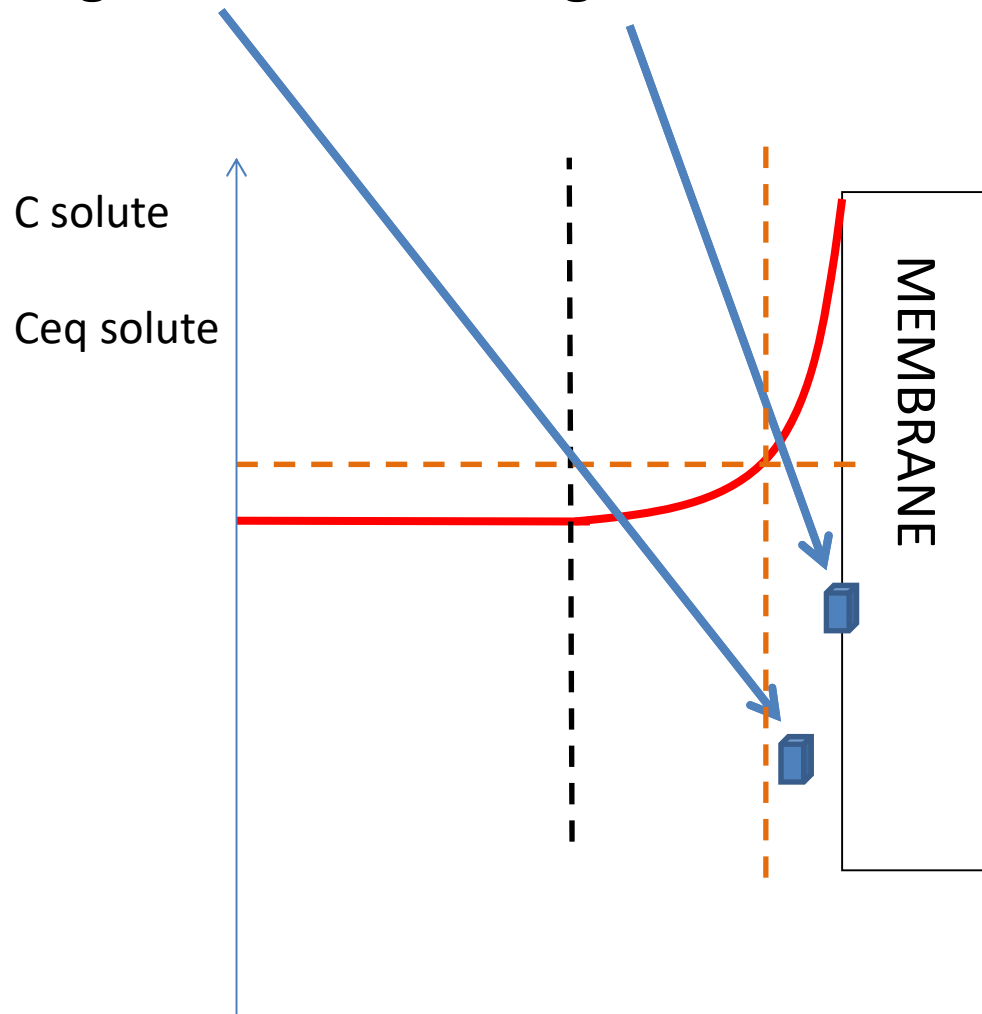
Taking advantage of polarization



NICE CORRIDOR FOR CRYSTALLIZATION! →
PRETREATMENT PROCESSES REMAIN FUNDAMENTAL

Take advantage of polarization

homogeneous or heterogeneous



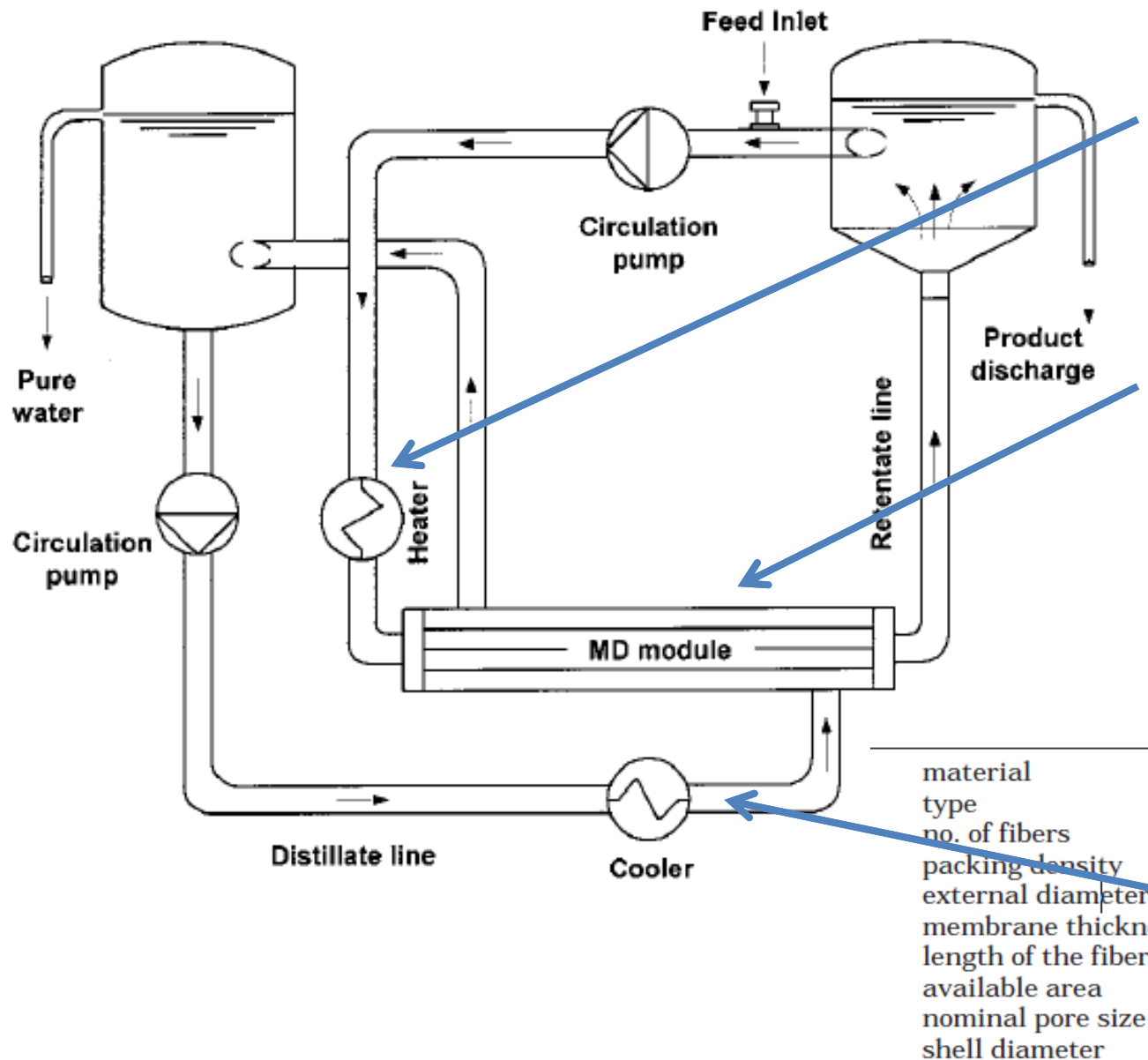
Nucleation may be ...

The second one is promoted at contact with the membrane surface, leading to severe fouling!

The first option needs impressive fine tuning, therefore advantage of

polarization is near to impossible...

Membrane crystallizers (by MD)



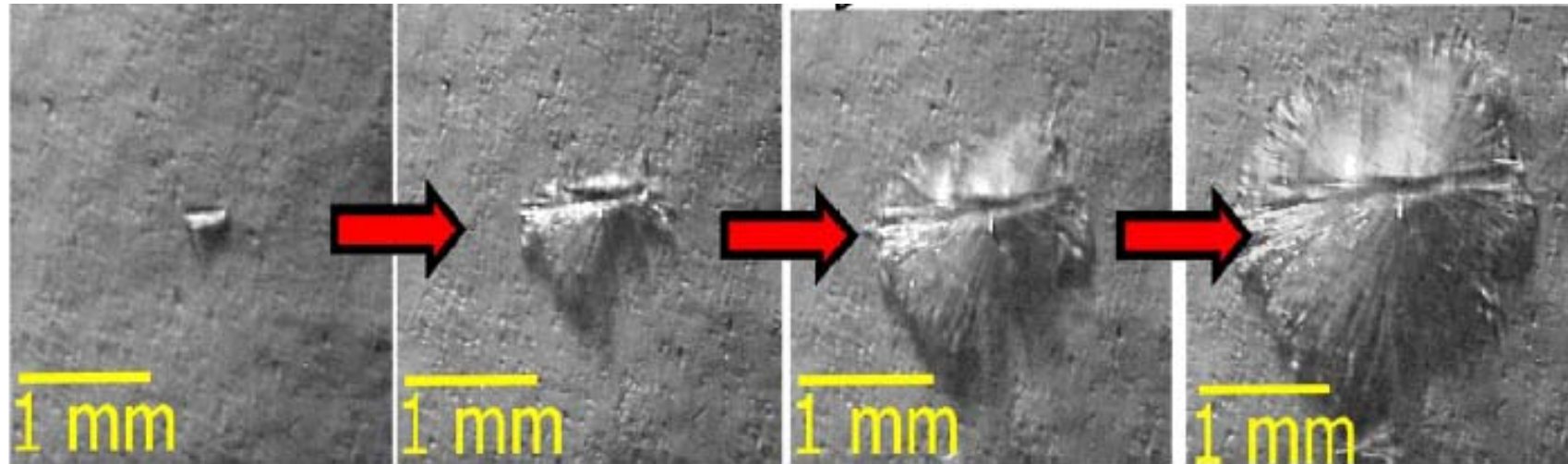
Heater assures below saturation conditions

Membrane removes solvent triggering nucleation as soon as the stream exists the system on the membrane surface. Fouling is the consequence, but may be taking into account for special productions.

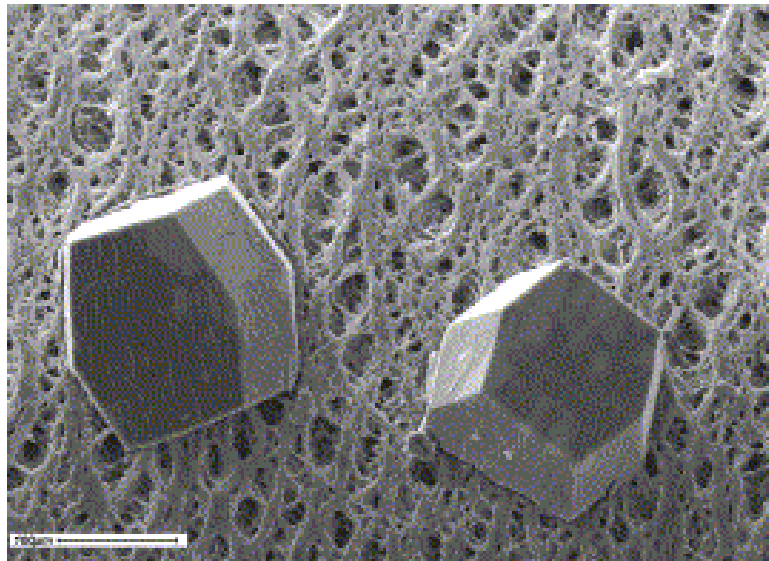
Cold permeate stream of pure solvent promote the solvent evaporation through the pores

Membrane crystallizers (MD)

Gypsum crystal on RO membrane

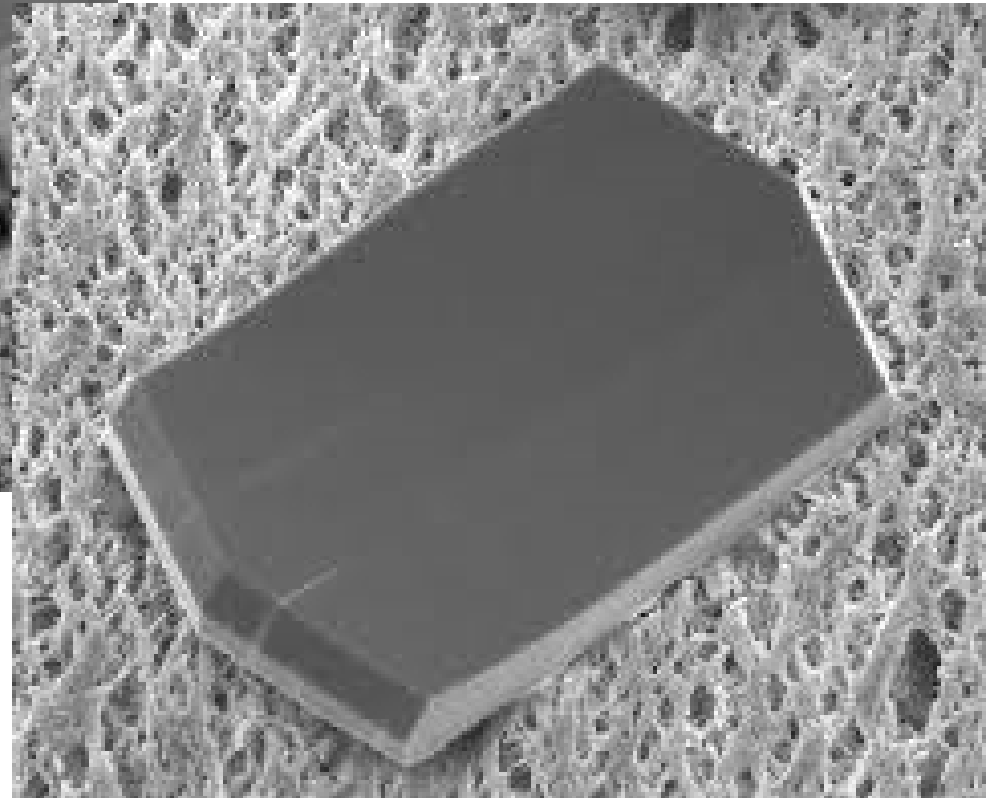


Lysozyme



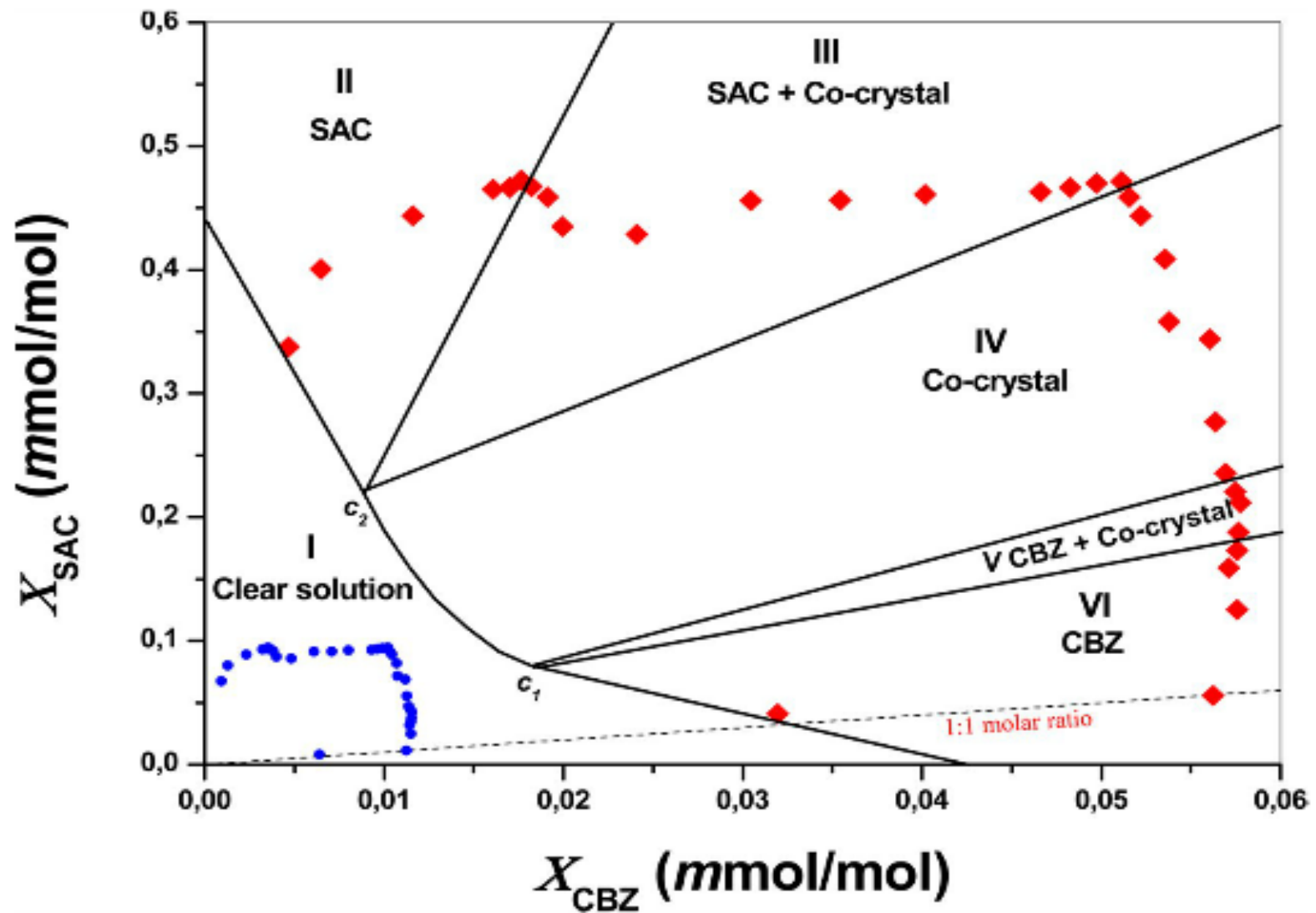
Membrane crystallizers (MD)

Protein crystal growth – **special crystal habits** are obtained by MC!

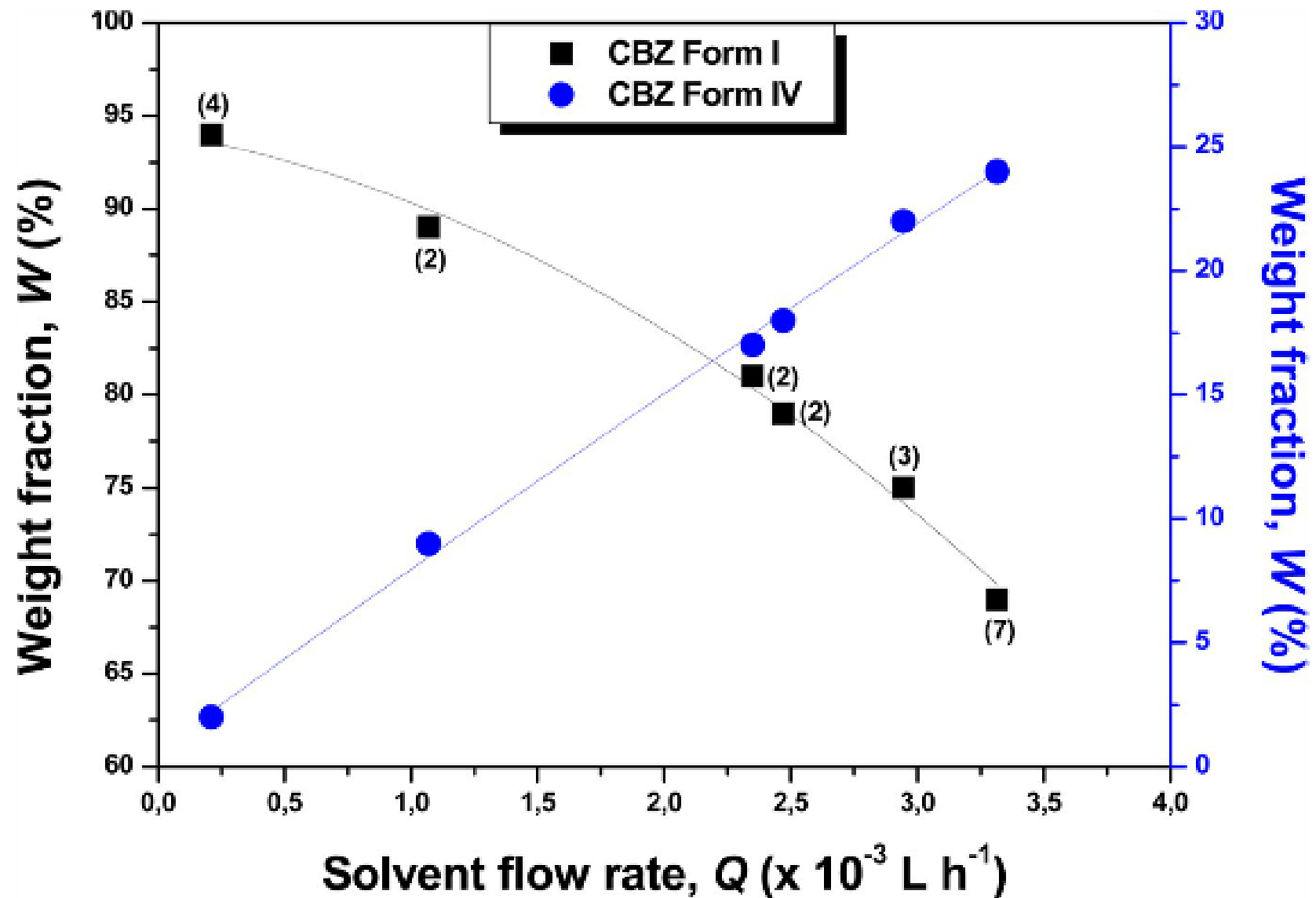


Membrane crystallizers (MD)

Carbamazepin (CBZ) – Saccharose (SAC) crystals from water/ethanol mixtures

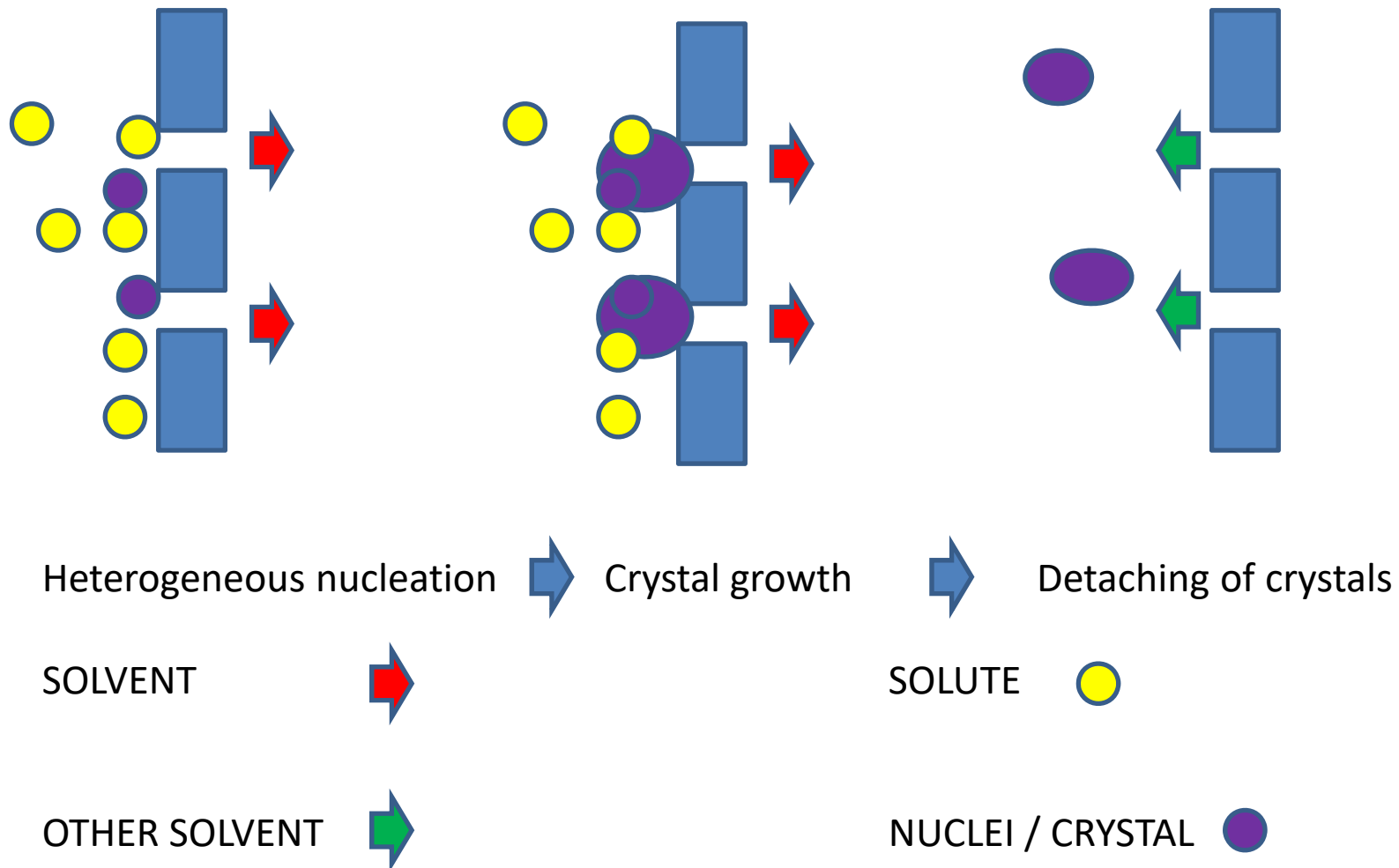


Membrane crystallizers (MD)



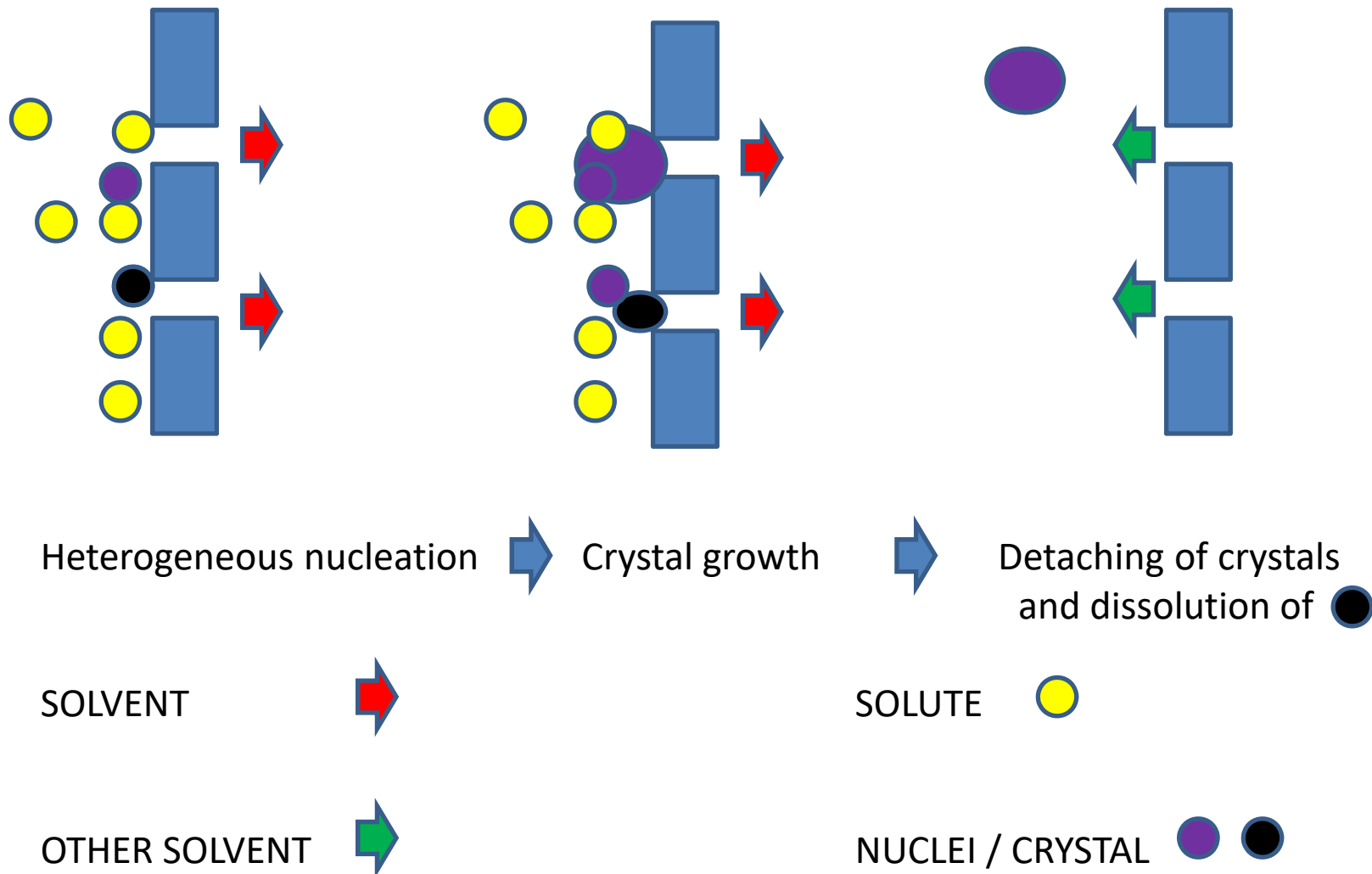
Membrane crystallizers (Heterogeneous)

Two solvent strategy

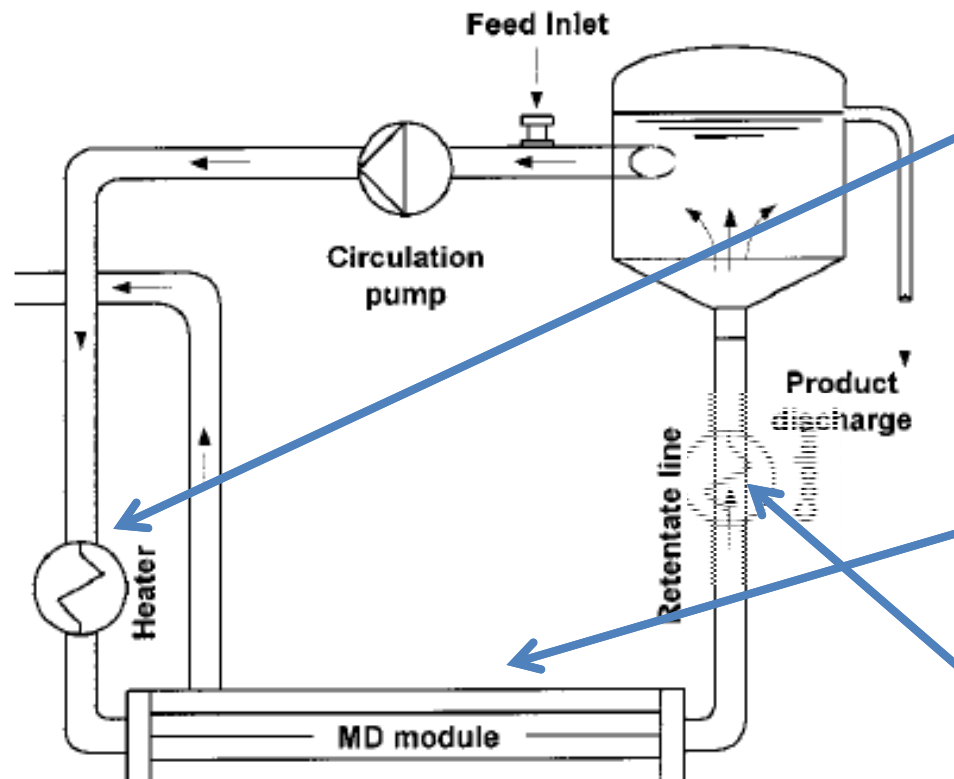


Membrane crystallizers (Heterogeneous)

Two solvent strategy to inhibit polymorphism



Membrane crystallizers (assisted)



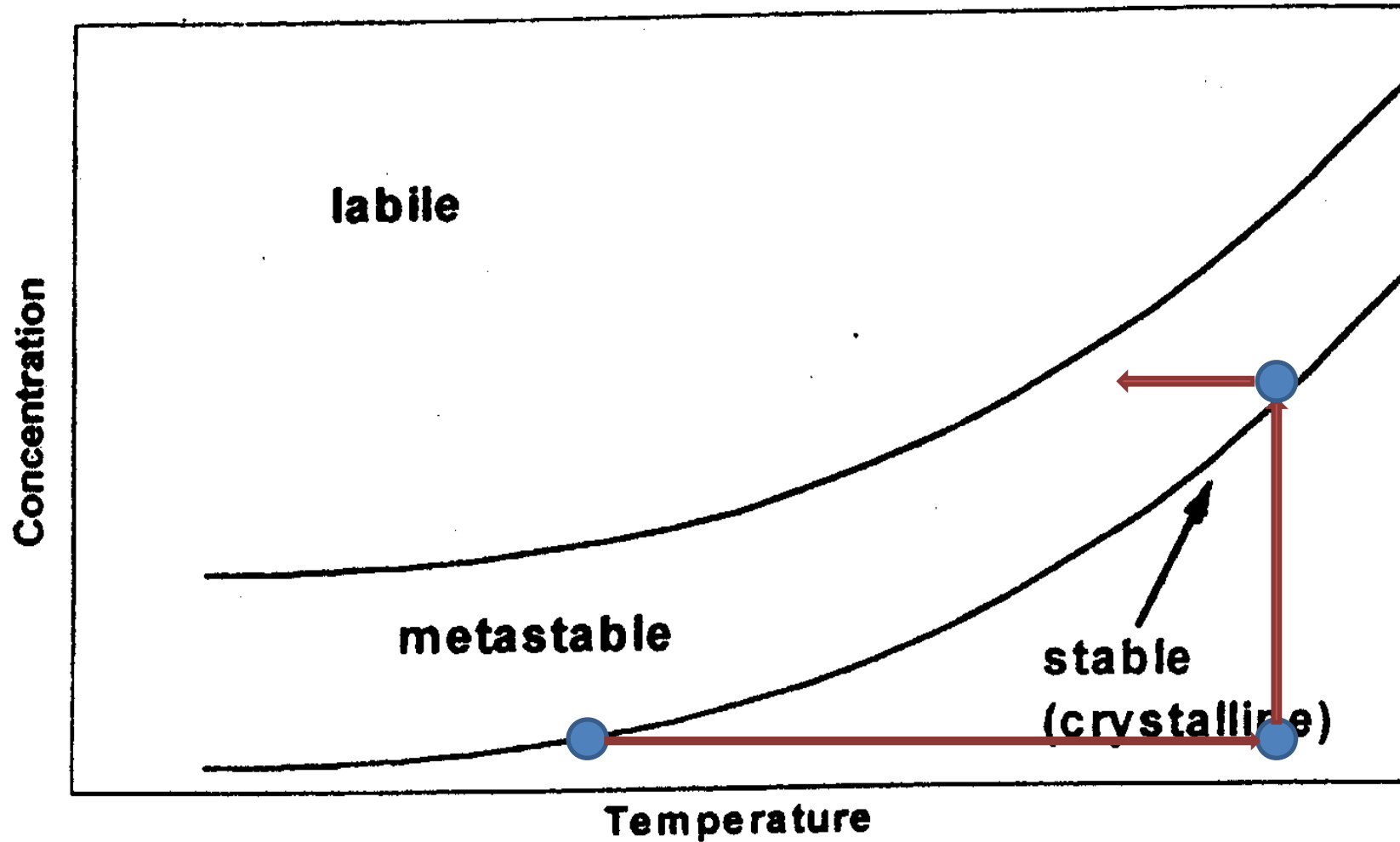
Heater assures below saturation conditions

Membrane removes solvent triggering nucleation as soon as the stream exists the system

Nucleation/growth is promoted in the reactor tank at lower T

material	PP
type	hollow fiber
no. of fibers	40
packing density	70%
external diameter of the fibers	1.8 mm
membrane thickness	120 μm
length of the fibers	45 cm
available area	0.1 m^2
nominal pore size	0.20 μm
shell diameter	2.1 cm

Back to crystallization fundamentals



Membrane crystallizers (assisted)

For the membrane crystallizer of NaCl crystals the following correlation was found:

$$B_0 = 7.3 \cdot 10^{18} M^1 G^{2.08}$$

Therefore, compared to other systems, membrane crystallization should be taken into account in the framework of process intensification.

Table 3. Semiempirical Power Law Relations for Different Conventional Crystallizer Configurations (Impeller Speed N Generally Ranges from 10 to 30 rps)

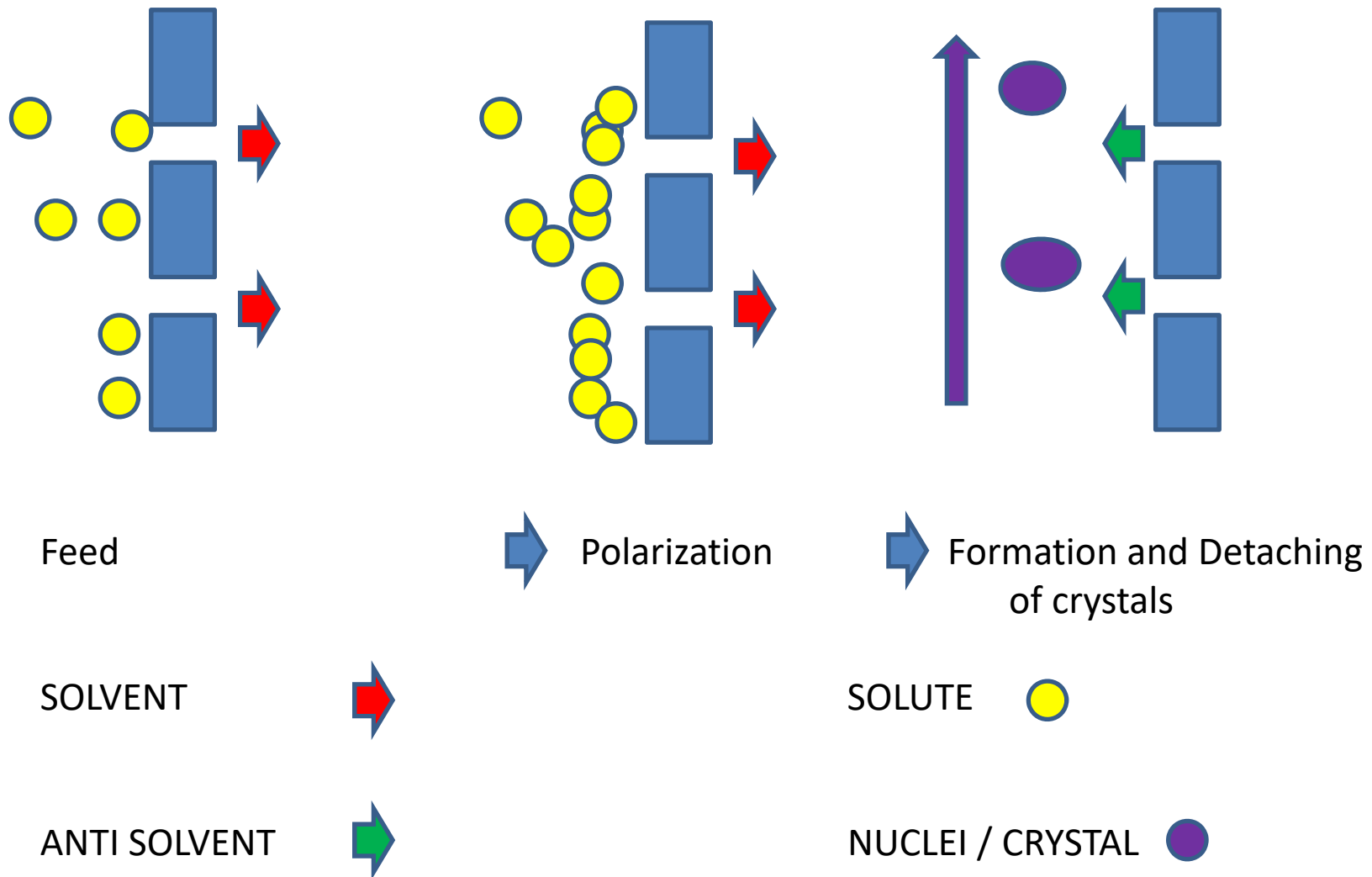
crystallizer	volume (m ³)	correlation
MSMPR	0.055	$8 \times 10^{16} N^2 M G^2$
MSMPR	0.091	$(3.5/11) \times 10^{16} N^2 M G^2$
pilot unit	1.33	$(0.4/1.5) \times 10^{16} N^2 M G^2$
pilot unit	1.0–1.8	$(0.5/1.5) \times 10^{16} N^2 M G^2$
Weston Point	280	$2.5 \times 10^{16} N^2 M G^2$
Swenson Evap.	121	$(10/20) \times 10^{16} N^2 M G^2$

Advantage: no fouling of the membrane

Disadvantage: Operating conditions are defined by design, restriction of design may not allow the production of the desired crystal phase and/or CSD (crystal growth).

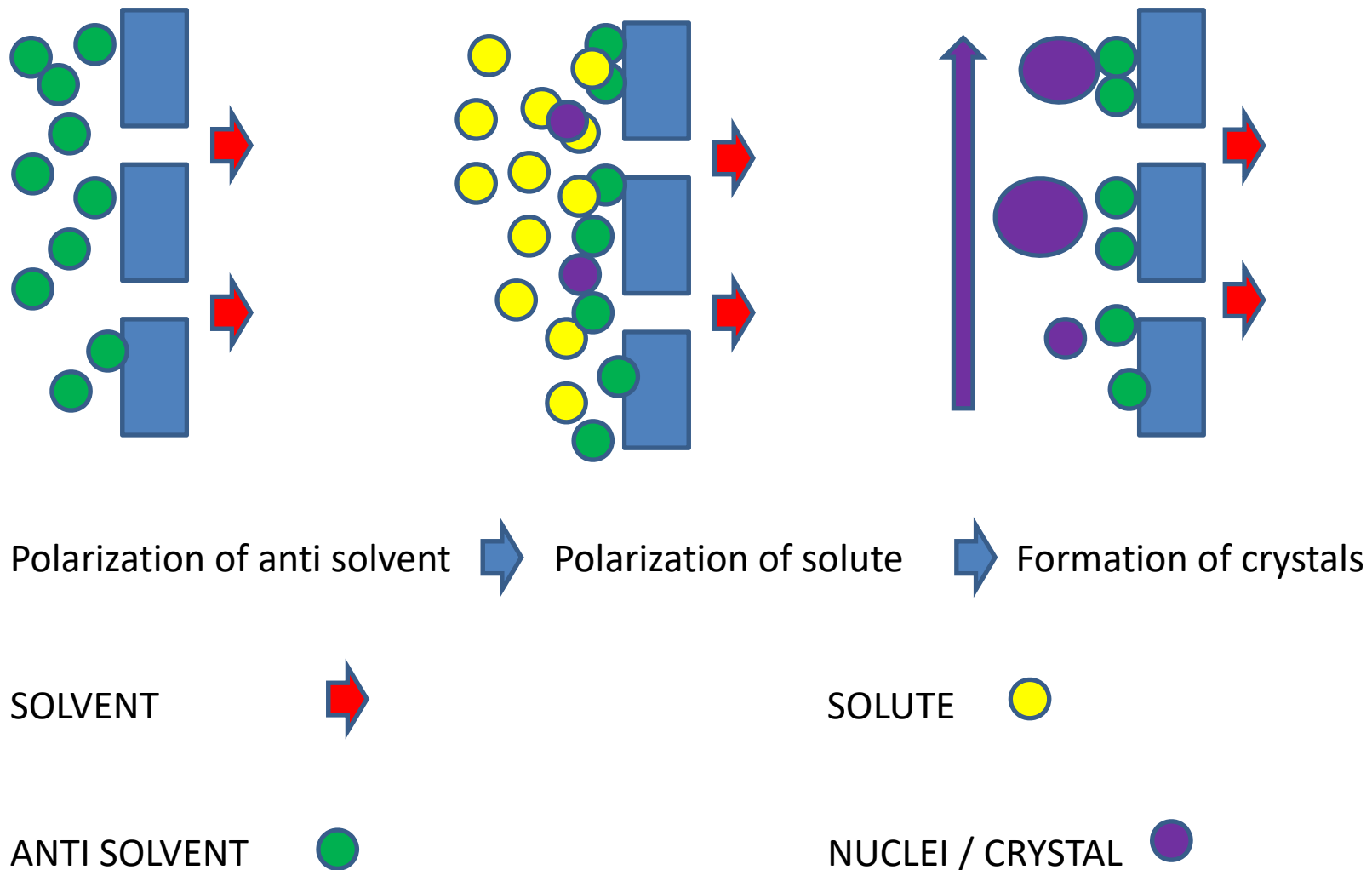
Membrane crystallizers

Anti-solvent strategy (batch)



Membrane crystallizers

Anti-solvent strategy (continuous)



SUMMARY

Membrane crystallizers generates supersaturation by:

1. Membrane assisted crystallization where solvent is separated to an extent that permits after cooling to reach desired supersaturation in the crystallizer
2. Membrane distillation or osmotic distillation, where solvent passes the membrane at vapor phase thus leaving solutes dry on the membrane surface
3. Impermeable hollow fibers used as micro heat exchanger for cooling crystallization
4. Antisolvent forced as liquid in the feed stream trough the membrane pores
5. Antisolvent dosed in the feed stream and concentrated on the membrane due to different selectivities.