Crystallization of salts in a porous medium

A tribute to Gilles Chanvillard

George W. Scherer , Princeton University

July 5, 2016

Salts in a porous medium

- What is the problem?
- Gilles' approach to the equilibrium state
- Non equilibrium considerations
- Experimental study of growth in pore networks

Mirabilite in Limestone

- Indiana limestone pores contain thenardite (Na_2SO_4)
- Precipitation of mirabilite ($Na_2SO_4 \bullet 10H_2O$) destroys stone

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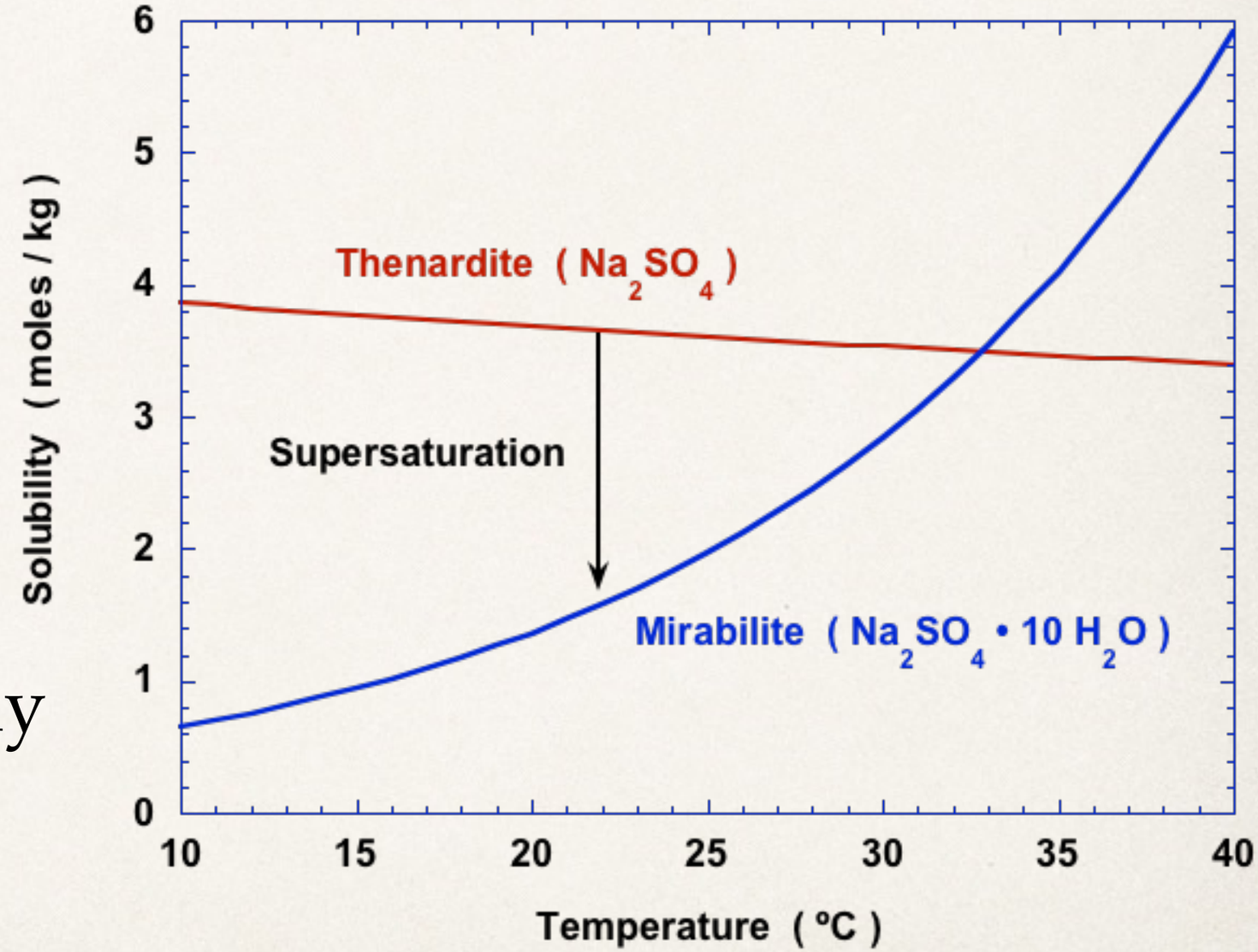
Stress from Mirabilite

- Dry salt dissolves until solution is saturated with respect to thenardite
- That solution is highly supersaturated with respect to mirabilite



Driving Force for Growth: Supersaturation

- Dissolution of hydrated salt

$$Na_2SO_4 \cdot 10H_2O \rightleftharpoons 2Na^+ + SO_4^{2-} + 10H_2O$$

Solubility product: $Q = \left[Na^+\right]^2 \left[SO_4^{2-}\right] \left[H_2O\right]^{10}$

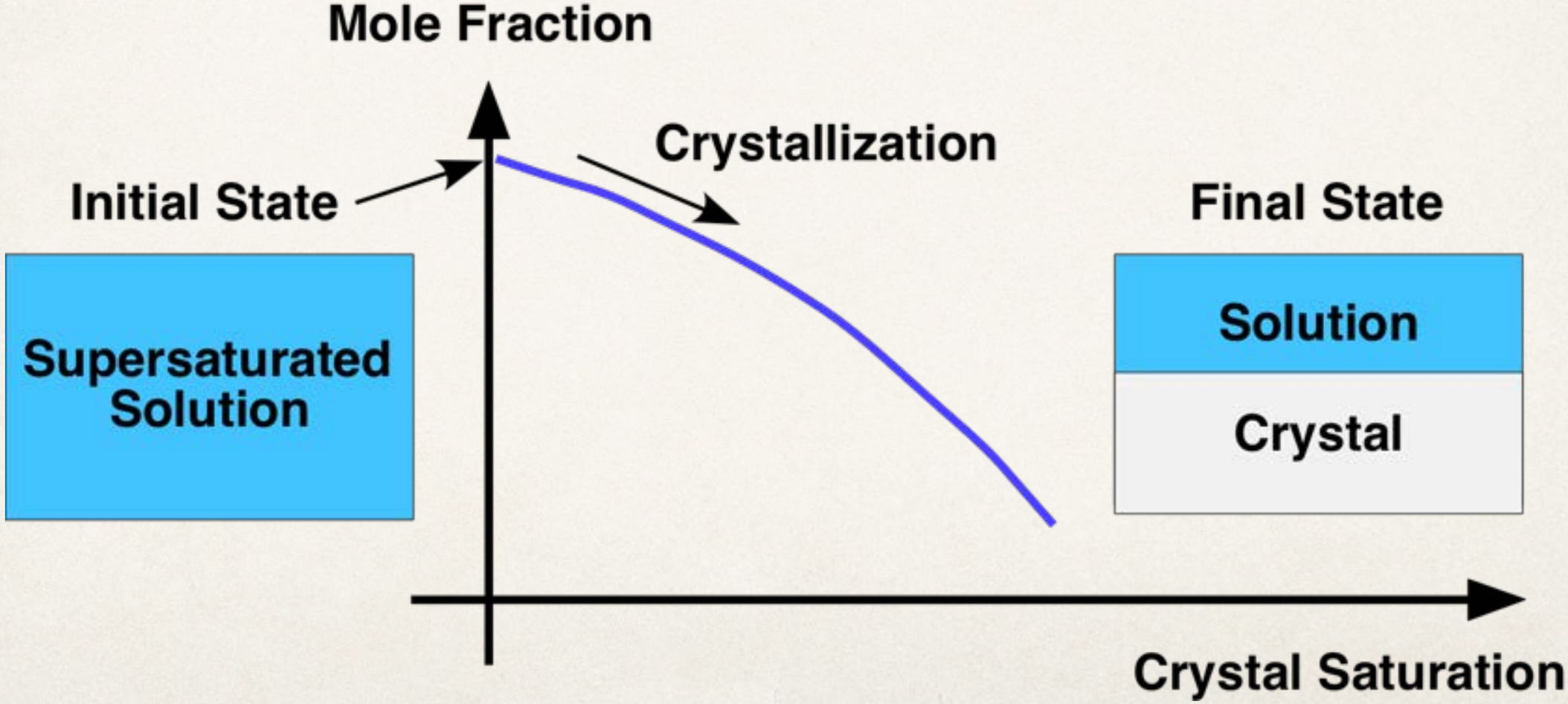
Equilibrium constant: $Q = K\left[T\right]$

- Pressure needed to suppress growth of a macroscopic crystal

$$p = \frac{RT}{V_M} \ln\left[\frac{Q}{K\left[T\right]}\right] \approx \frac{R_g T}{V_M} \ln\left[\left(\frac{c}{c_s}\right)^3\right]$$

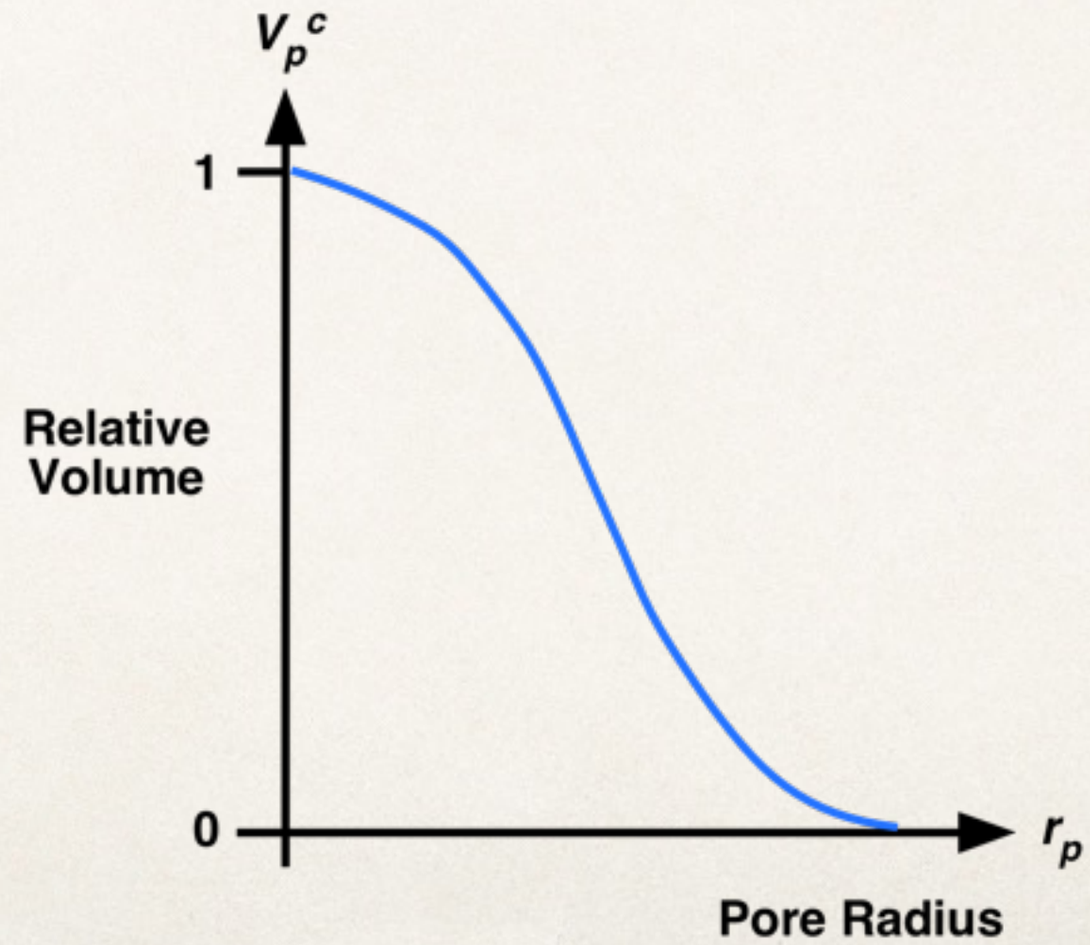
Concentration versus Saturation

- As degree of saturation with crystals increases, mole fraction of solute decreases



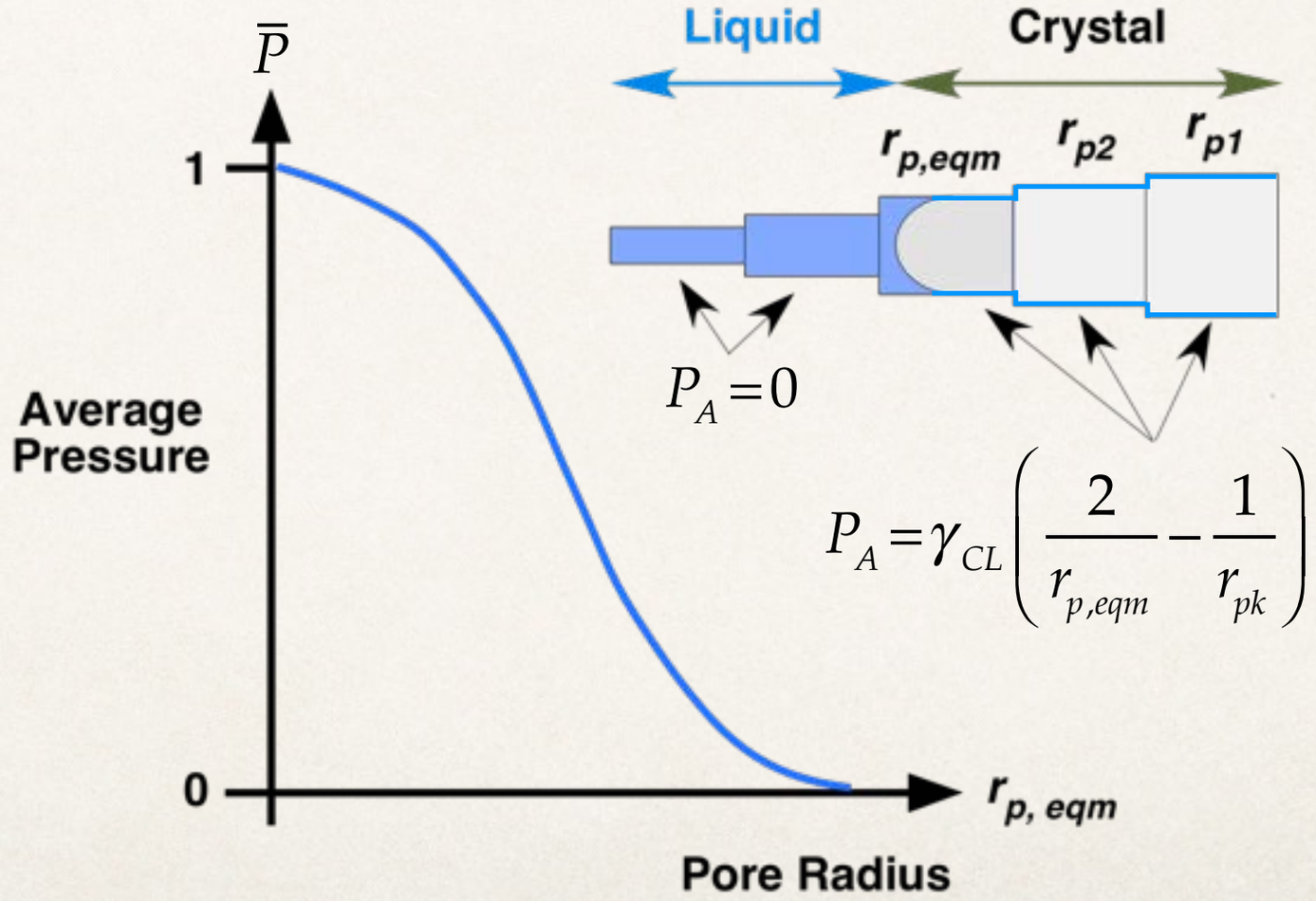
Saturation versus Pore radius

- Crystals progressively invade smaller pores, reaching full saturation as $r_p \to 0$



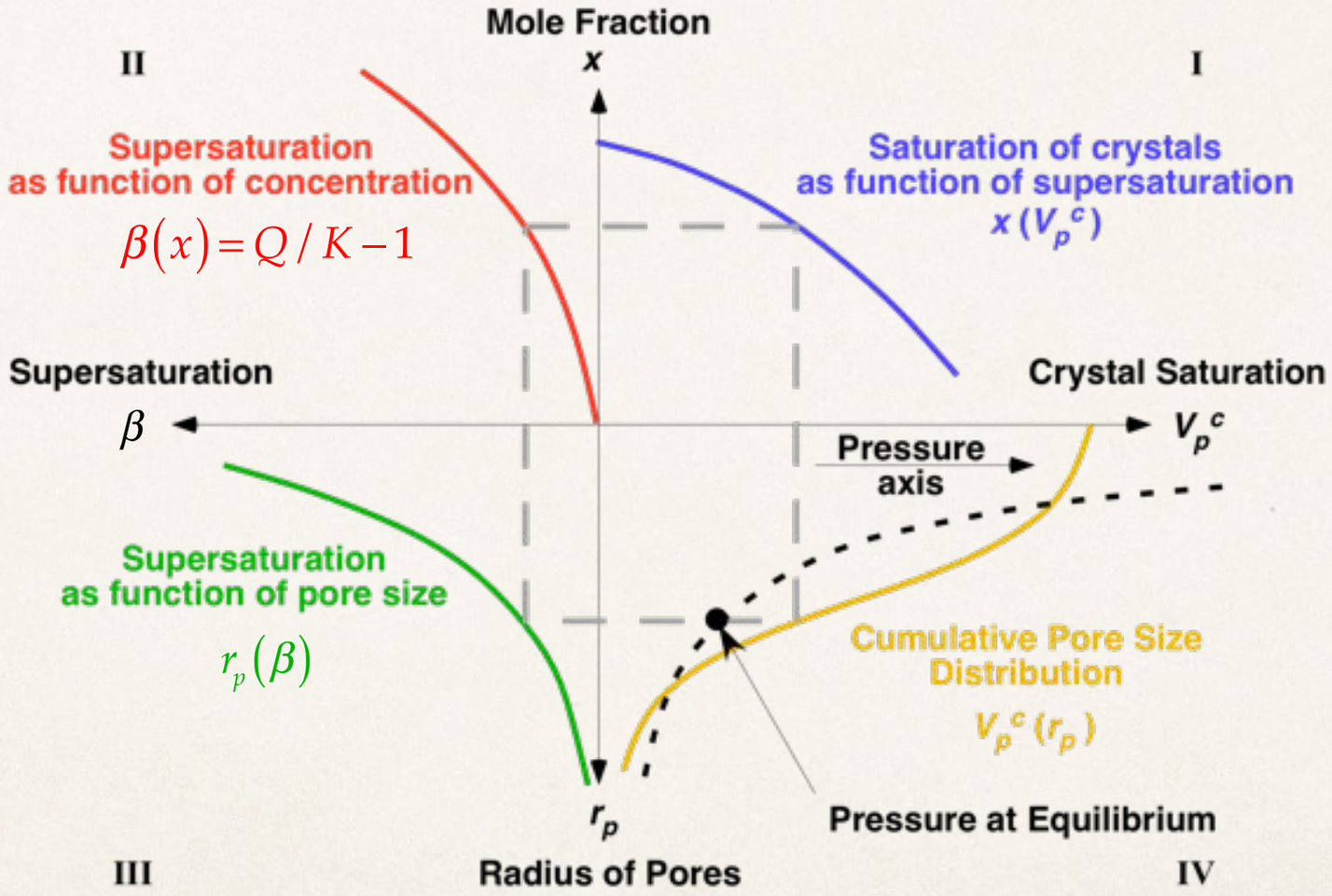
Crystallization pressure vs Radius

- As smaller pores are invaded, the pressure applied to the pore walls, $P_{A,}$ increases



Chanvillard Diagram

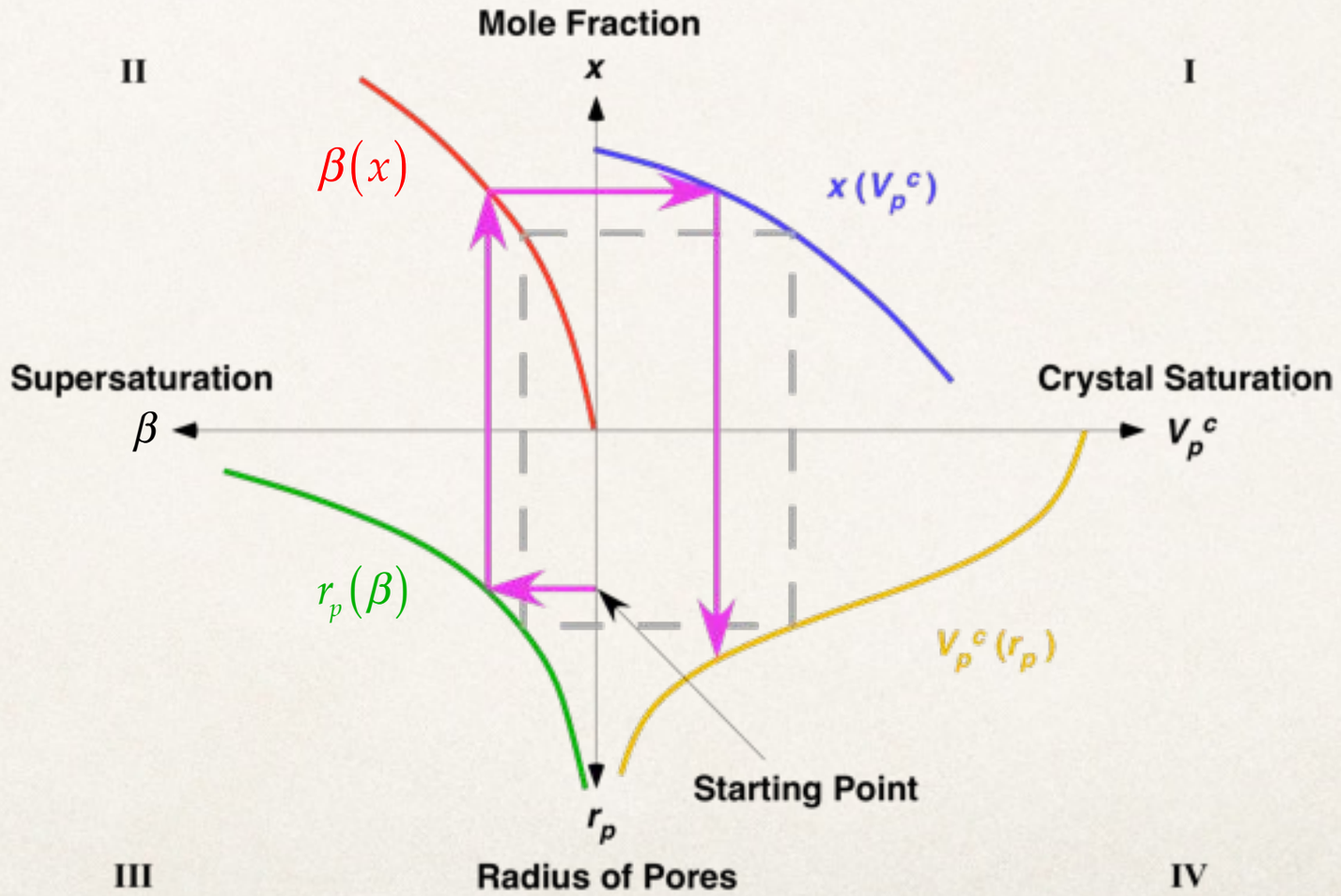
- Equilibrium state corresponds to osculating rectangle



Chemistry | Microstructure

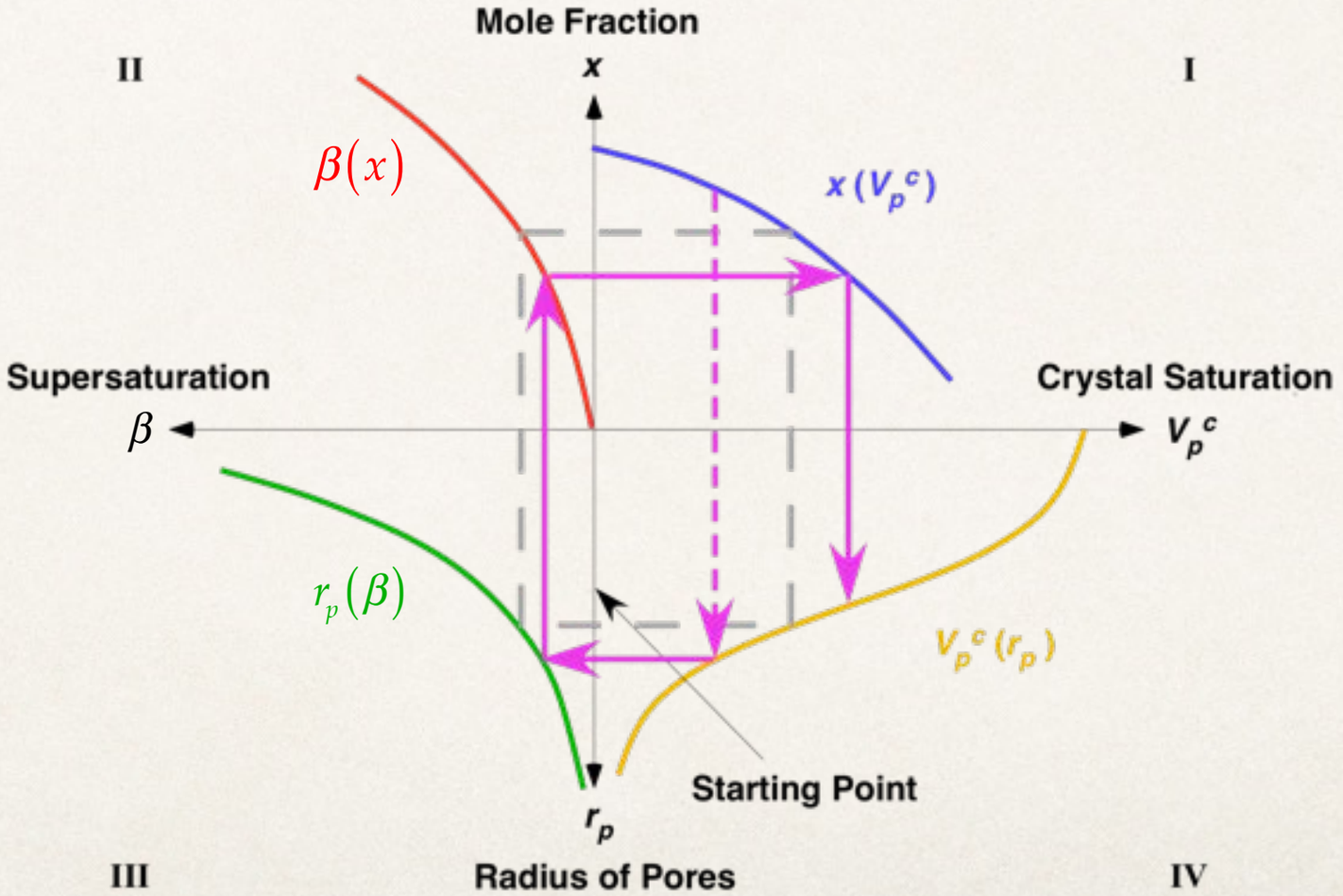
Approaching equilibrium

- First cycle from arbitrary starting point



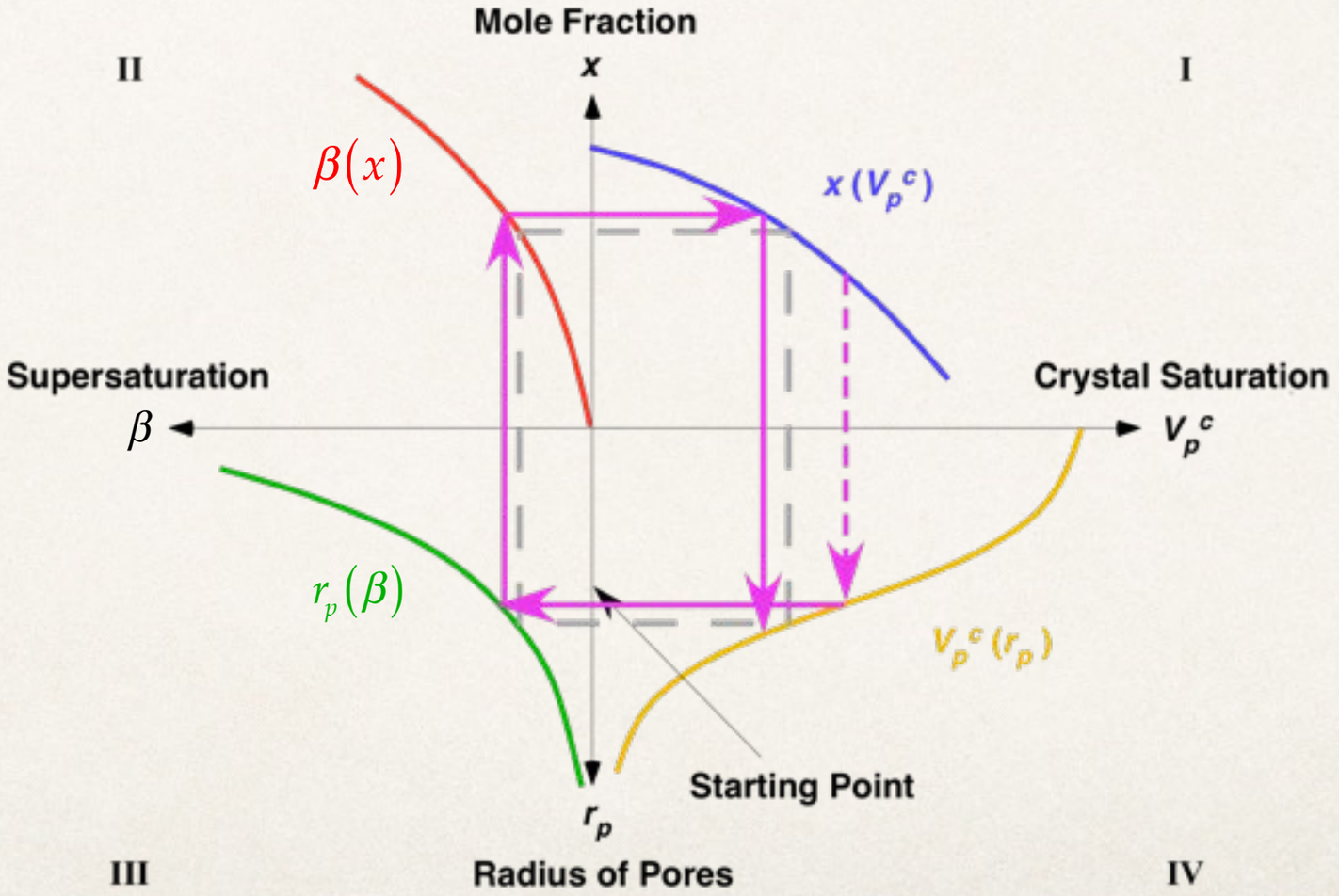
Approaching equilibrium

- Second cycle



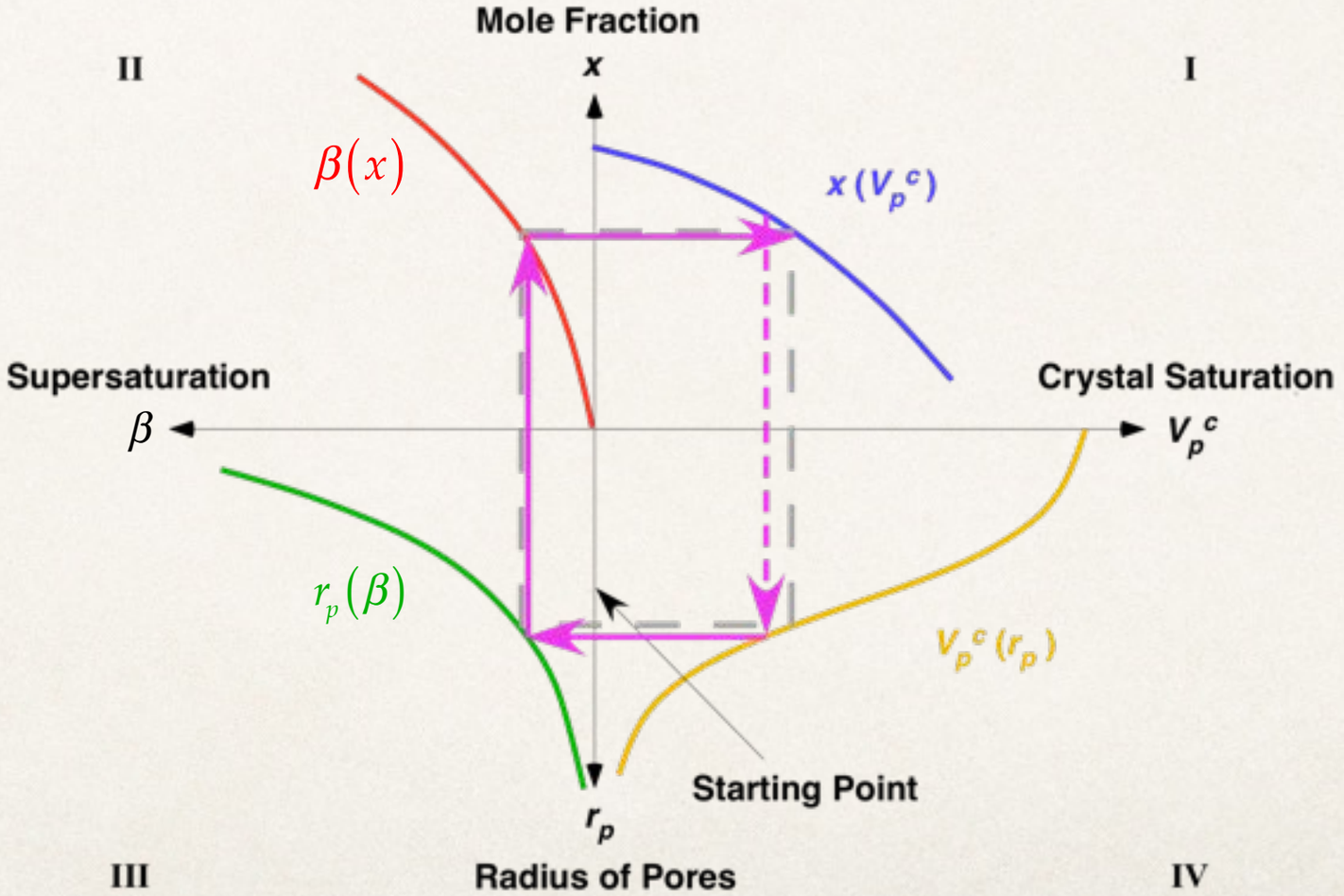
Approaching equilibrium

- Third cycle



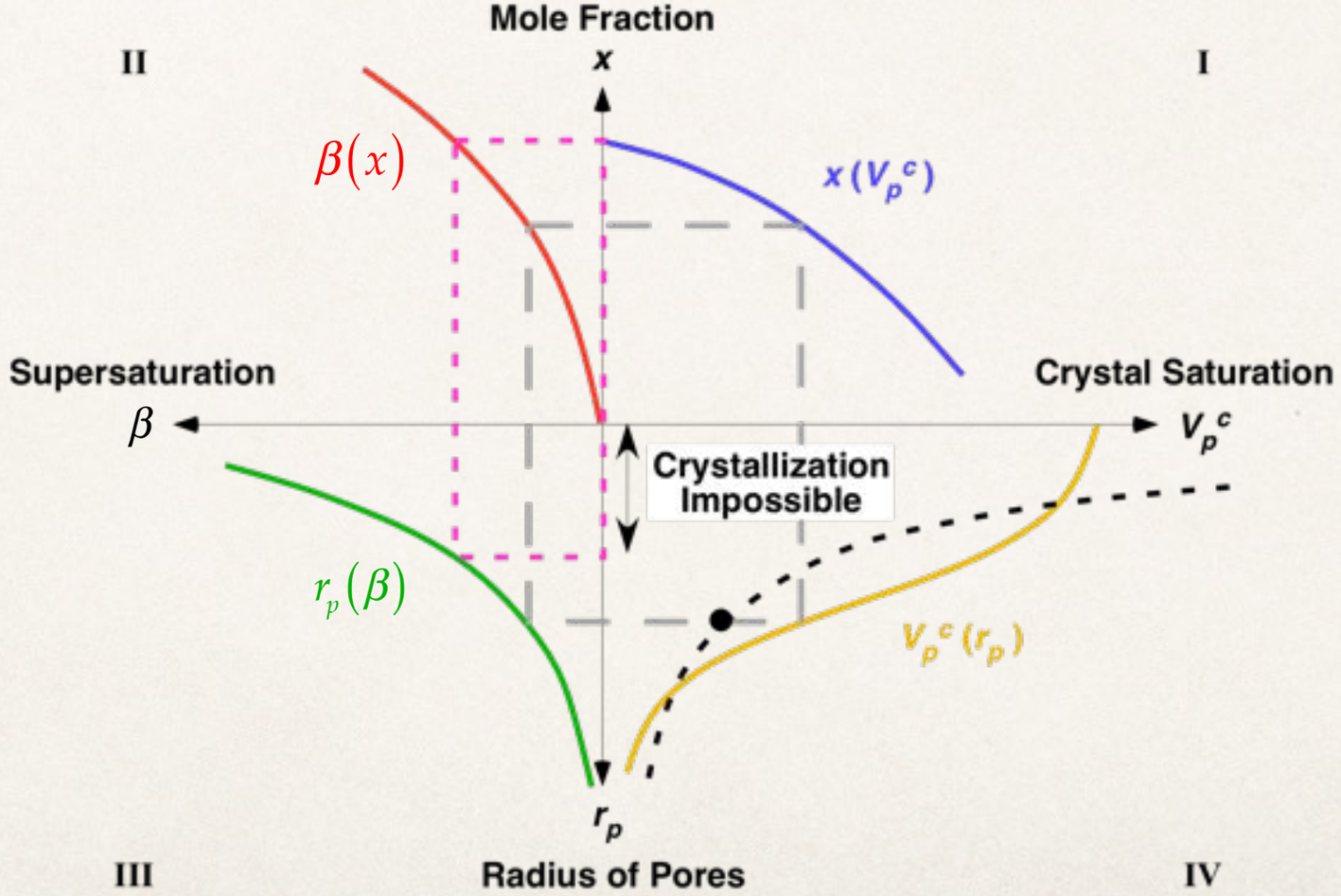
Approaching equilibrium

- Fourth cycle → approaching equilibrium



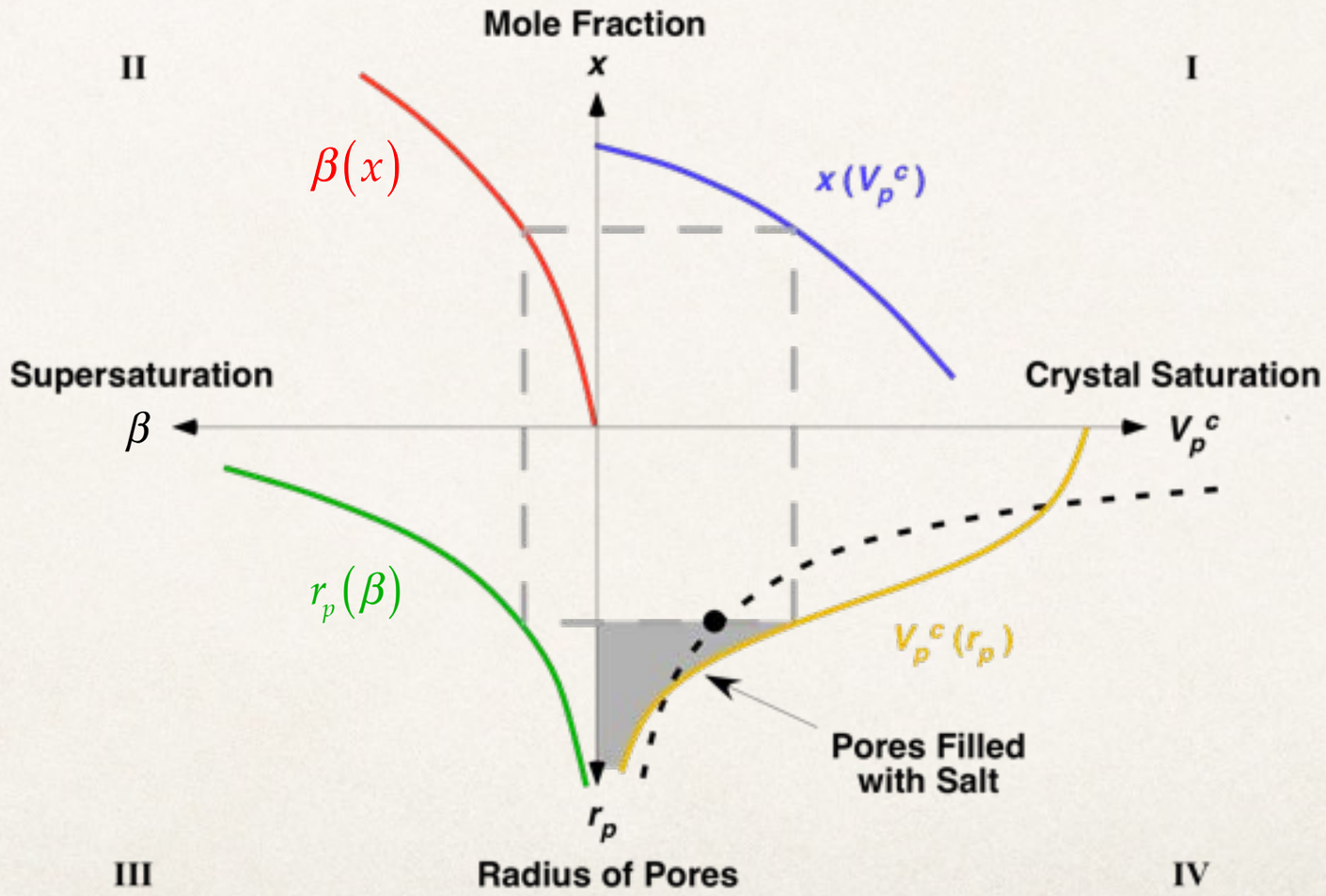
Inaccessible pores

- Initial concentration limits size of pores that salt can enter



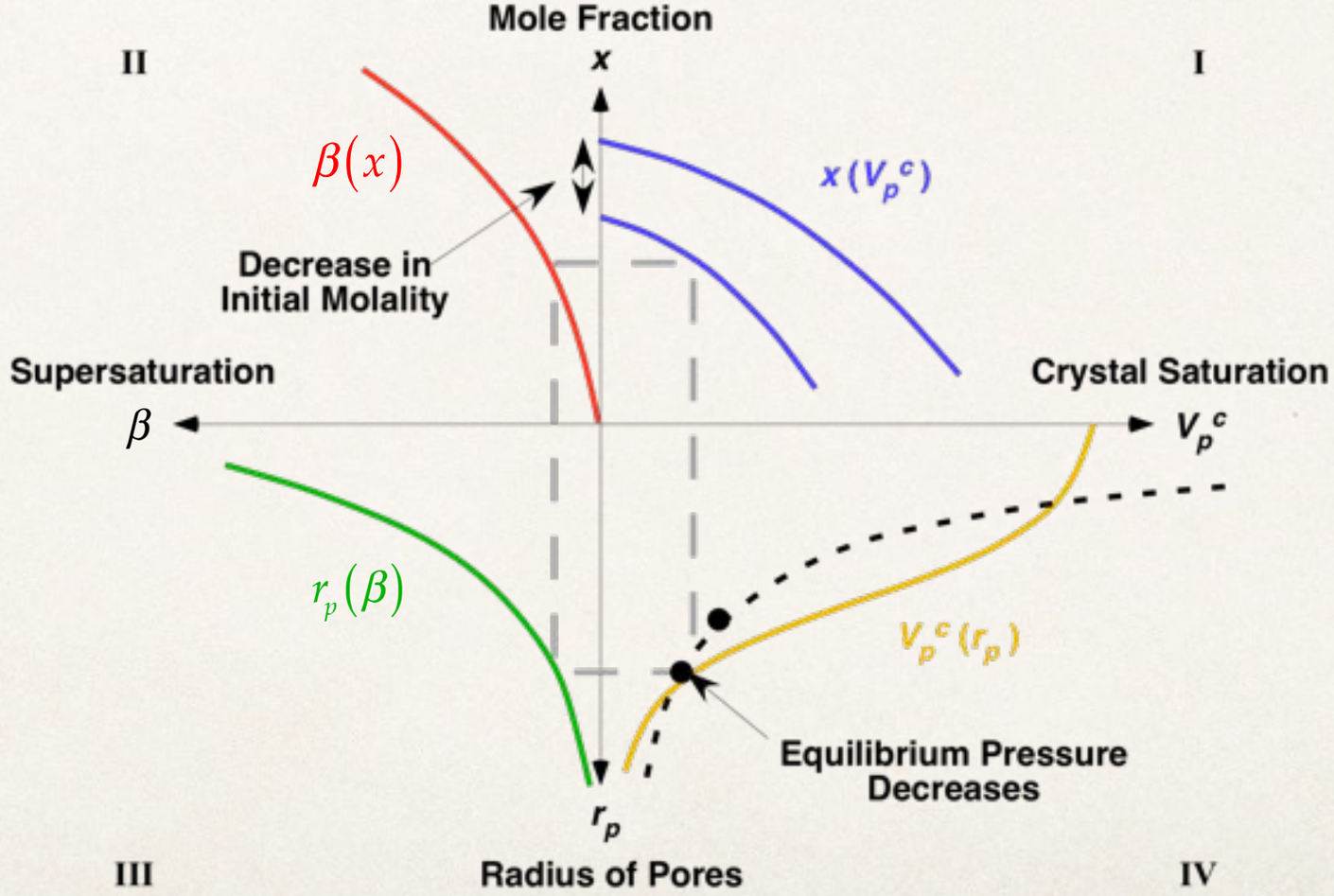
Crystal saturation

- Equilibrium box bounds salt-filled pores



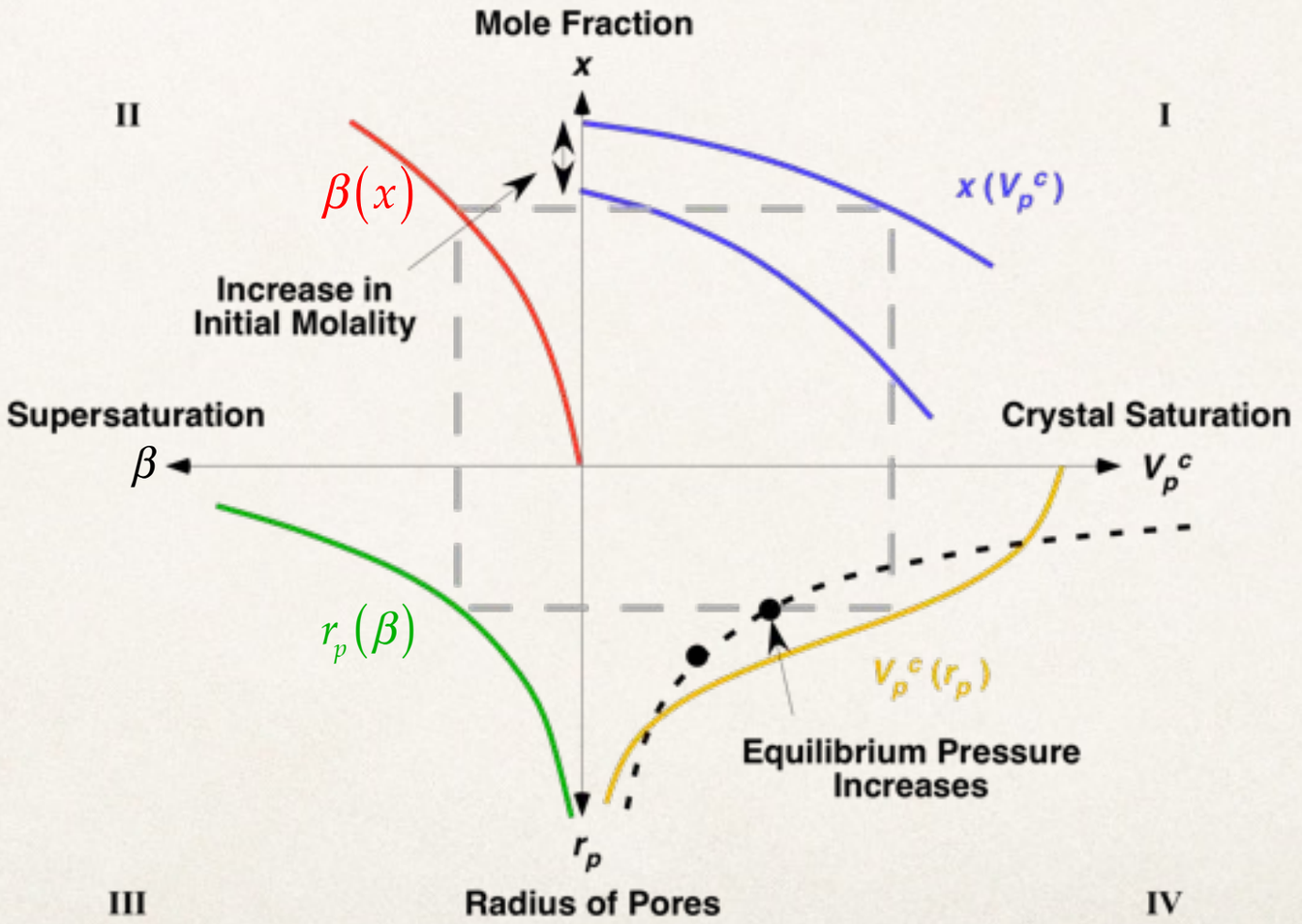
Effect of concentration

- Decreasing x decreases pressure on pore walls



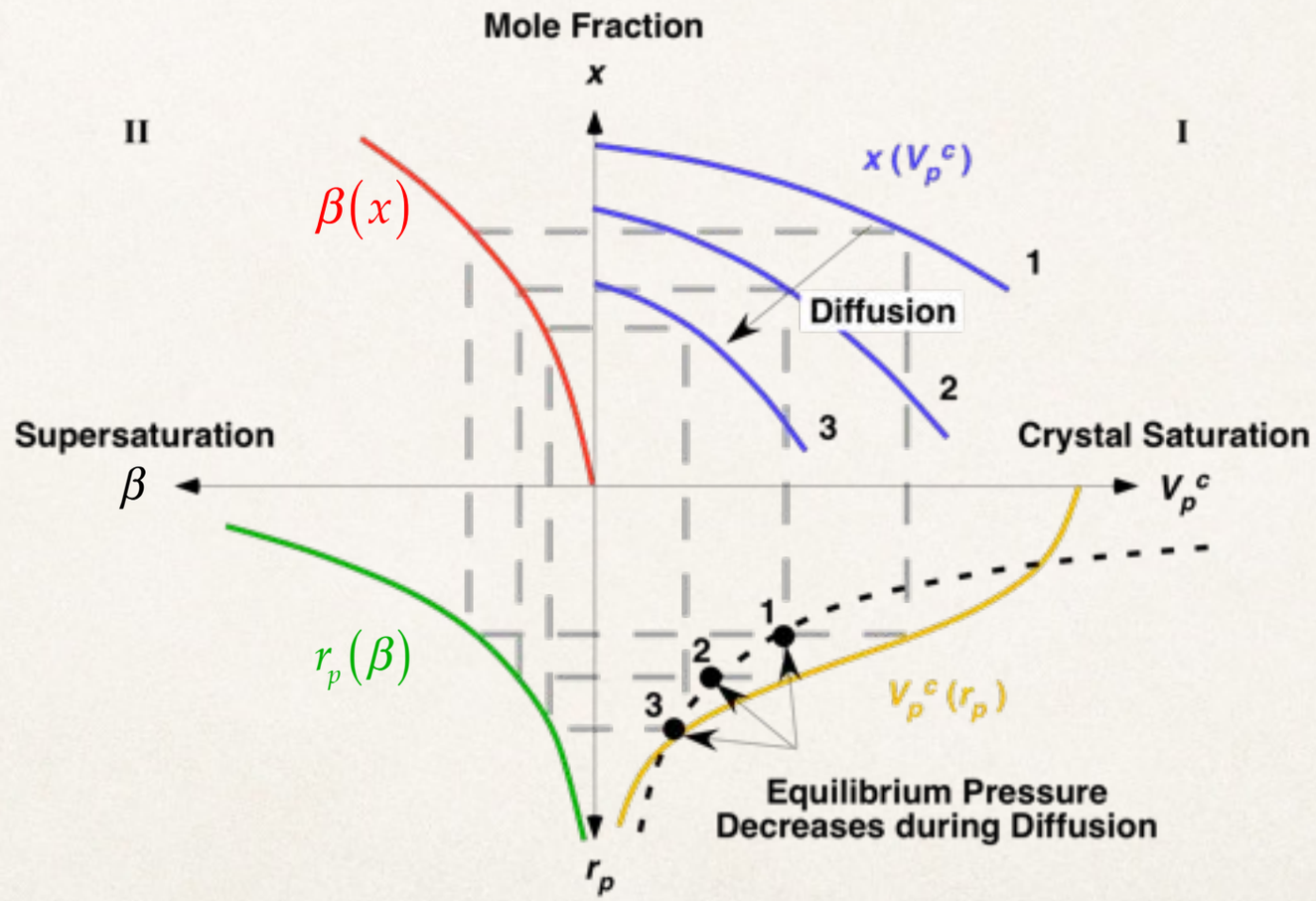
Effect of concentration

- Raising x increases pressure on pore walls



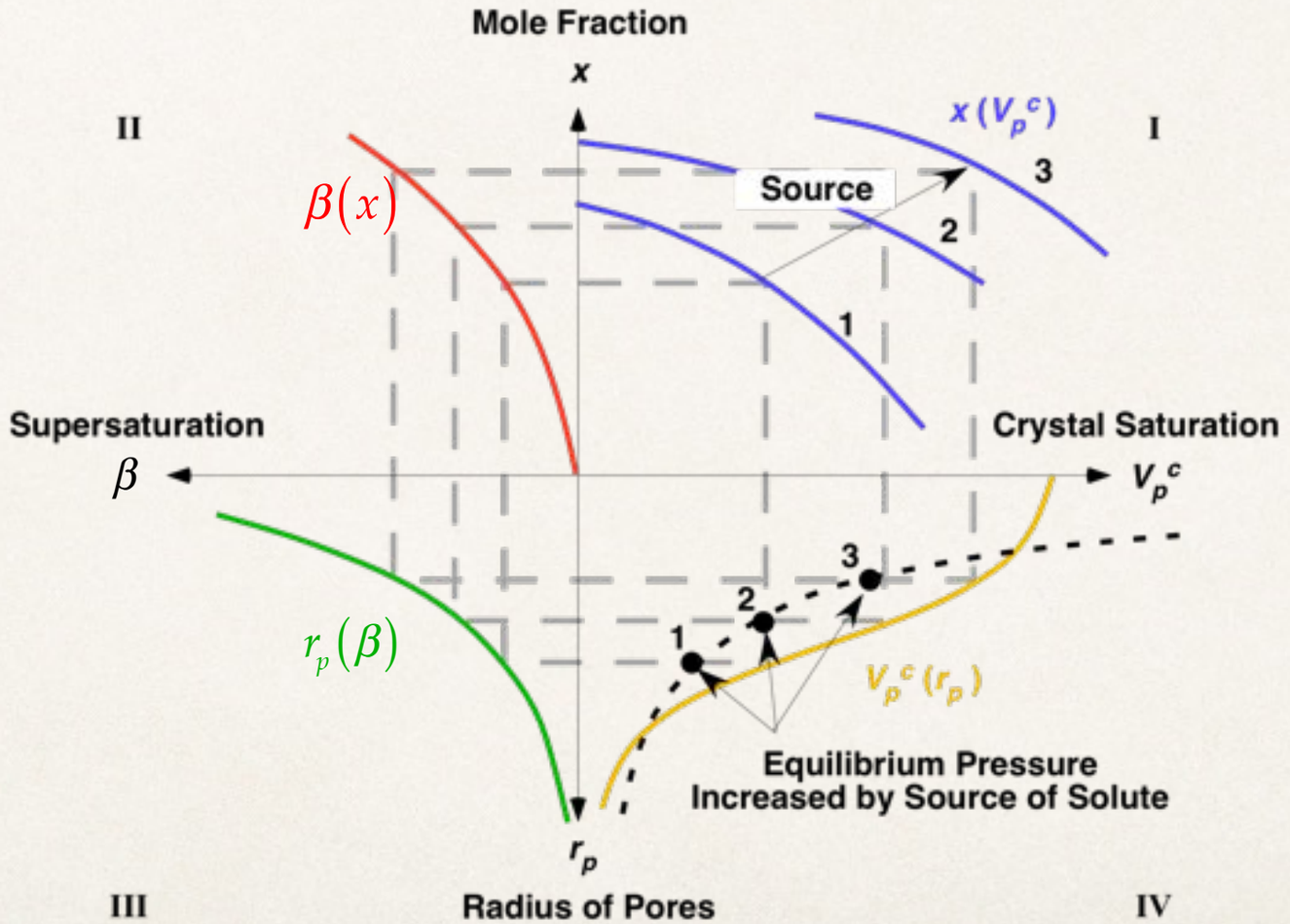
Coarsening

- Diffusion of salt out of the body reduces P_A



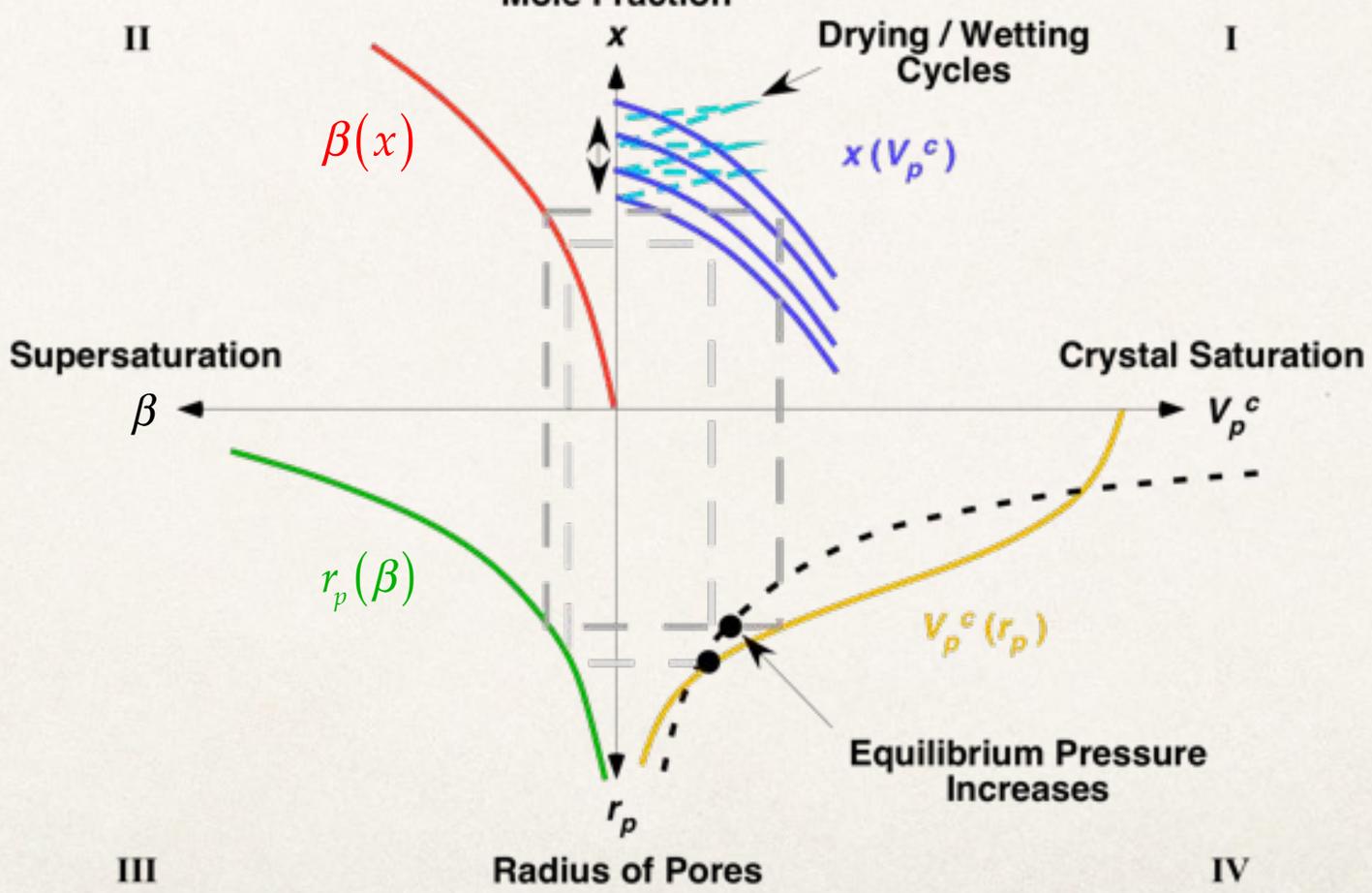
External source of salt

- Entry of salt, evaporation, or cooling raises x and P_A



Wetting / Drying Cycles

- Rewetting with salt-rich solution raises x and P_A



Limitations of equilibrium analysis

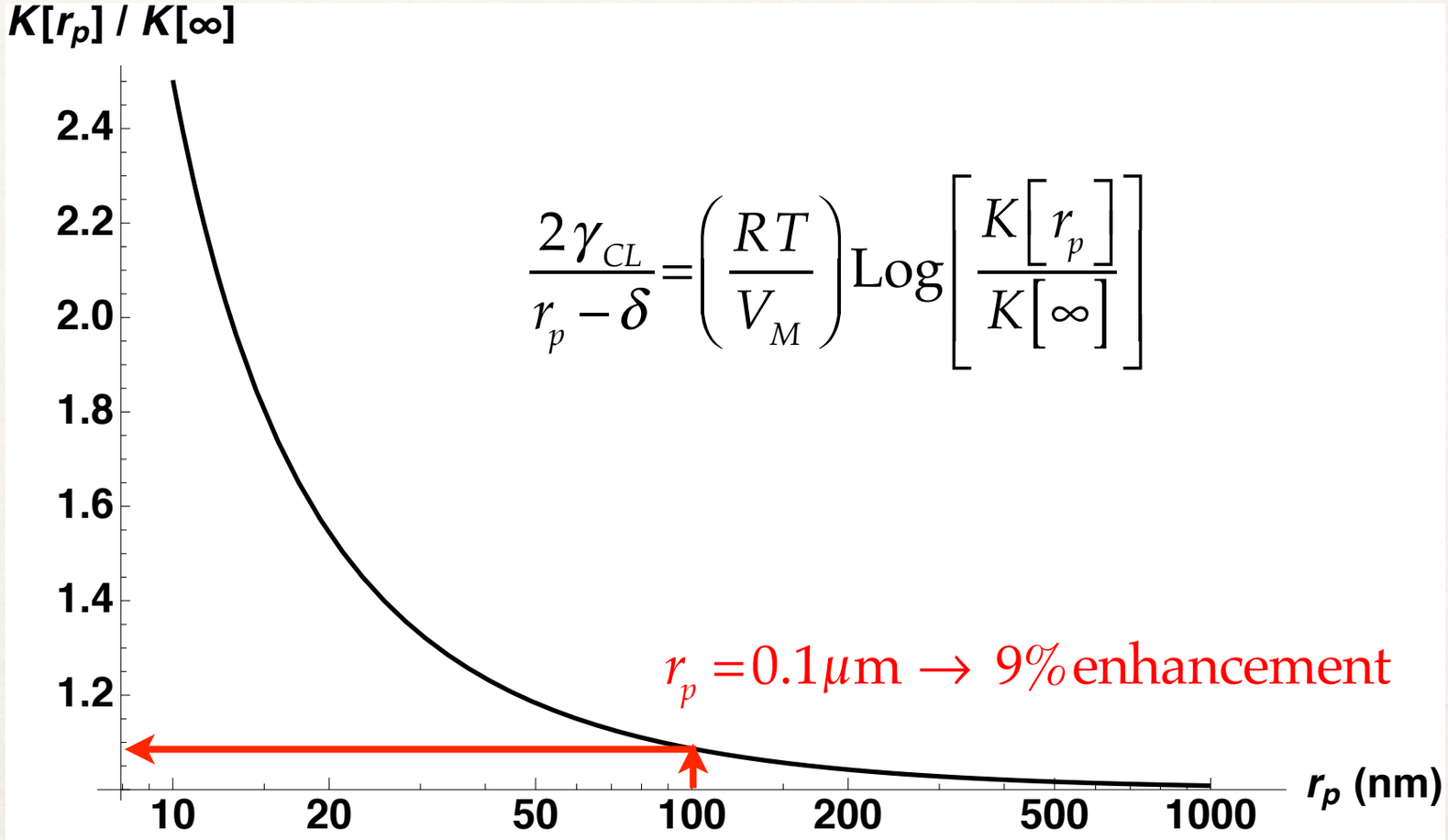
- Pores in stone are usually too large for curvature to affect solubility significantly

- All pores fill simultaneously

- Propagation from large into small pores leads to diffusion control, so no pressure

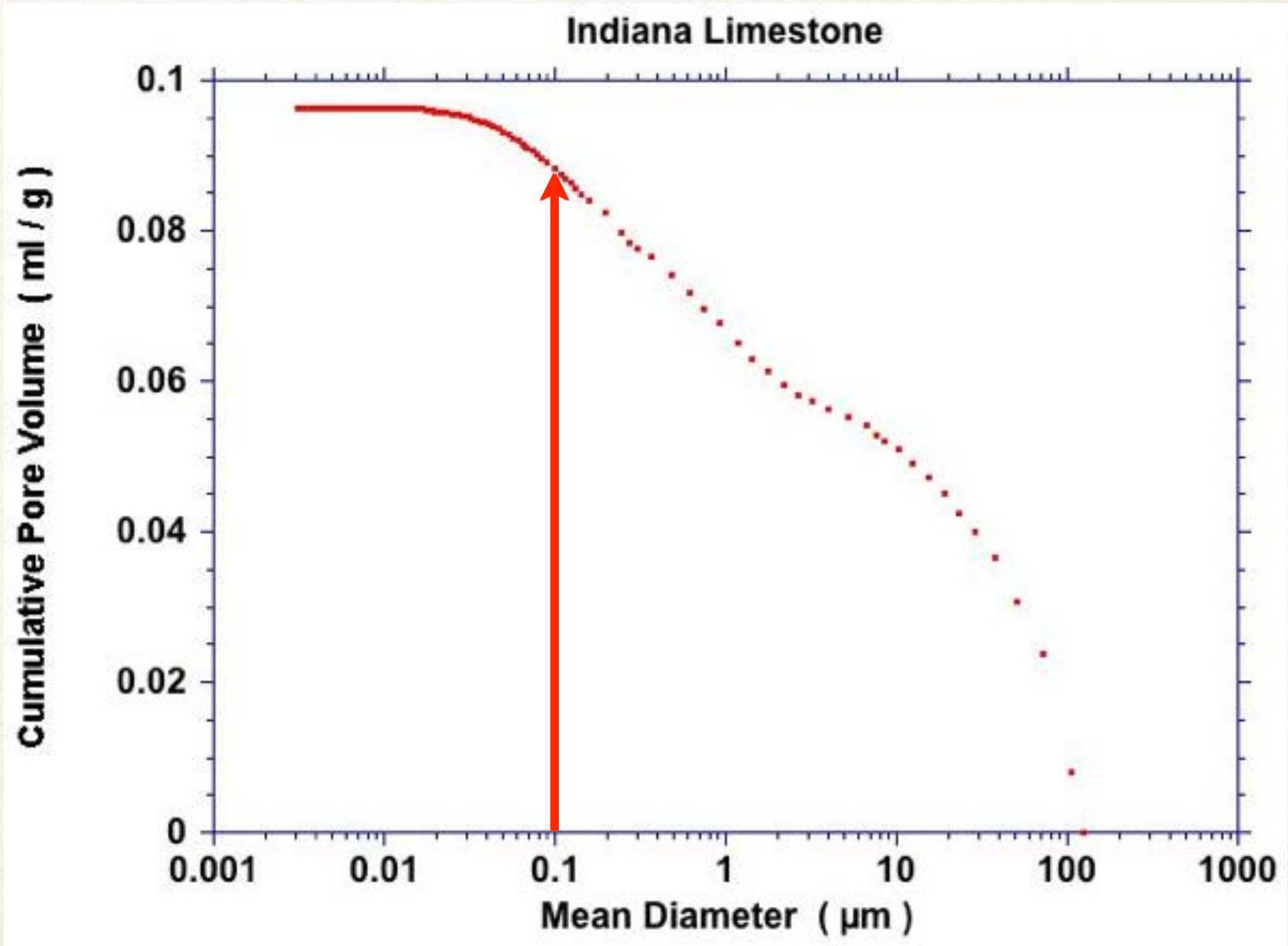
Solubility versus Pore size

- Freundlich equation relates solubility product, *K*, to crystal size



Indiana Limestone

- Bimodal pore size distribution
  - Peaks near 0.3 and 30 μm
  - Few pores smaller than 0.1 μm

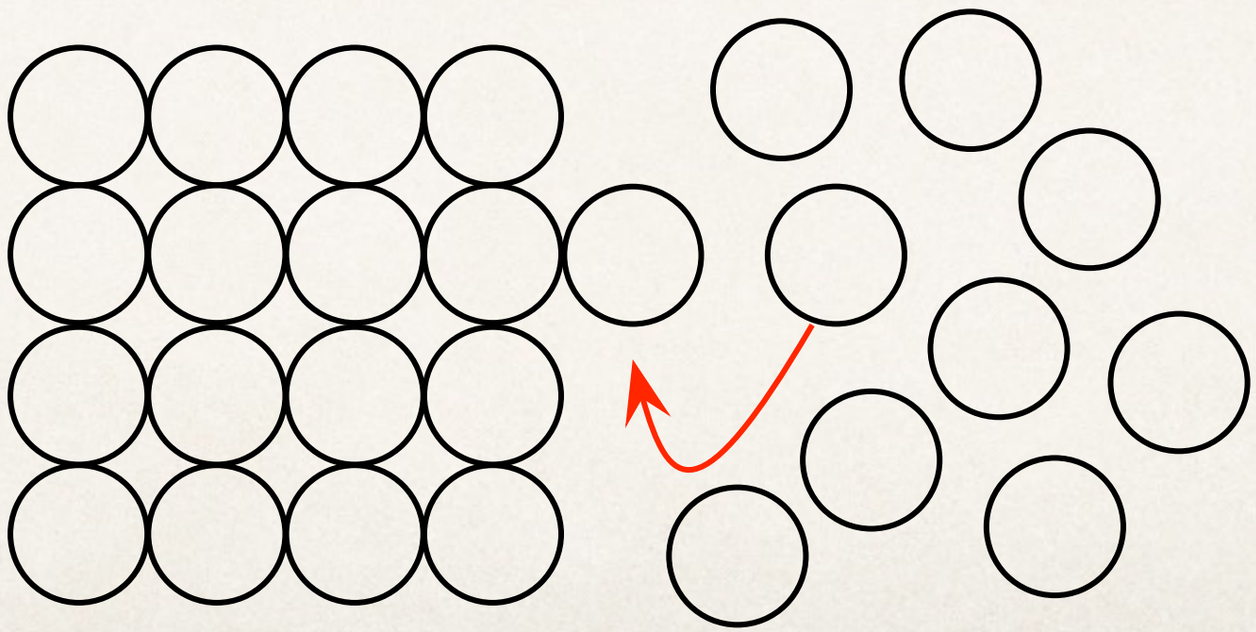


Kinetic considerations

- Interface- versus Diffusion-controlled growth
- Frequency of nucleation
- Transport in the film
- Growth through a network of pores

Interface Control

- Rate of growth is determined by the kinetics of attachment of atoms to the interface
  - Not all sites are equally likely to accommodate attachment
- Driving force for growth is supersaturation, $Q/K - 1$



Crystal Growth

- Interface attachment kinetics
  - Growth rate, G, depends on mobility, η, driving force, ΔG_f and accommodation probability (interface site factor, f)

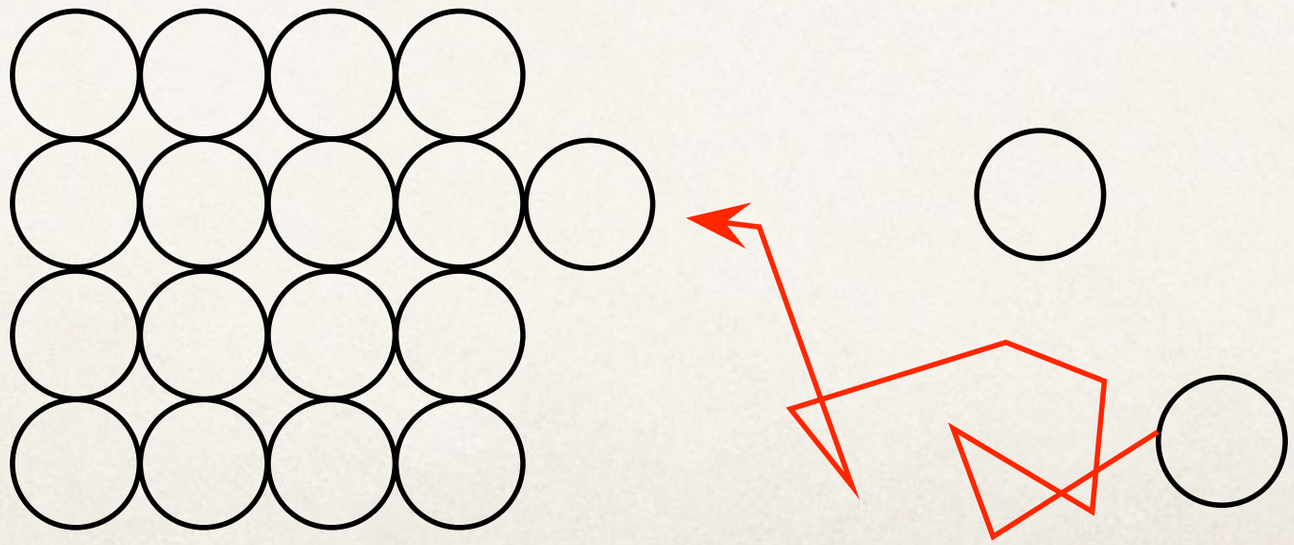
$$G = \frac{f\,kT}{2\pi\lambda^2\eta}\left(1-\exp\left[-\frac{\Delta G_f}{kT}\right]\right)$$

- Precipitation: $\Delta G_f = kT\ln\left(\frac{Q}{K}\right) \equiv kT\ln(\beta)$

$$G = \frac{f\,kT}{2\pi\lambda^2\eta}\left(\frac{\beta-1}{\beta}\right)$$

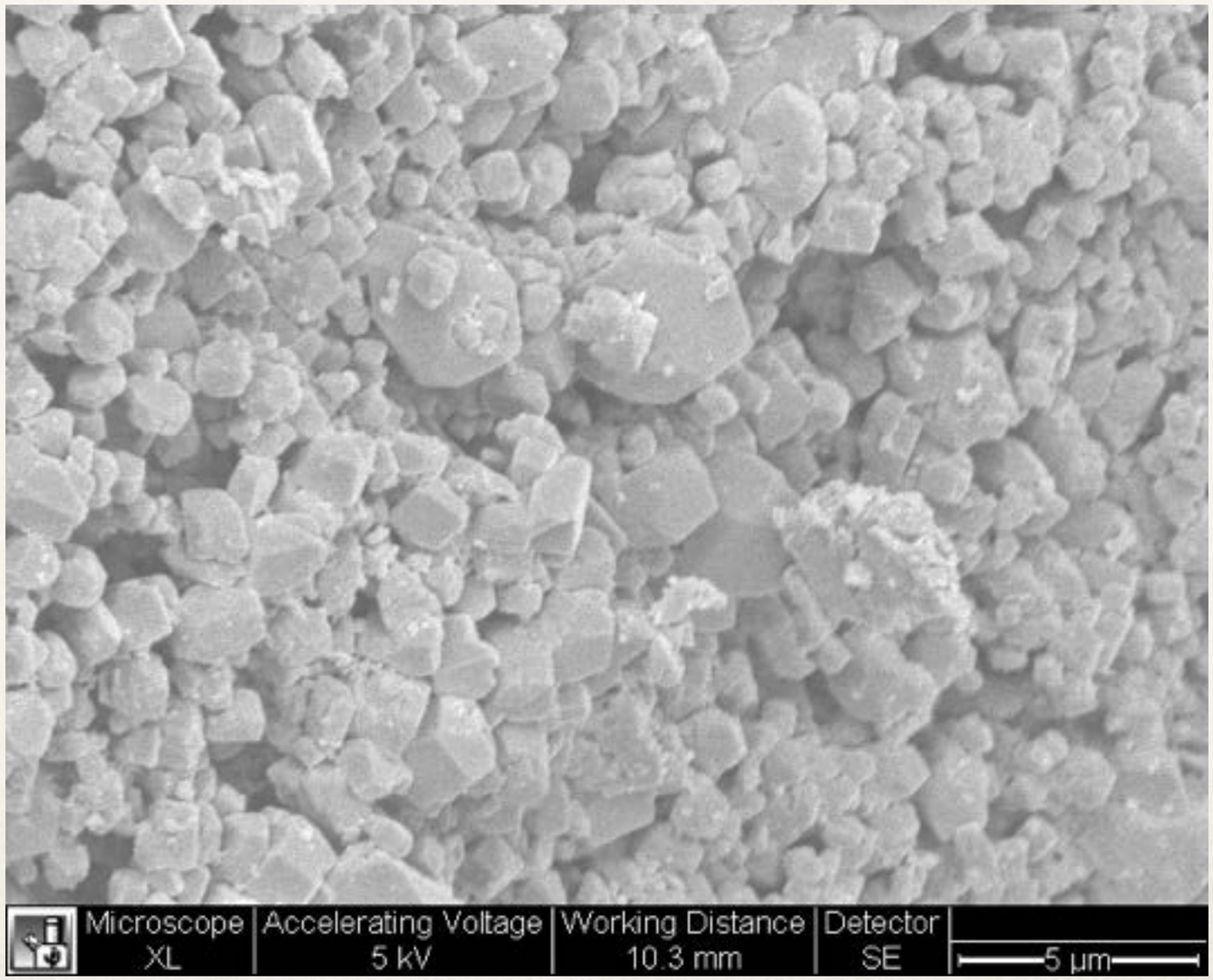
Diffusion control

- If the supply of atoms is small, the rate of arrival of atoms may be slower than the rate of attachment
- Concentration at interface reaches equilibrium solubility
- Since no supersaturation exists, no pressure can be exerted



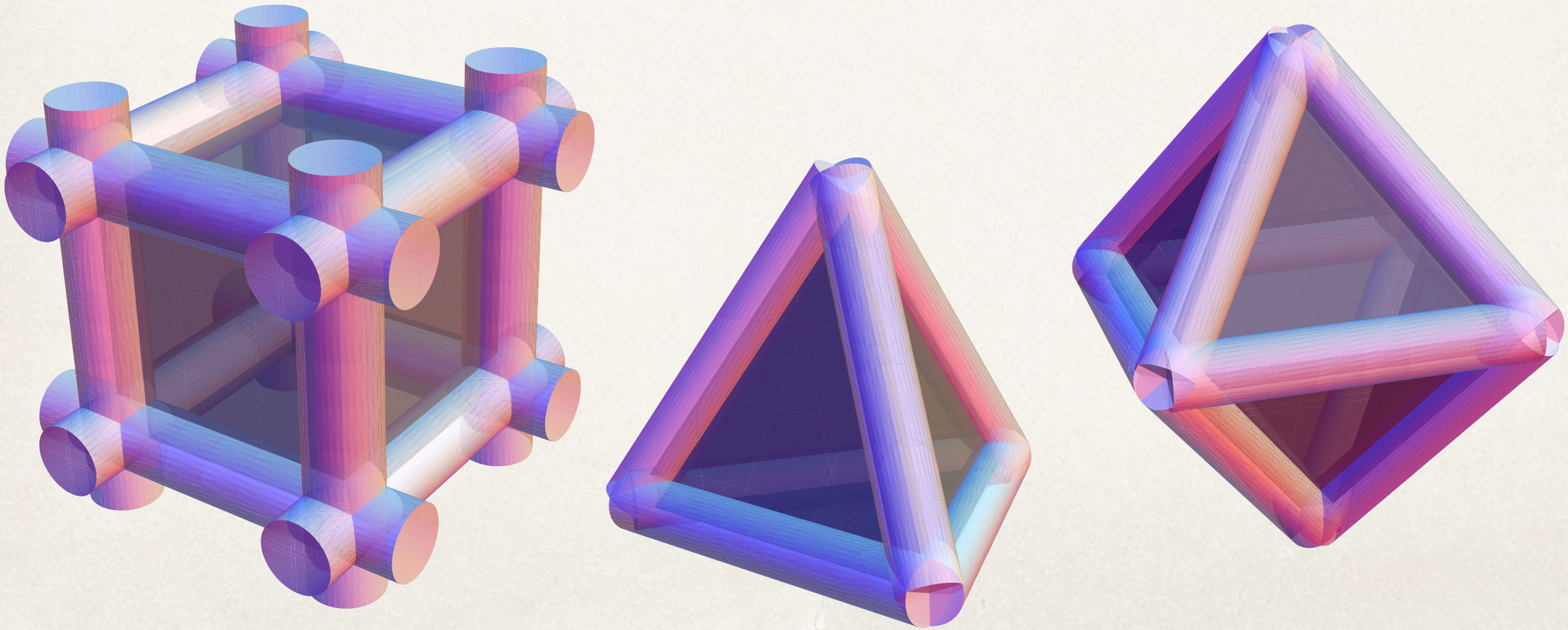
Growth in pores

- Pores in Indiana limestone



Model Networks

- Polyhedral grains with cylindrical pores along edges
  - For typical stone with 15% porosity, 0.5 m^2/g surface area, node spacing is 4-6 times the pore diameter



Crystallization Pressure

- Crystallization pressure is possible only if the crystal is in contact with a supersaturated solution

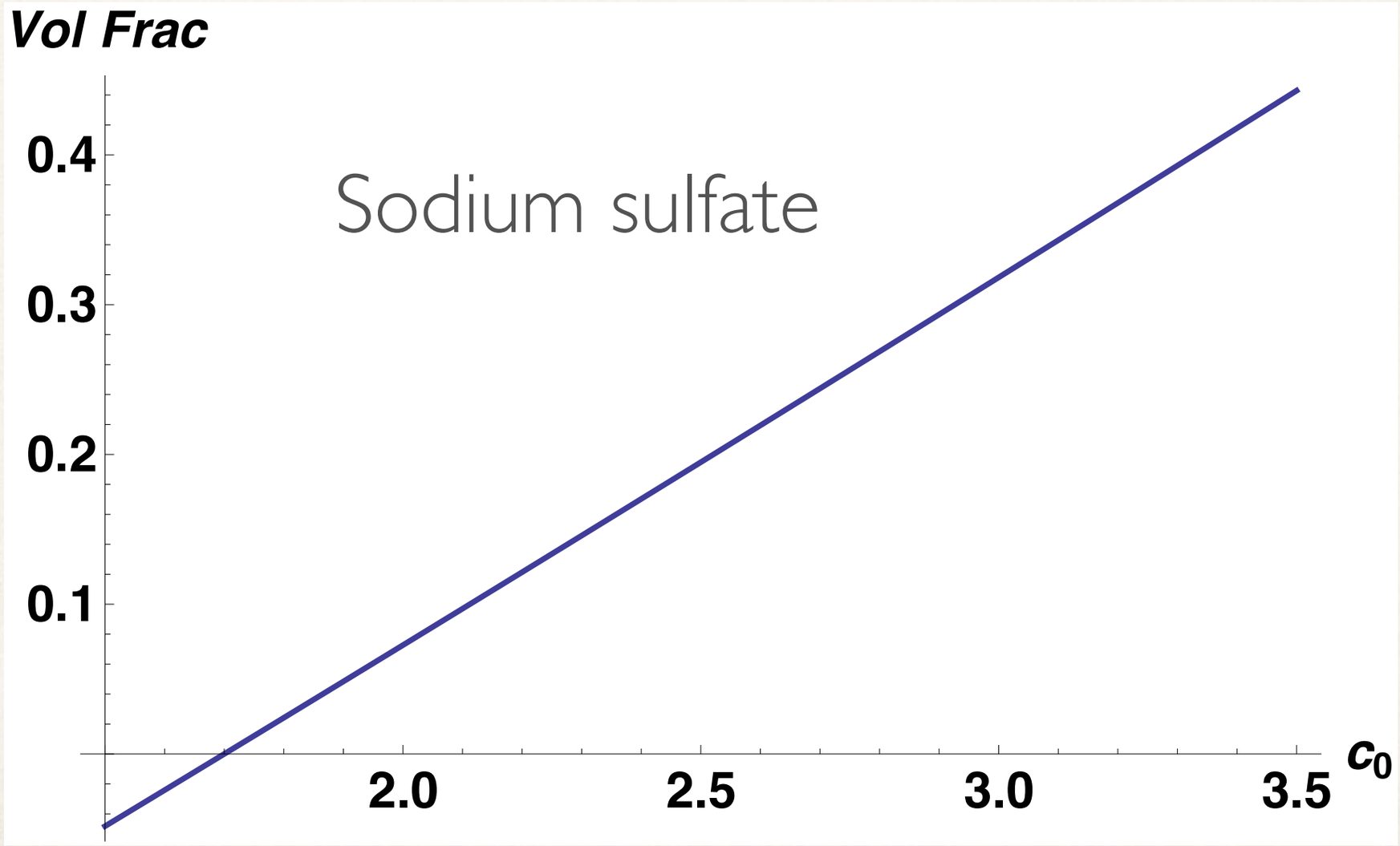
$$p_C \approx \frac{R_g T}{V_M} \ln\left[\left(\frac{c}{c_s}\right)^{\nu}\right]$$

- Under diffusion control, the interface concentration is c_s , so it cannot grow against resistance

- Crystallization pressure is present *only* if the crystal is growing under interface control

Pore - Filling

- Volume fraction of salt is insufficient to fill the pores



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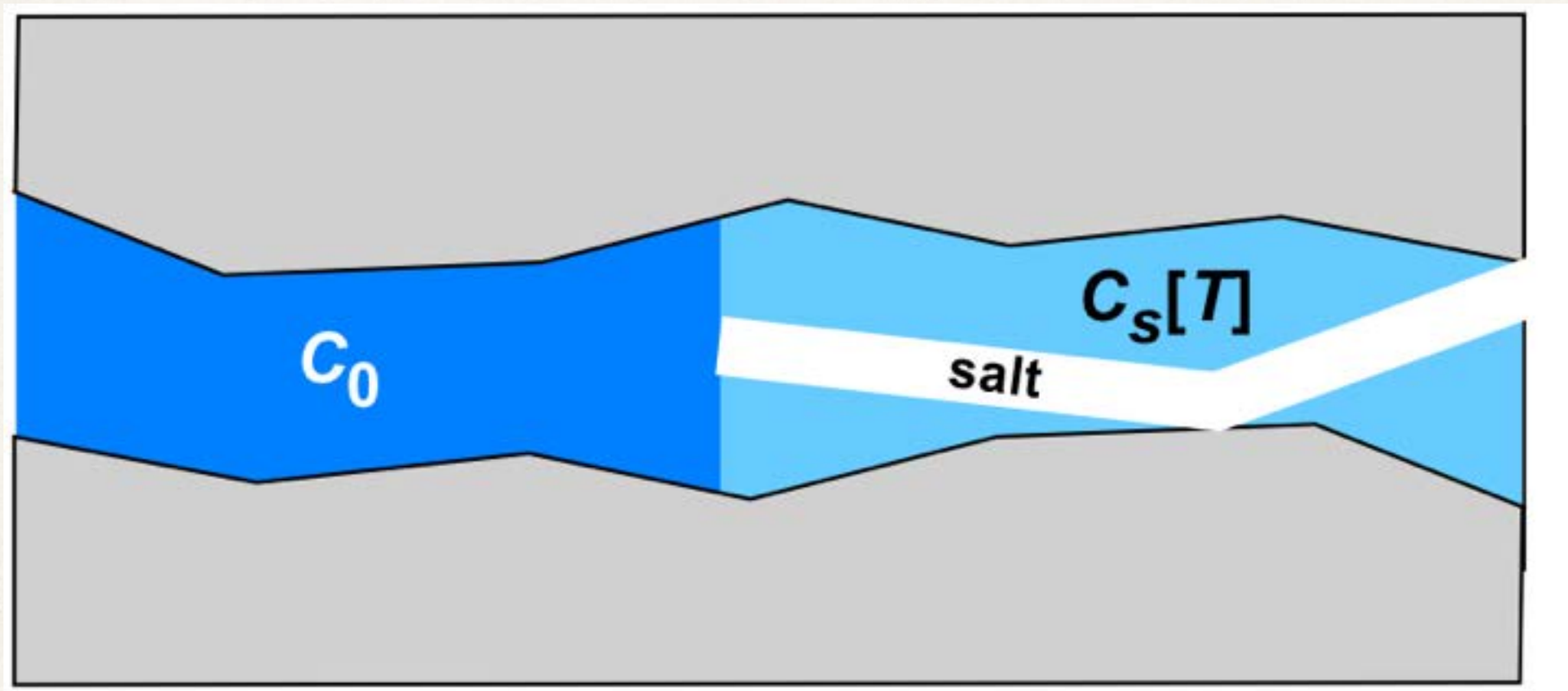

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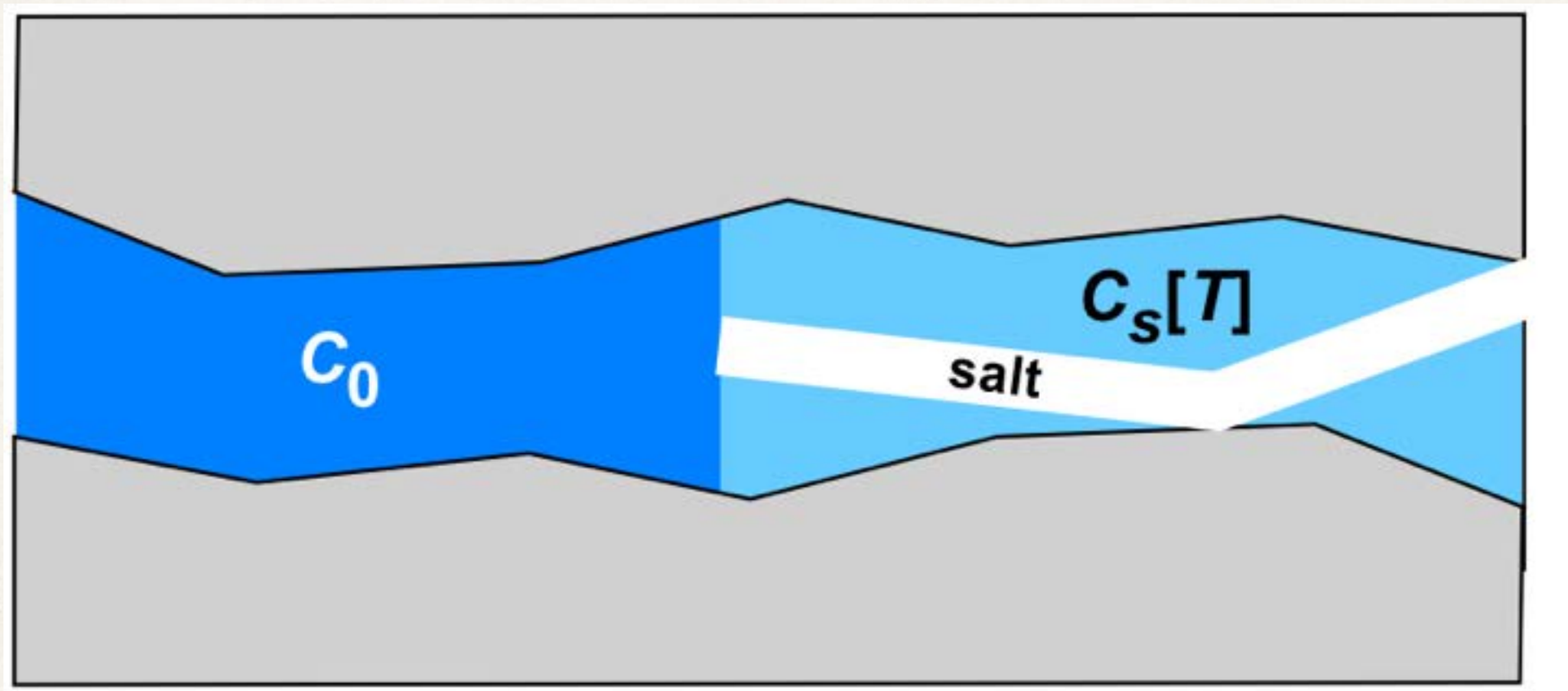


To generate pressure, must diffuse salt from adjoining pores *while maintaining supersaturation*

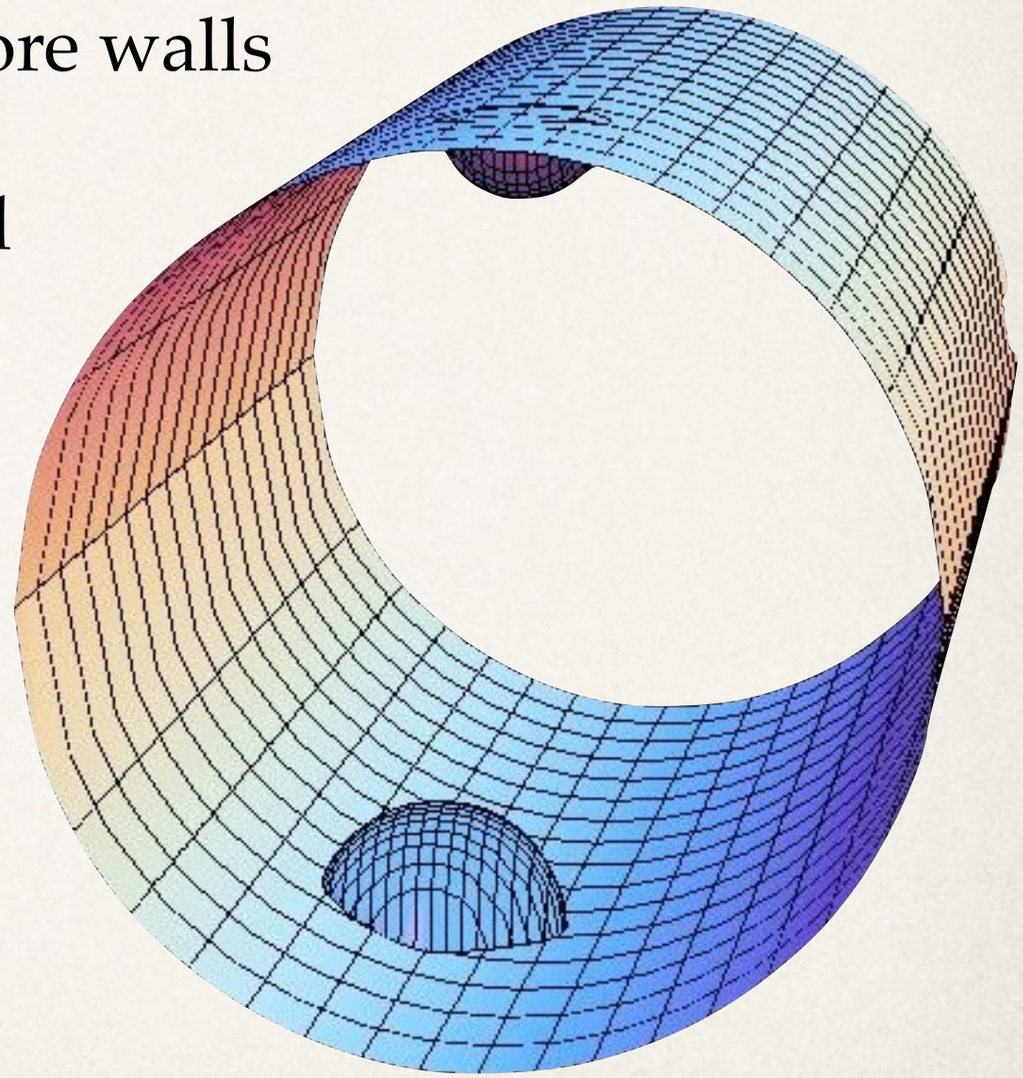
Generating Pressure

- Expect heterogeneous nucleation on pore walls
  - No pressure generated unless crystal touches the opposite wall
- When a spherical crystal makes contact (radius = diameter of pore) its volume is

$$V_{sphere} = 8\left(\frac{2\pi}{3} - \frac{8}{9}\right) r_{pore}^3$$

$$= \pi r_{pore}^2 \ell v_{frac}$$

so solute comes from pore length $\ell \approx 3 r_{pore} / v_{frac}$



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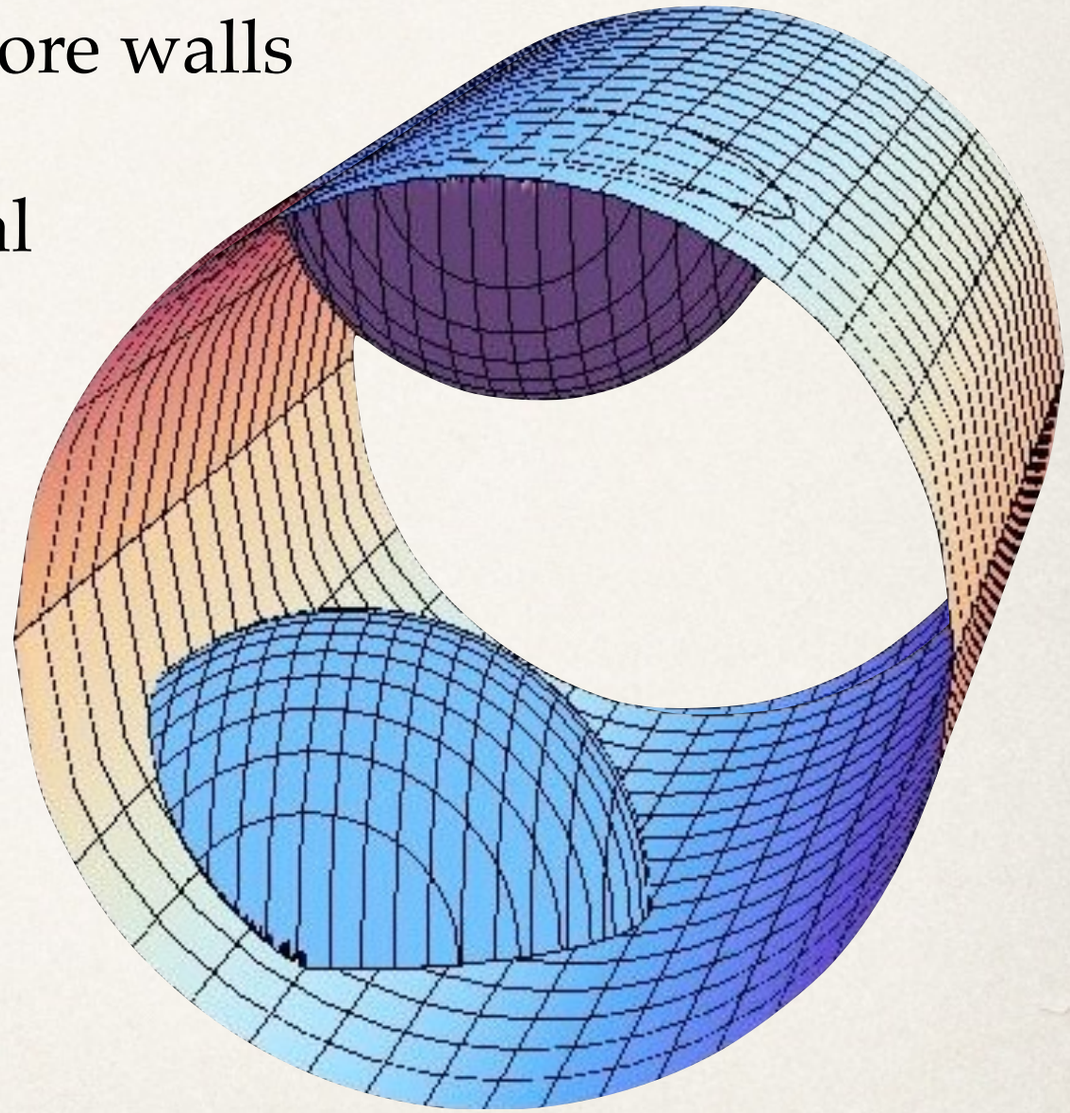


Diffusion Control?

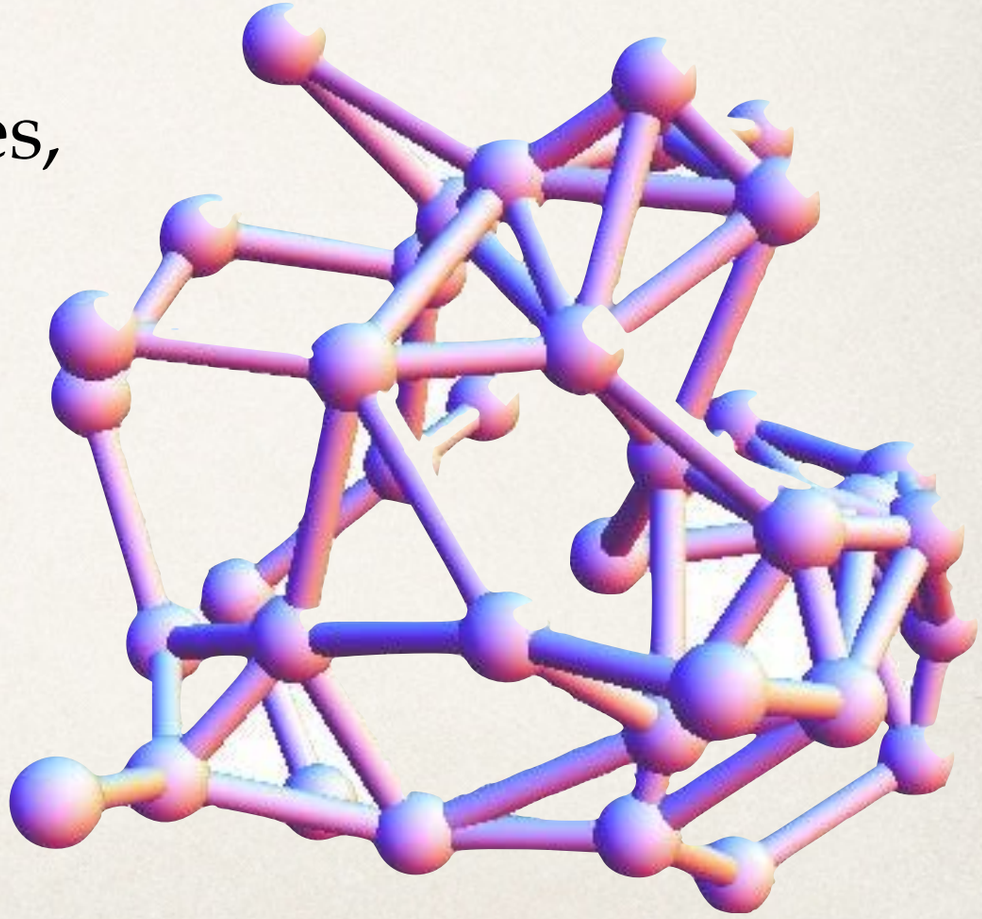
- Solute must come from distance $\ell / 2 \approx 1.5\, r_{pore} / v_{frac}$
- Time for crystal to grow into contact is $t = 2\, r_{pore} / G$
- Distance homogenized by diffusion in this time is

$$x \approx \sqrt{D\, t} \approx \sqrt{2 r_{pore} D / G}$$

- Is $x > \ell / 2$?
- For sodium sulfate heptahydrate, G ~ 1-6 μm/s, $D \approx$ 0.65-2 x 10^{-9} m^2/s, so if pore radius is $r_{pore} \approx 2\ \mu$m, $x \approx$ 20-90 μm ≈ 10-45 $r_{pore} > \ell / 2$ for $v_{frac} >$ 0.03-0.15
  - Stress from hepta exerted w/o diffusion control

Nucleation on Walls

- Expect heterogeneous nucleation on pore walls
  - Few sites have favorable contact angle
- If number of nuclei ≥ 1 between nodes, the amount of solute is not sufficient to allow the crystal to grow into contact with the opposite side of the pore
  - Nucleation must be rare to generate crystallization pressure



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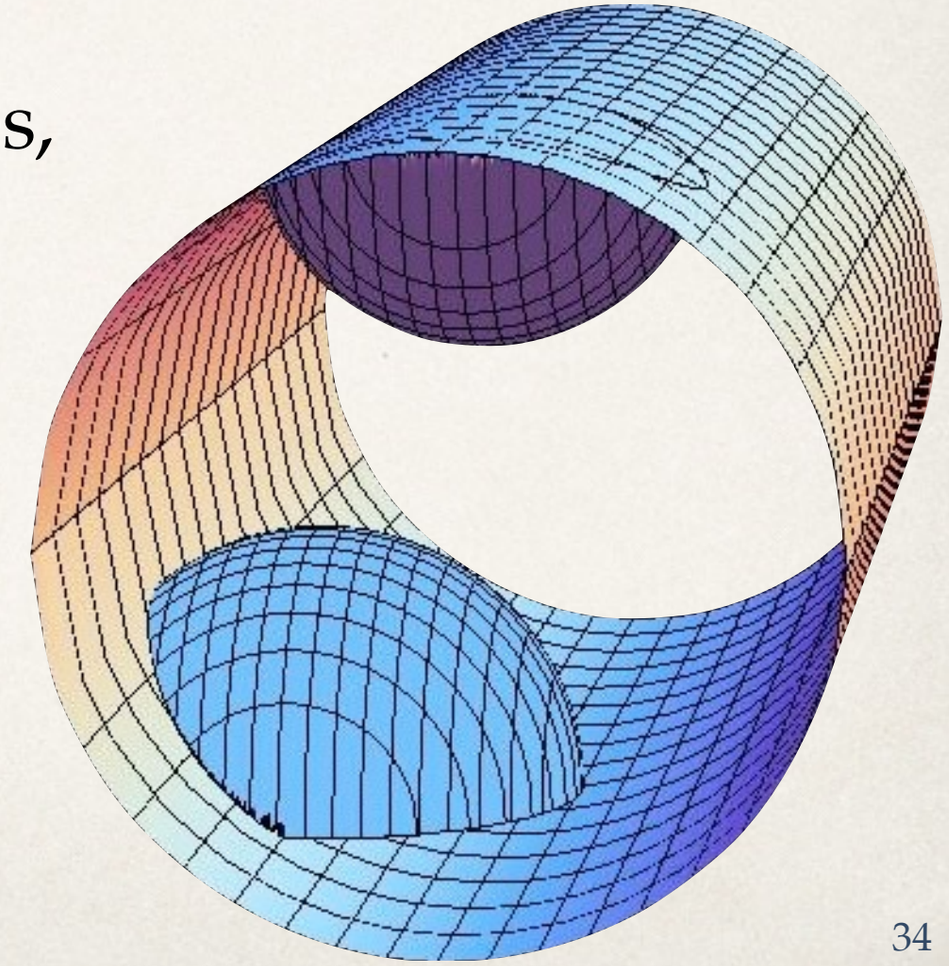
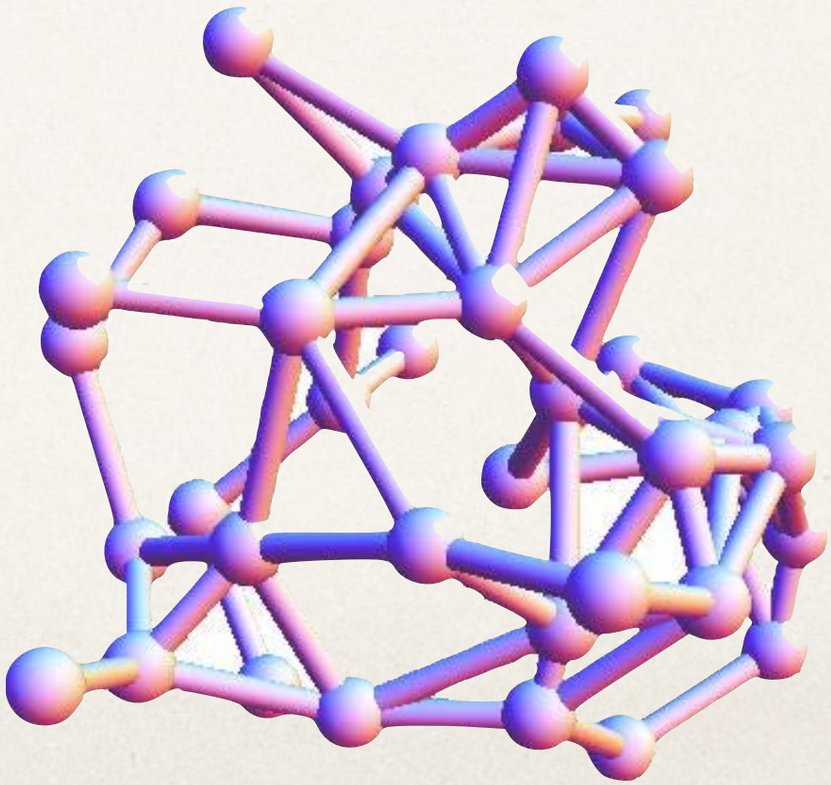


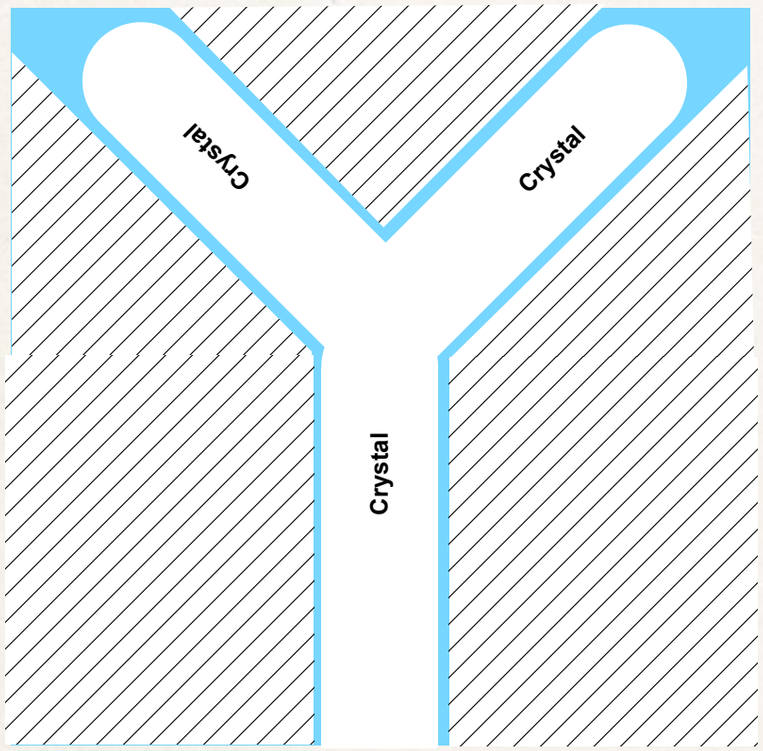
Pore Network

- Network consists of cylindrical pores and nodes (junctions)
- What happens when a crystal reaches a node?
  - Branch into all, some, or none of the intersecting pores?

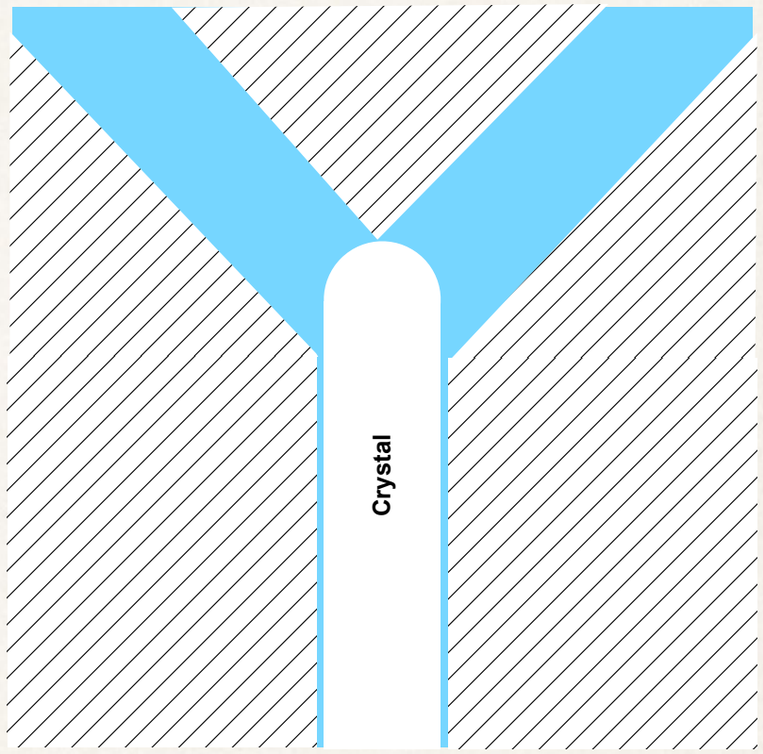


Branching at Nodes

- Can crystals branch freely at nodes, or are they trapped?



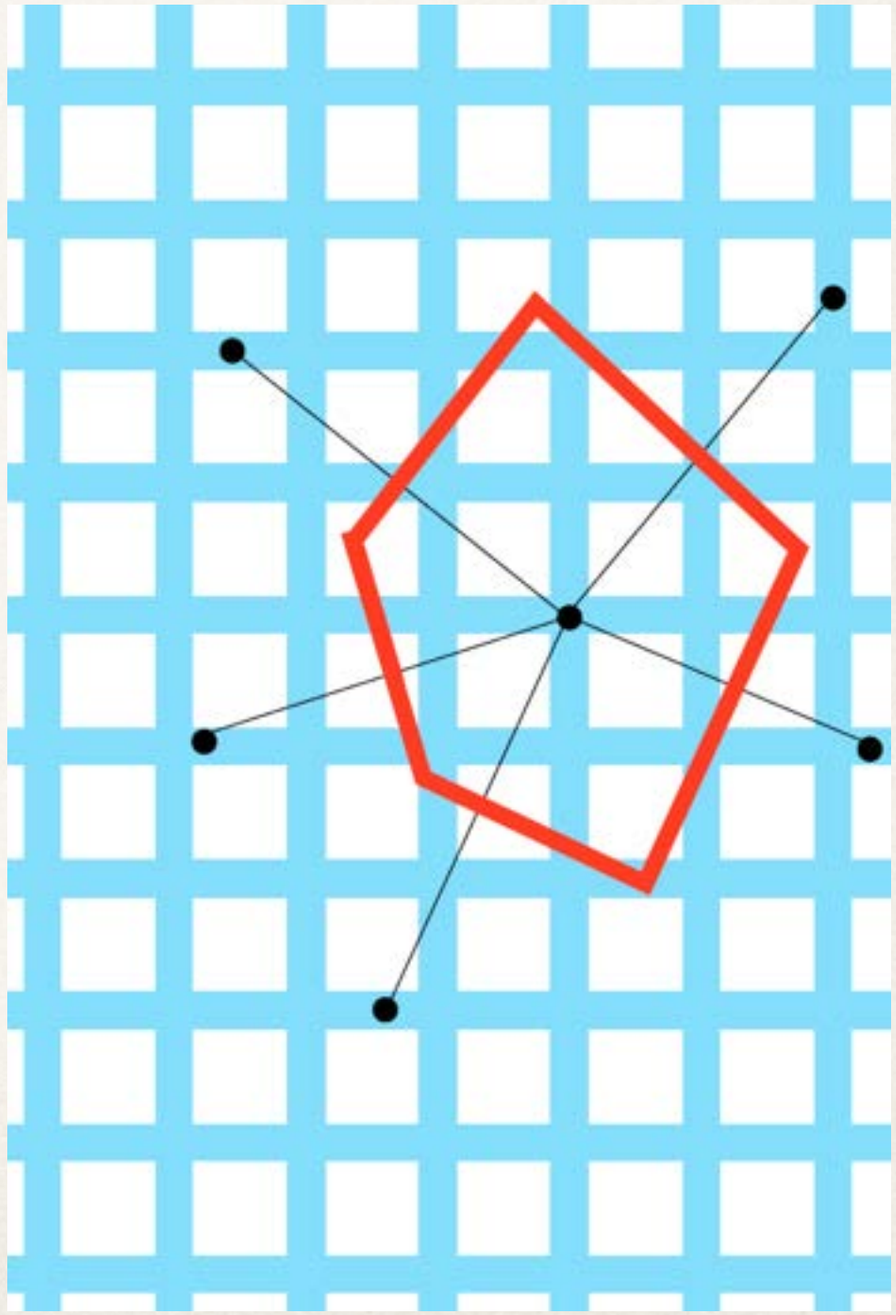
In this case, a single crystal can transform all the pore volume



In this case, diffusion to the trapped crystal generates crystallization pressure

Growth in a Network

- Nucleation must be rare to allow crystals to fill pores
- Diffusion must be fast compared to growth to allow interface concentration to be high ($\beta > 1$)
- If nuclei are not too far apart, neighborhood (red zone) has uniform concentration



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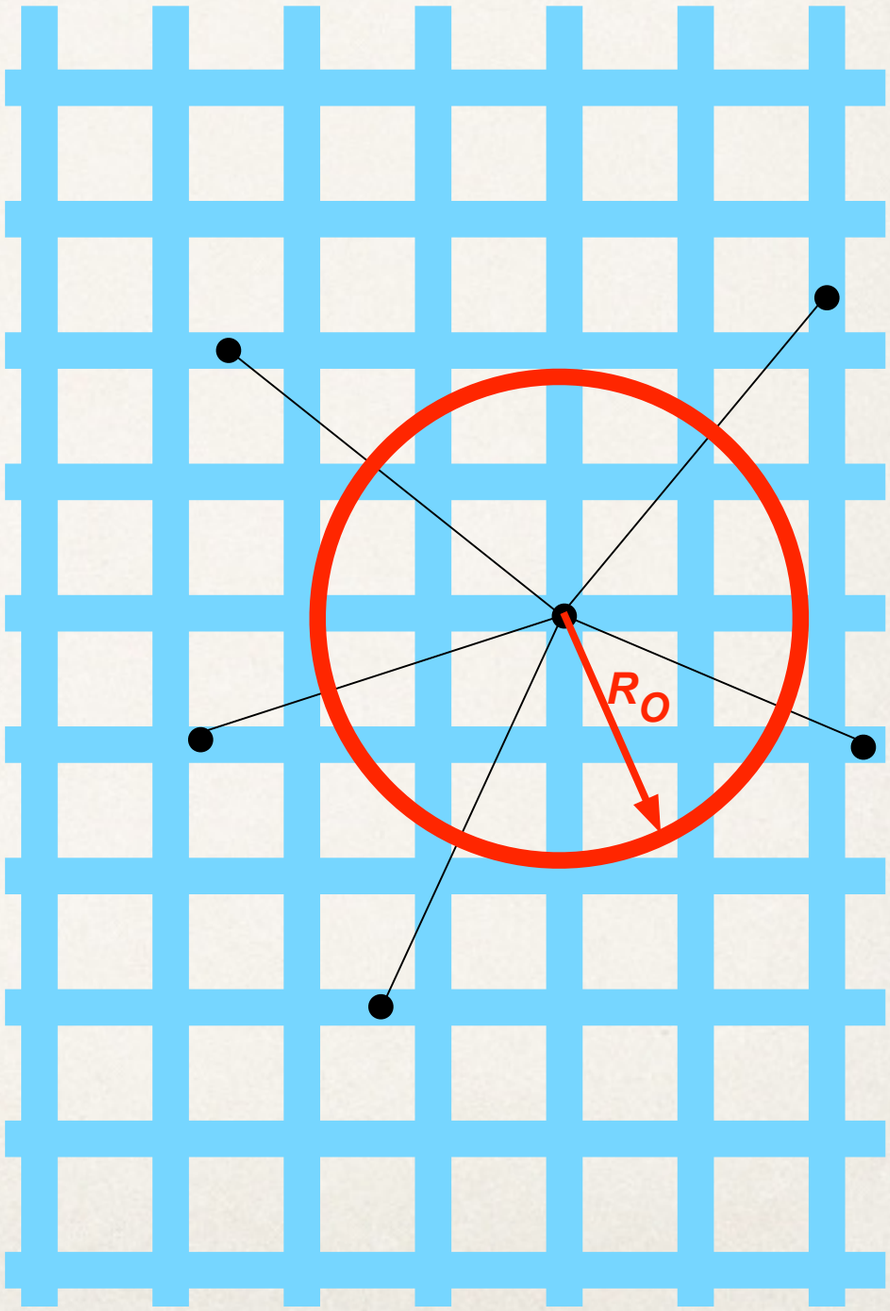
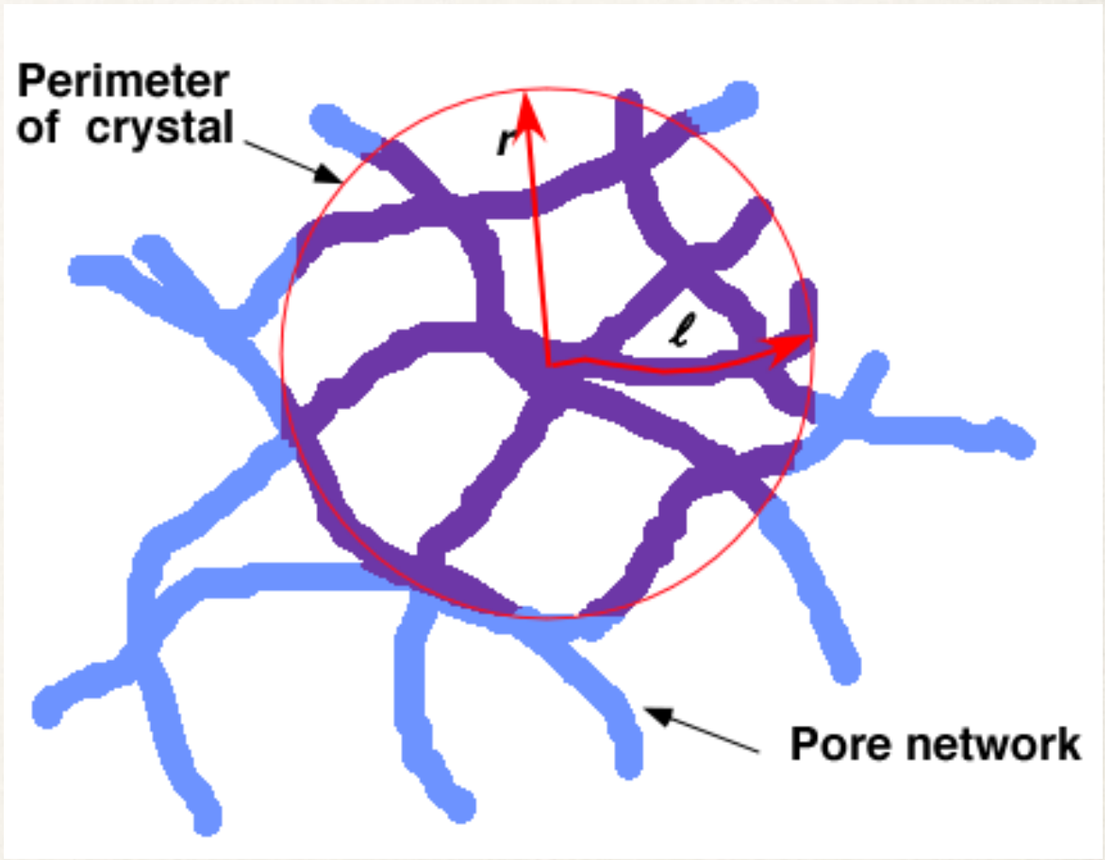


Growth & Branching

- If the crystal branches into all pores at junctions, a region with radius r transforms, but the growth distance is $\ell = r\,\tau$, where τ is the tortuosity of the pore network

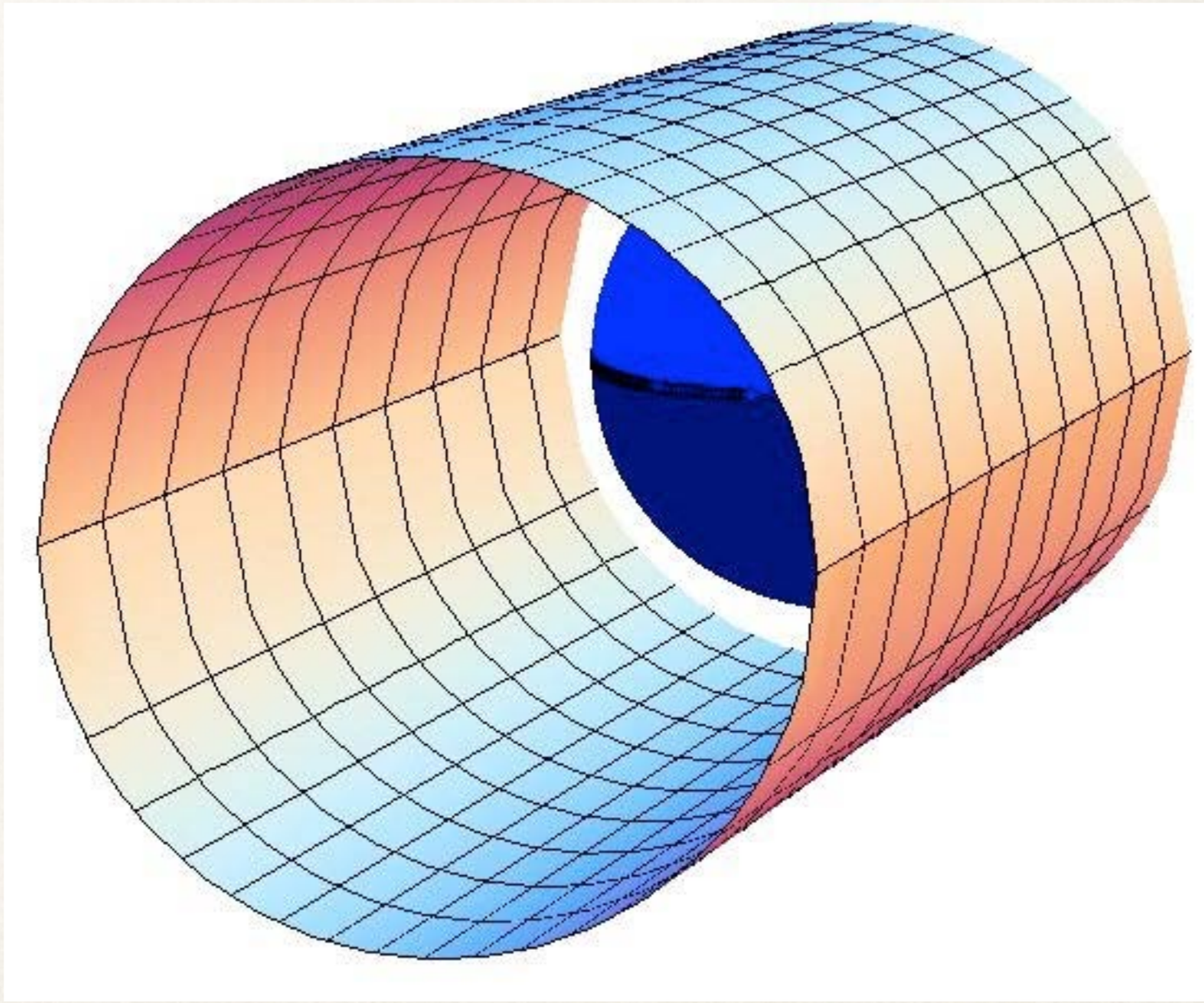


- Stress determined by composition of film between crystal and wall

- If diffusion in film is very slow, high pressure can be sustained on the pore wall

Trapping of Film

- Film of solution is trapped between crystal and pore wall
- Whether composition of film equilibrates with pore solution depends on diffusivity in the film



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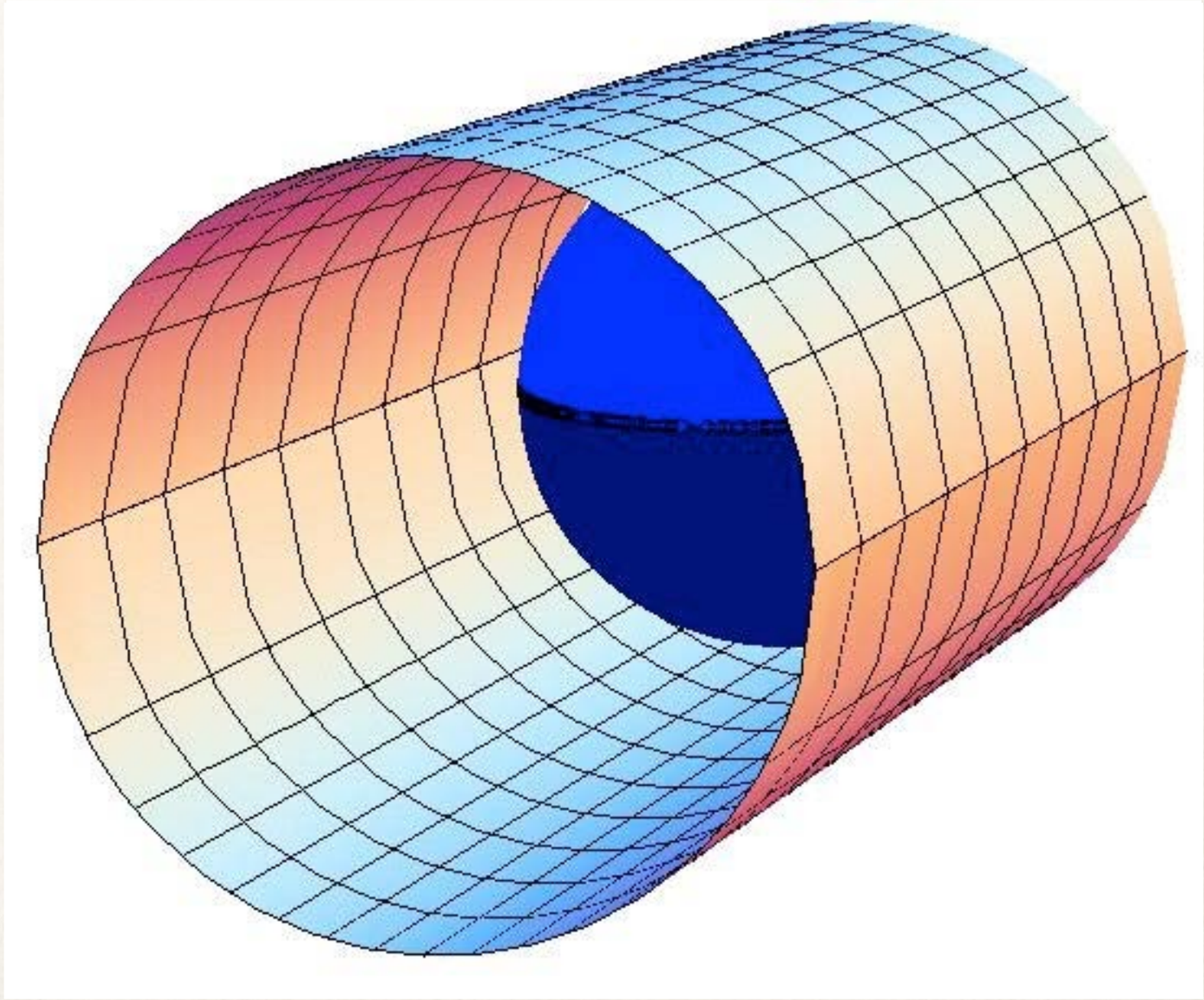

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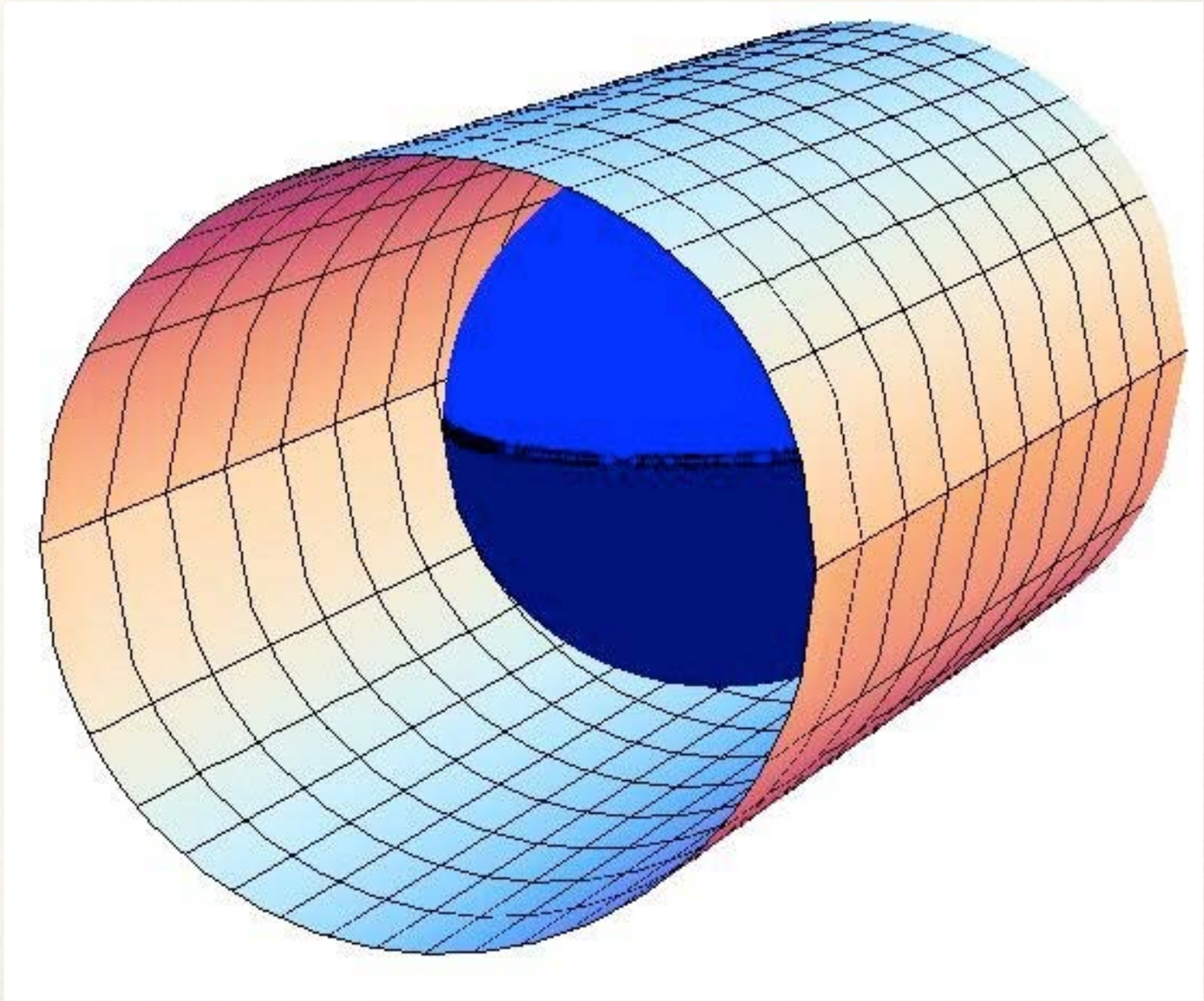

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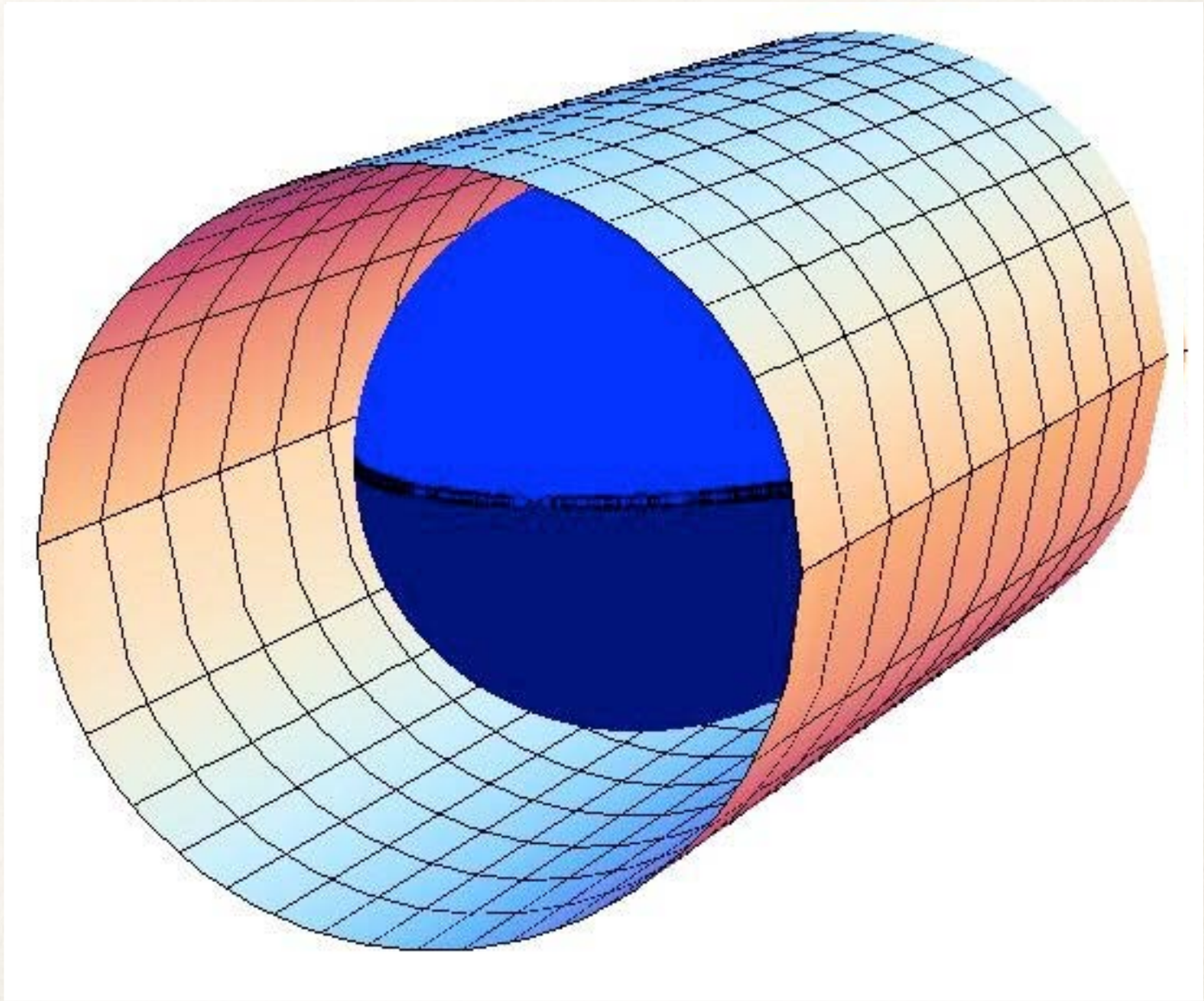

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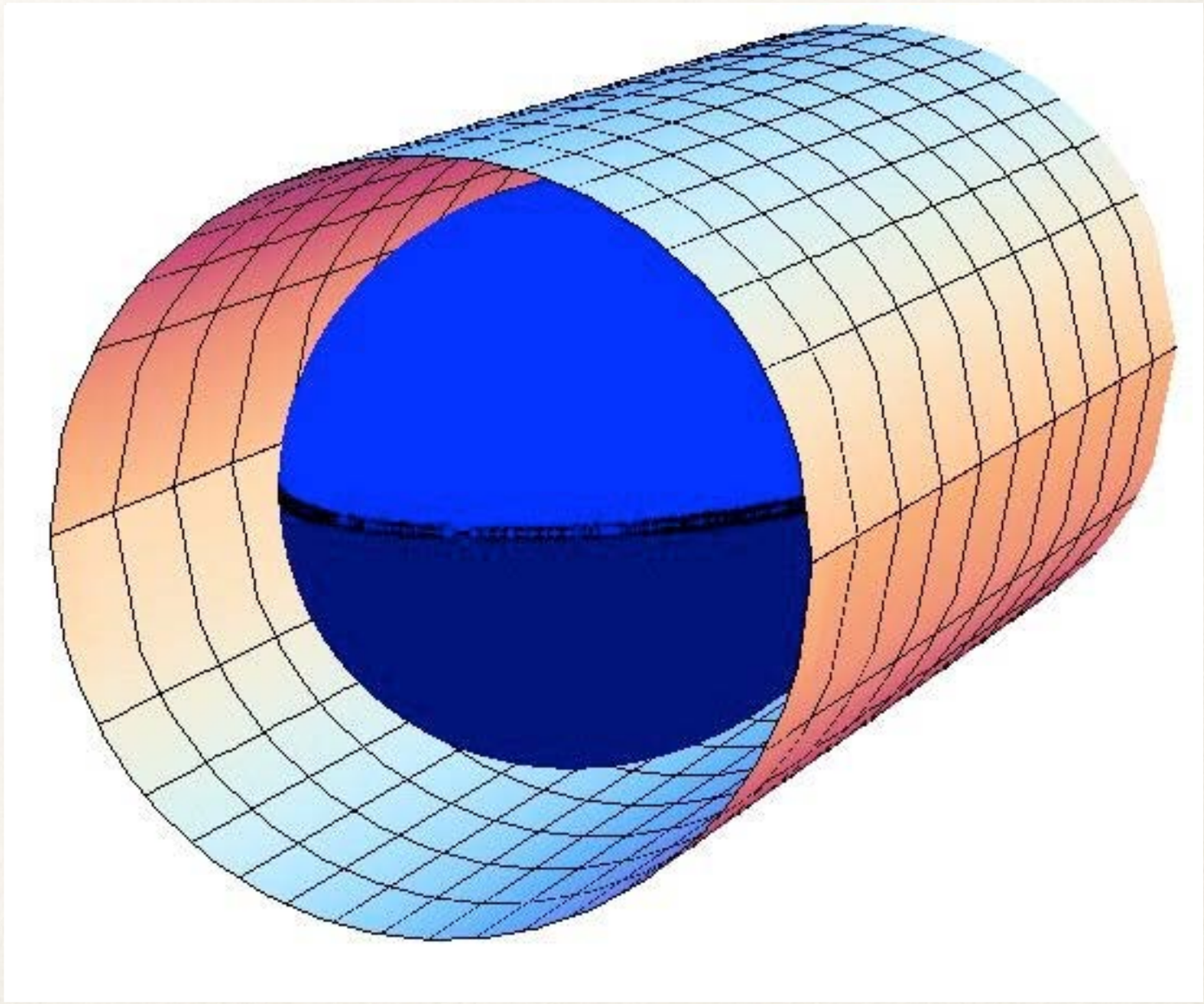

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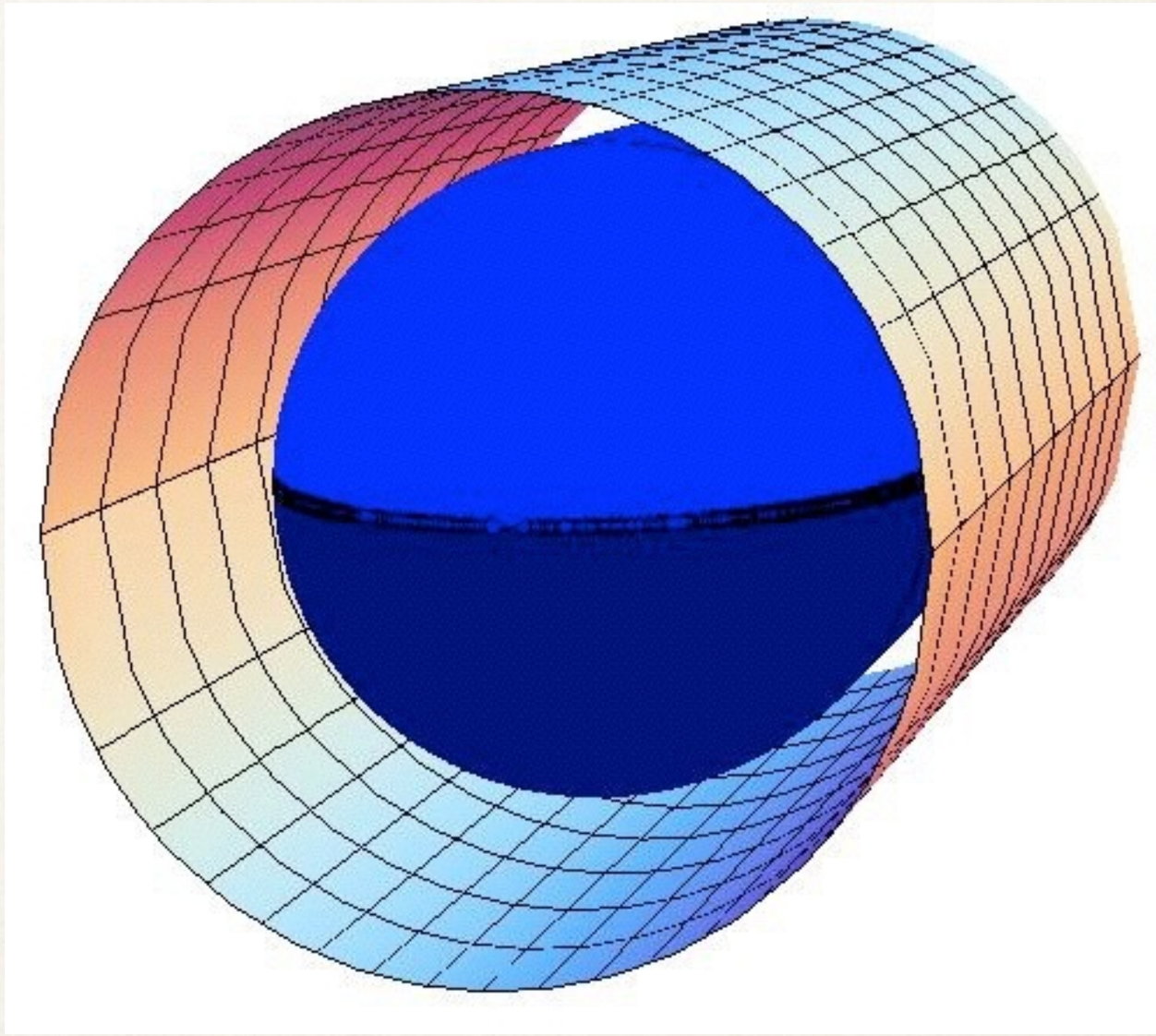

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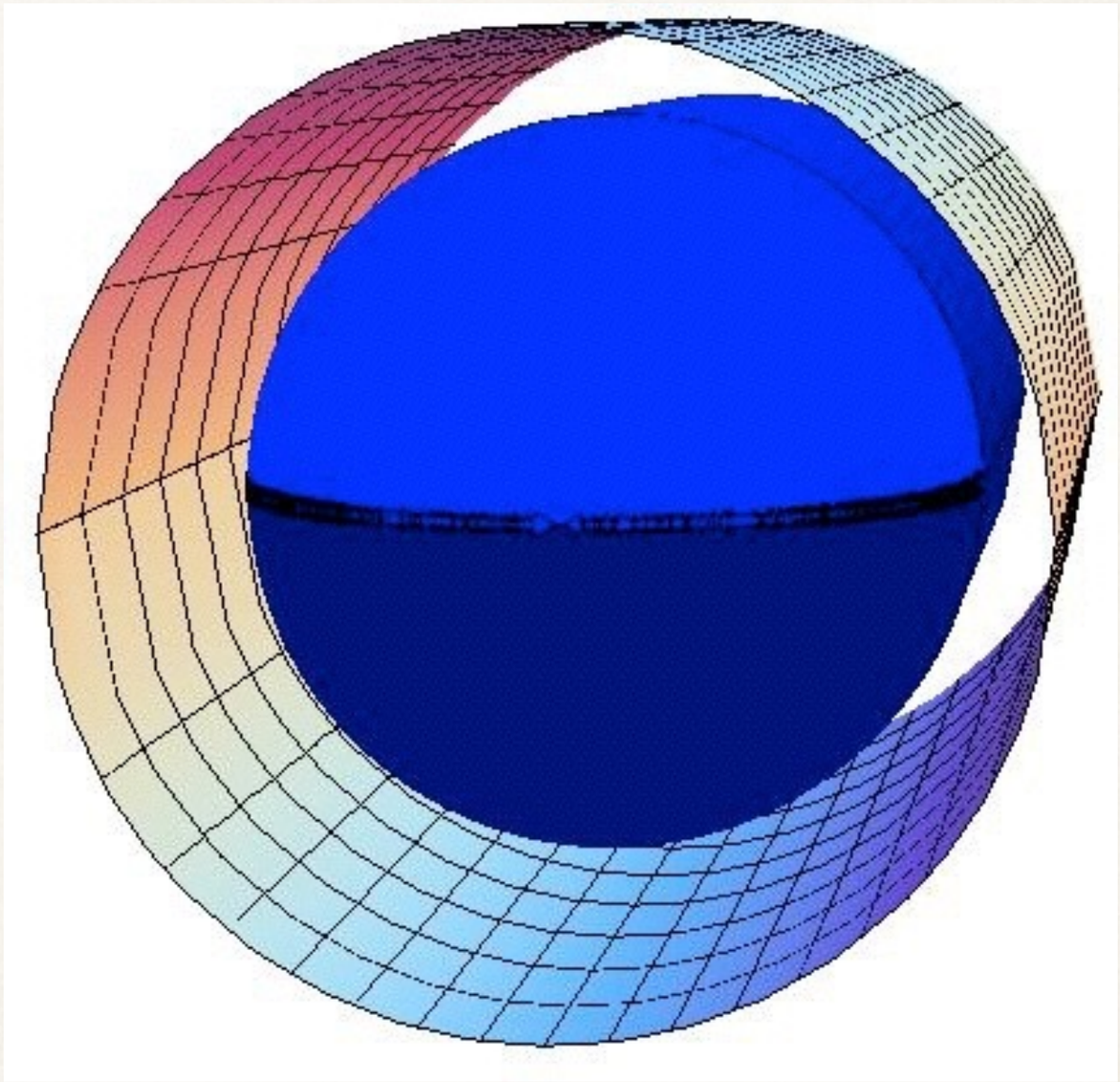

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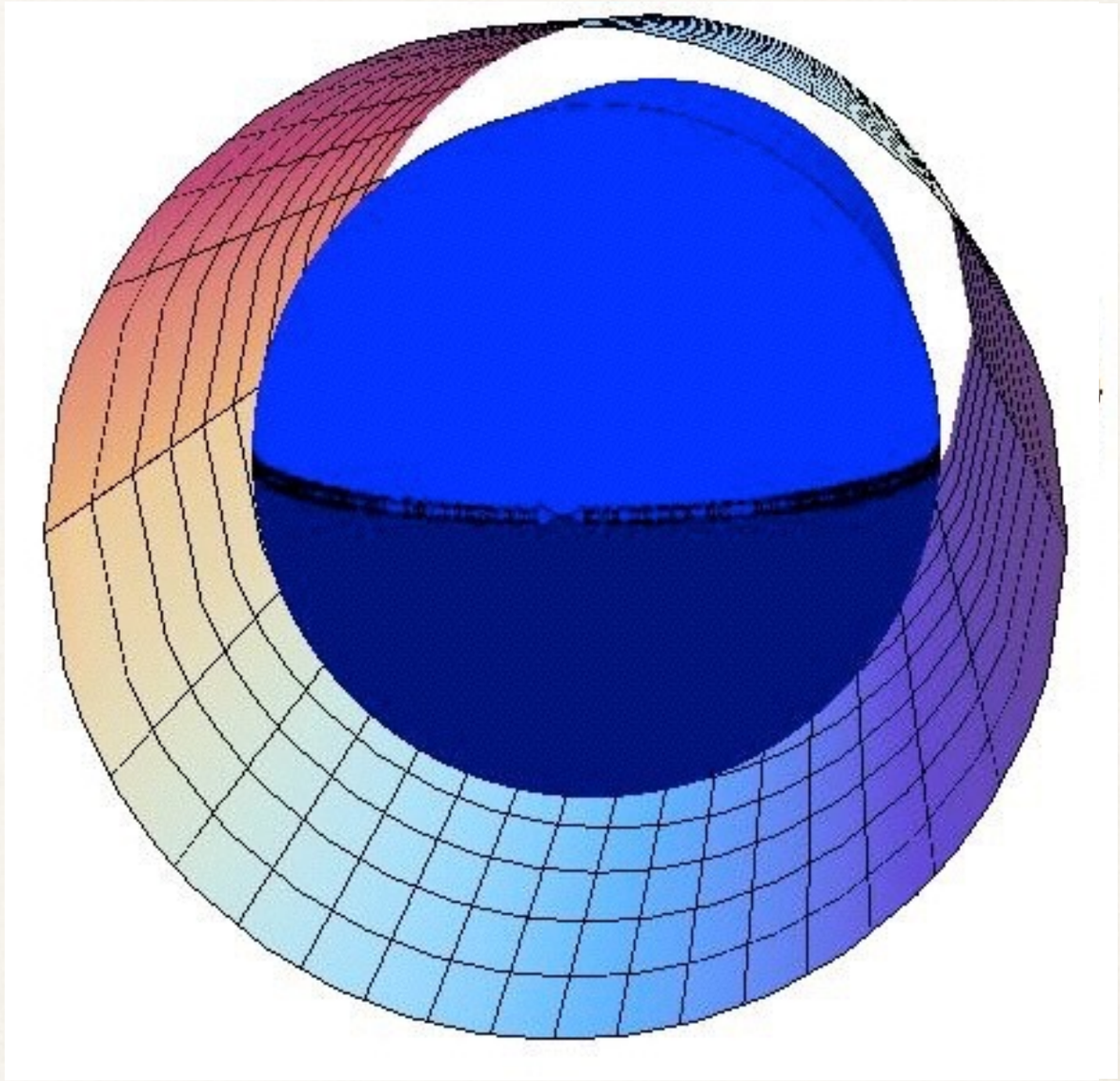
- Whether composition of film equilibrates with pore solution depends on diffusivity in the film



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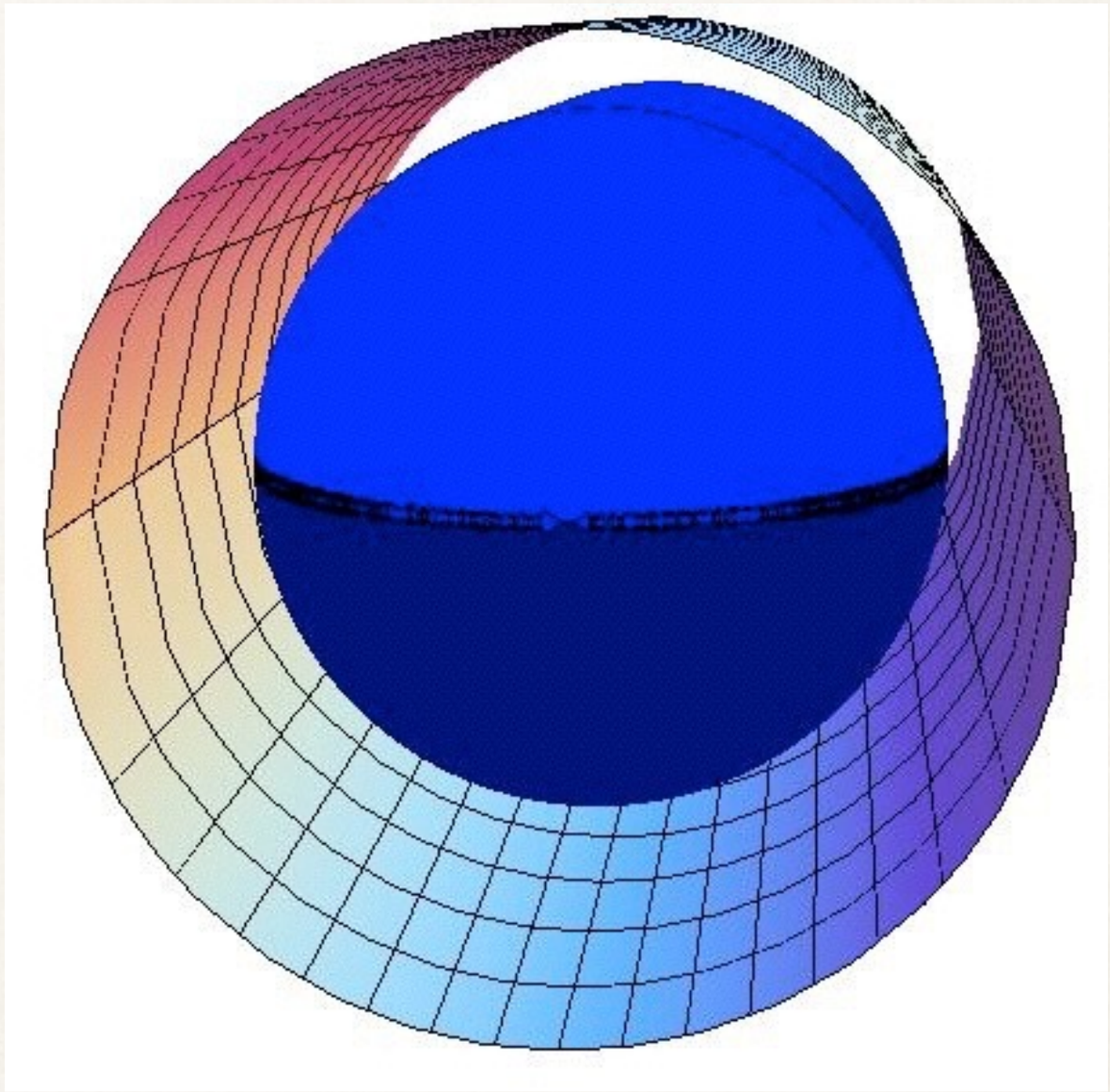
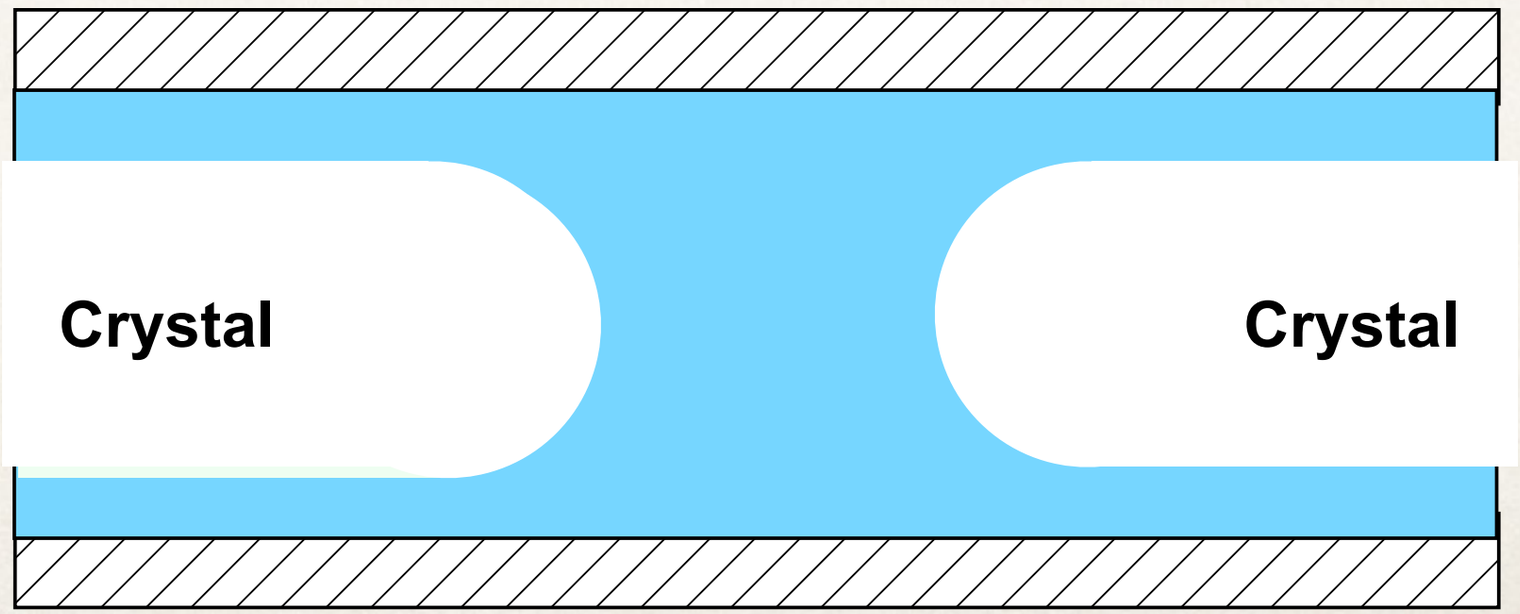


Fast diffusion in Film

- Suppose that growth is interface controlled
  - Concentration in pore liquid decreases as crystal grows, but interface concentration equals average composition, and *film composition is in equilibrium with pore liquid*



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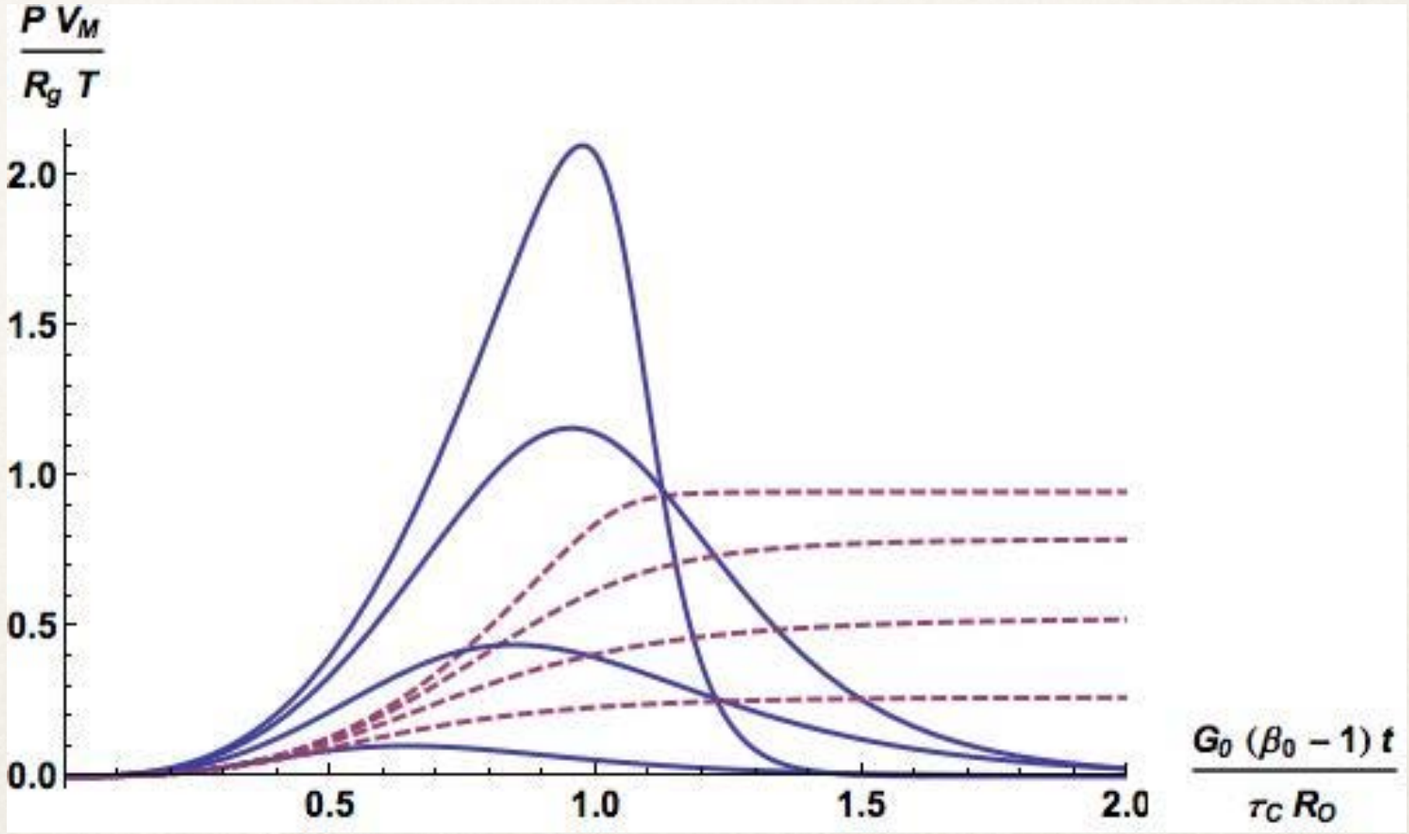
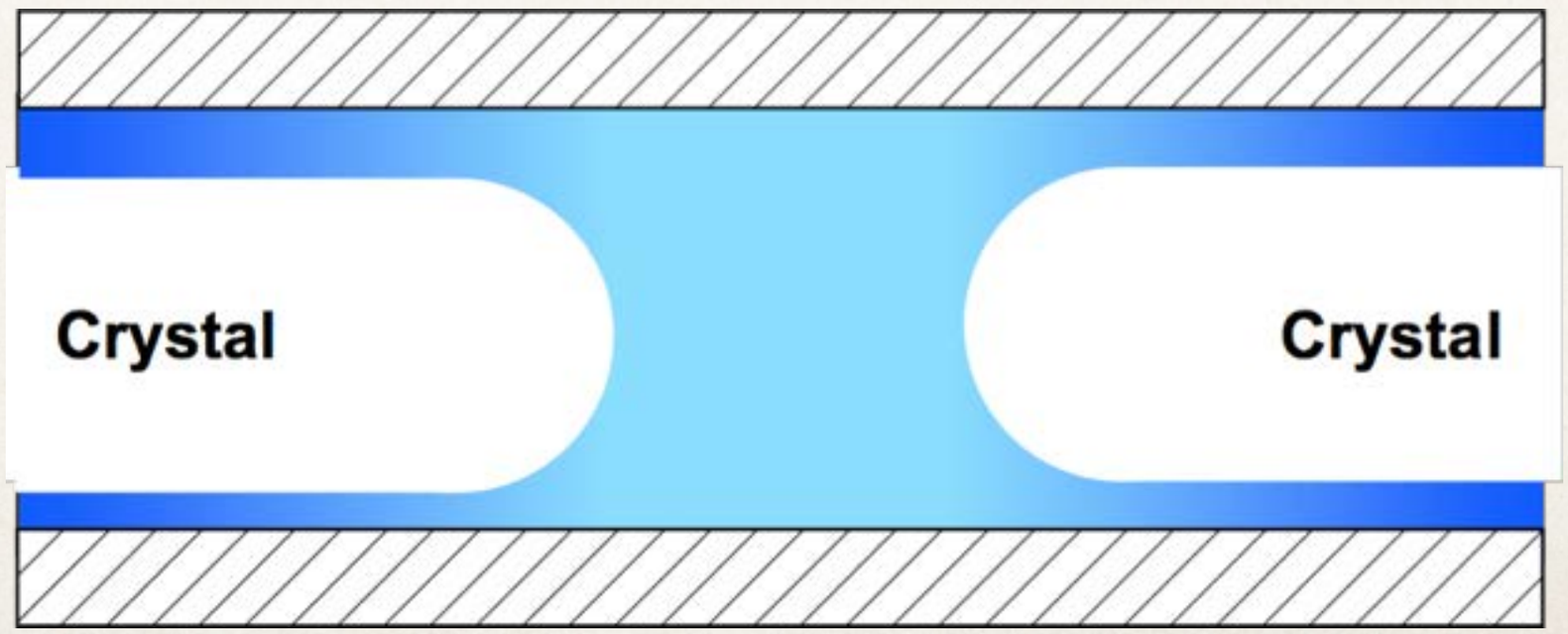
- Solid curve is crystallization pressure
- Dashed curve is fraction of pore filling with crystals
- $R_g T / V_M \approx 13$ MPa



Slow diffusion in Film

- Suppose that growth is interface controlled
  - Concentration in pore liquid decreases as crystal grows, and interface concentration equals average composition, but *film concentration does not equilibrate with pore*



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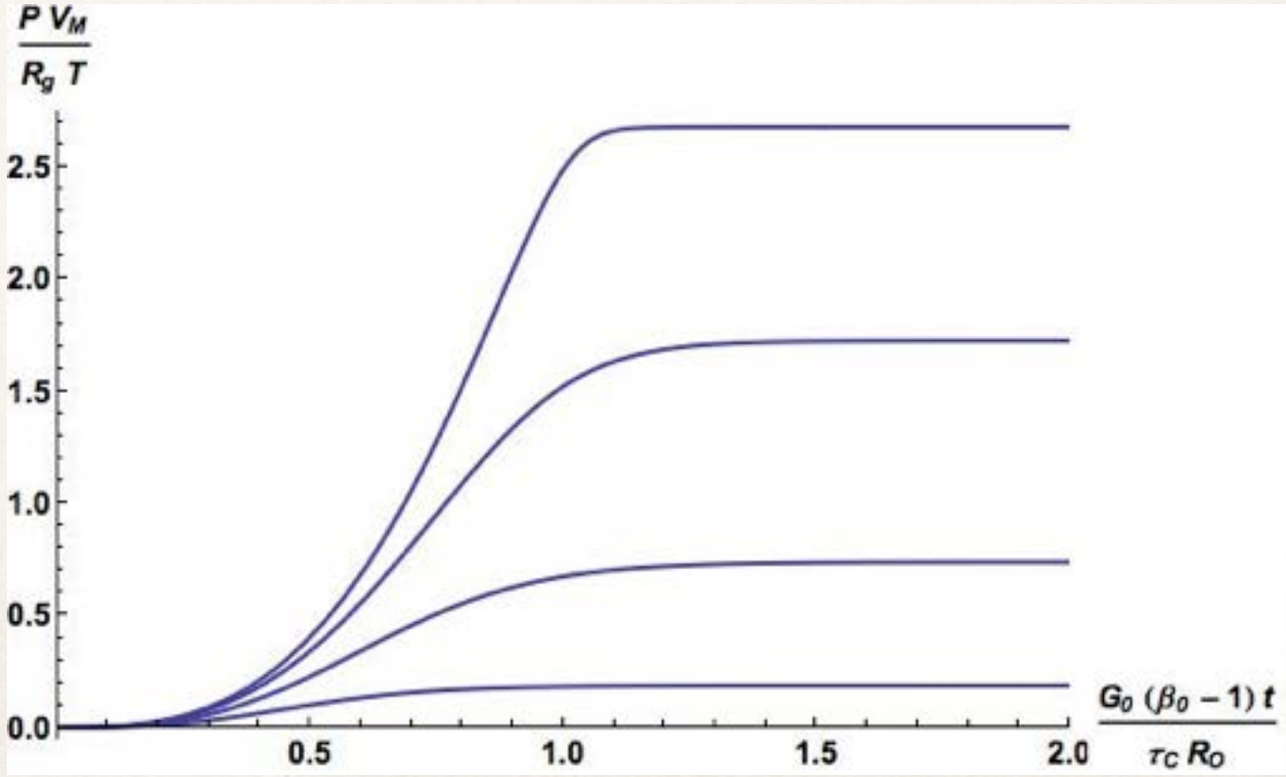
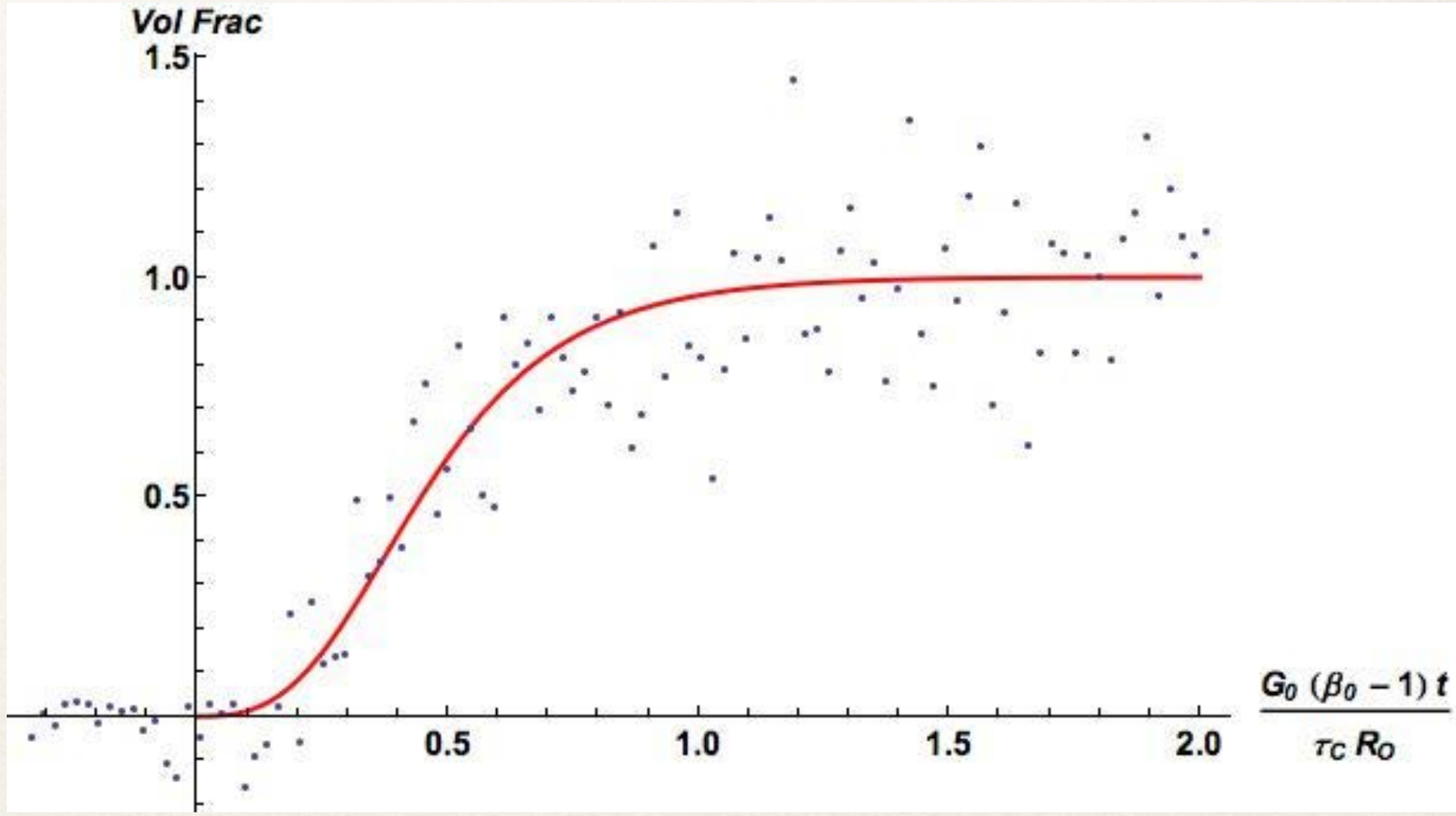


Comparison to Data

- NMR measurements of average solution concentration during growth of hepta in pores of stone
- Plot of normalized volume fraction versus normalized time indicates $R_O \approx 1$ cm
- If a single crystal grows that far, it must enter diffusion control



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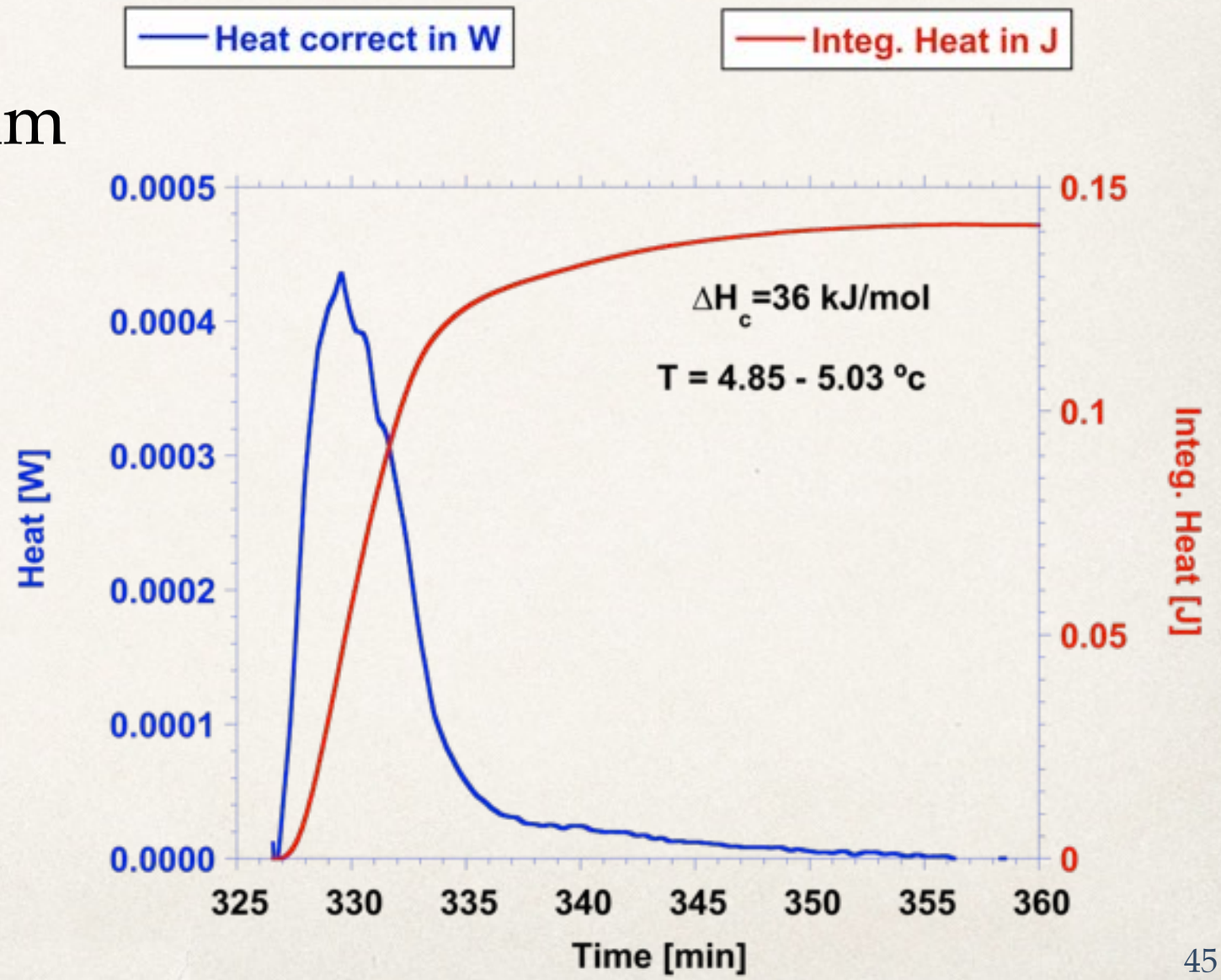
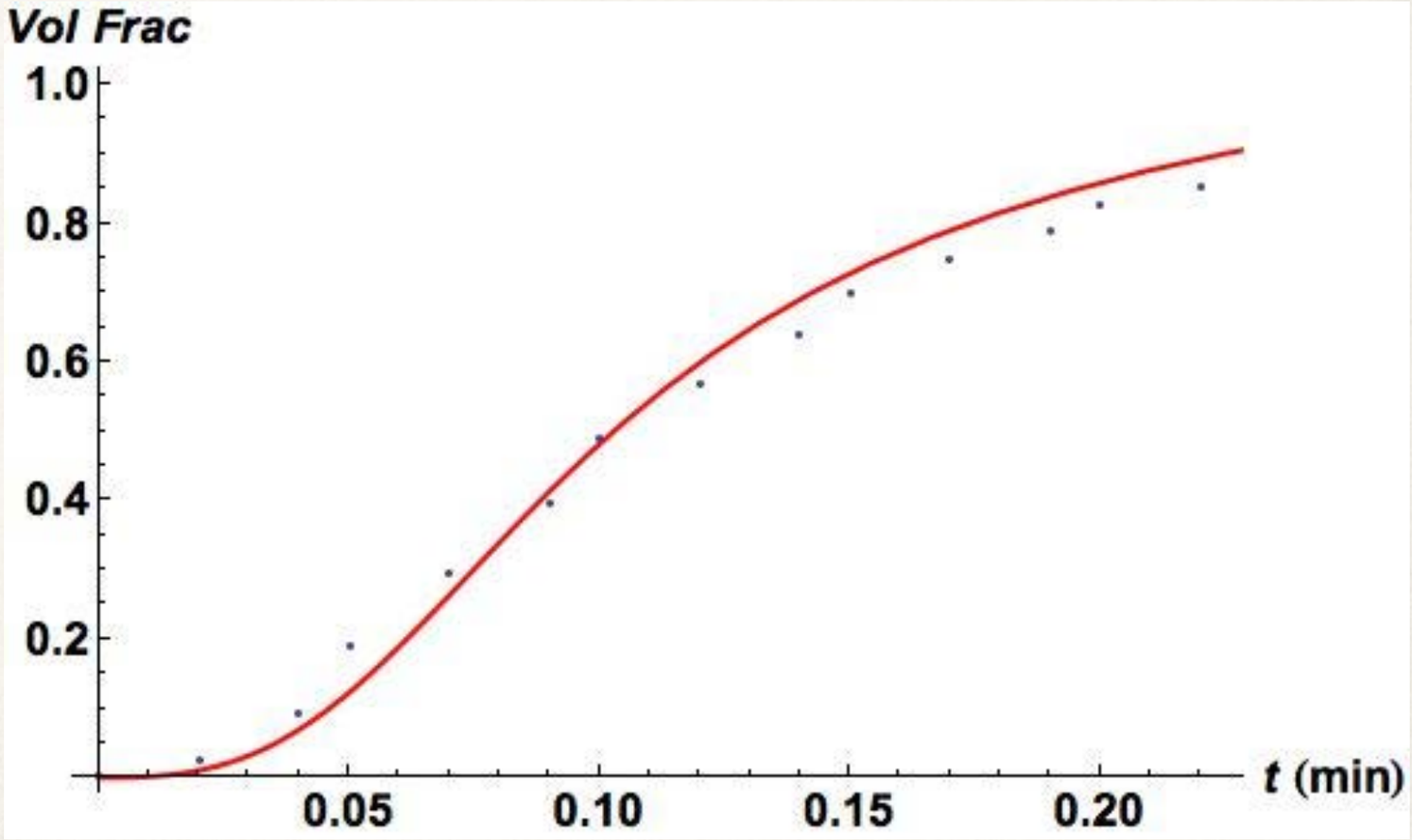
Comparison to Data

- DSC data for hepta in limestone
- Fit implies $R_0 \approx 0.3$ mm (similar to size of DSC sample)
- Implies growth of few crystals with high tortuosity or difficulty branching at nodes in network



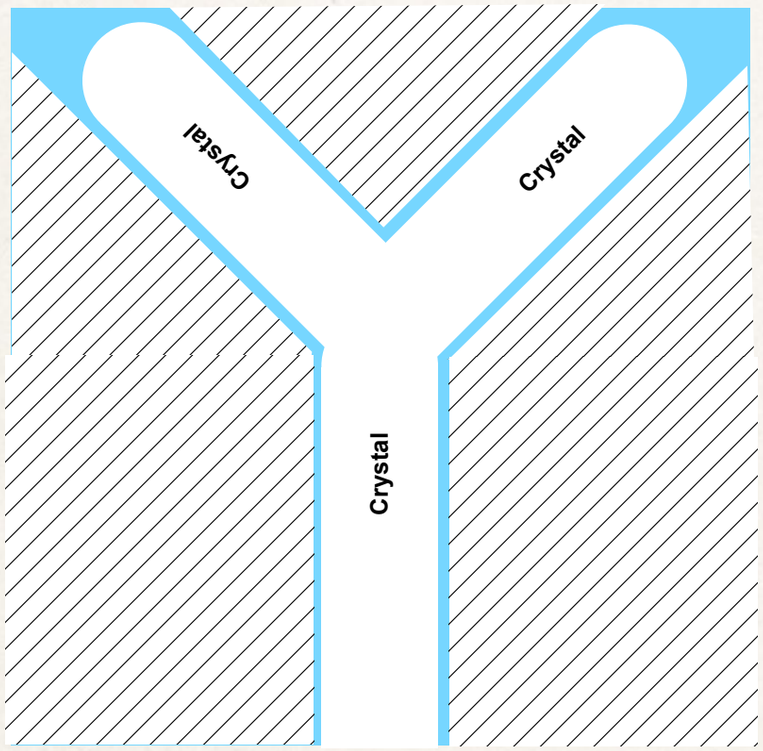
Comparison to Data

- DSC data for mirabilite in limestone (symbols) agree well with theory
- Duration of transition longer than time for one crystal to grow across the sample
- Implies growth of one crystal with high tortuosity or difficulty branching at nodes in network

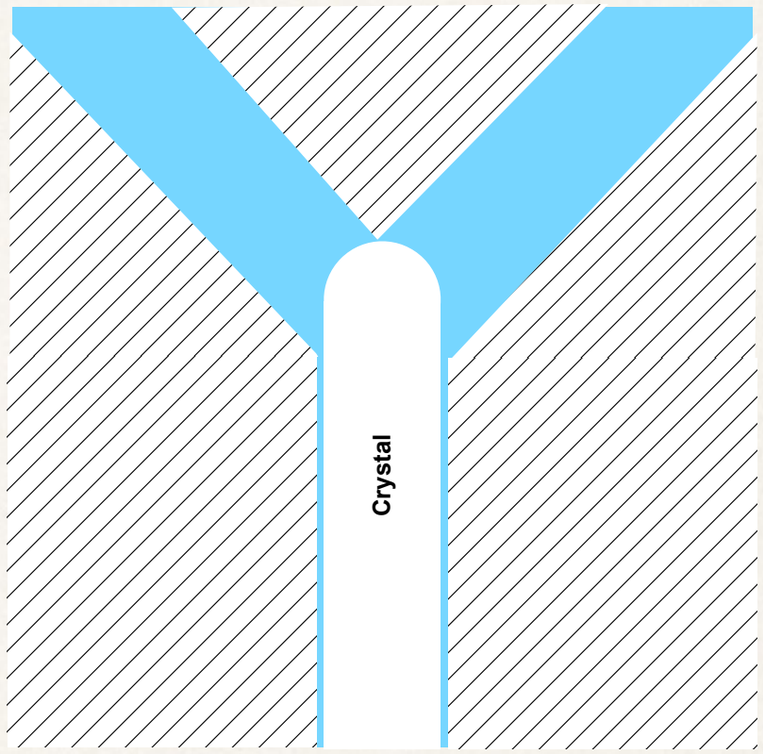


Branching at Nodes

- Can crystals branch freely at nodes, or are they trapped?



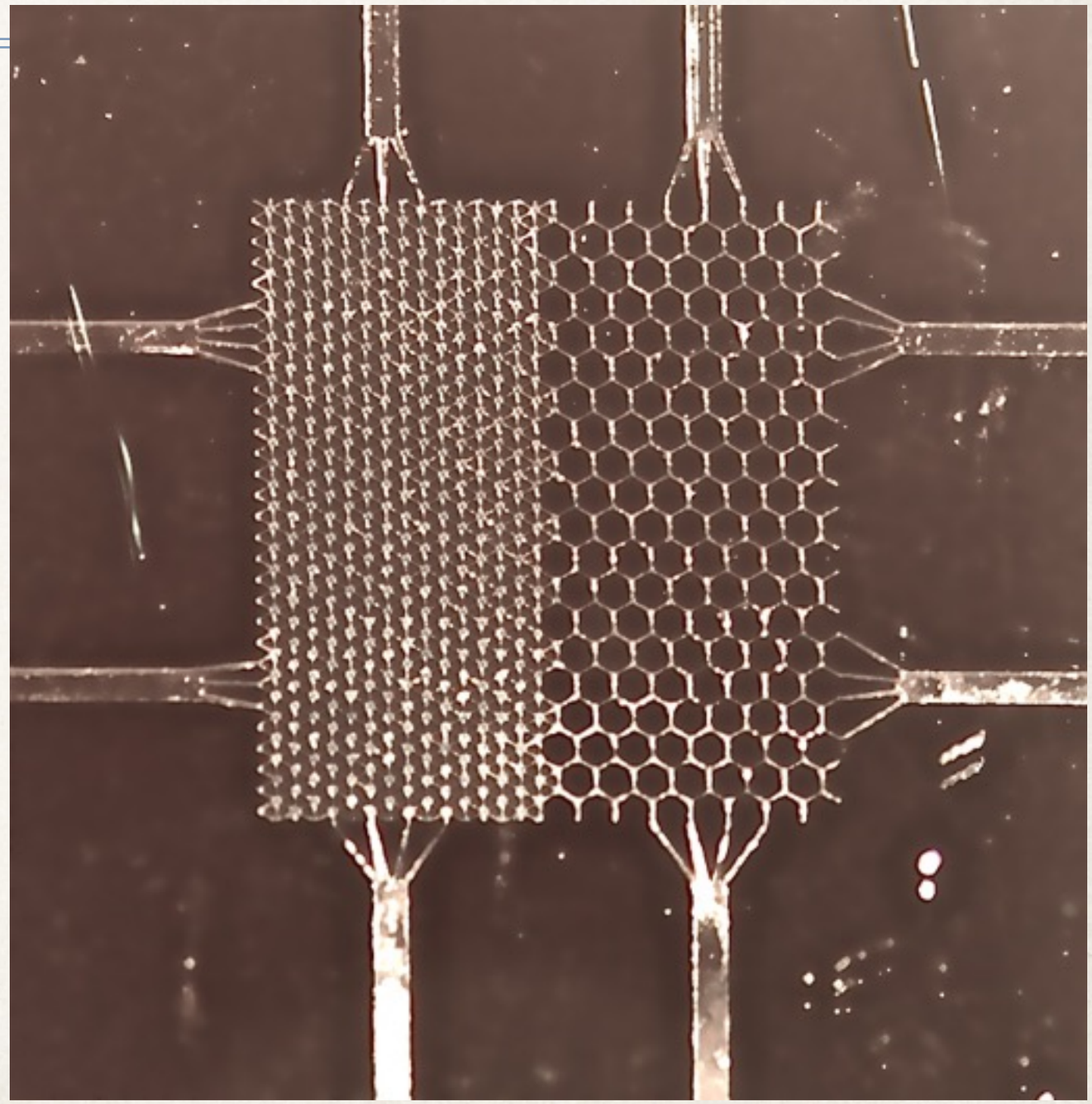
In this case, a single crystal can transform all the pore volume



In this case, diffusion to the trapped crystal generates crystallization pressure

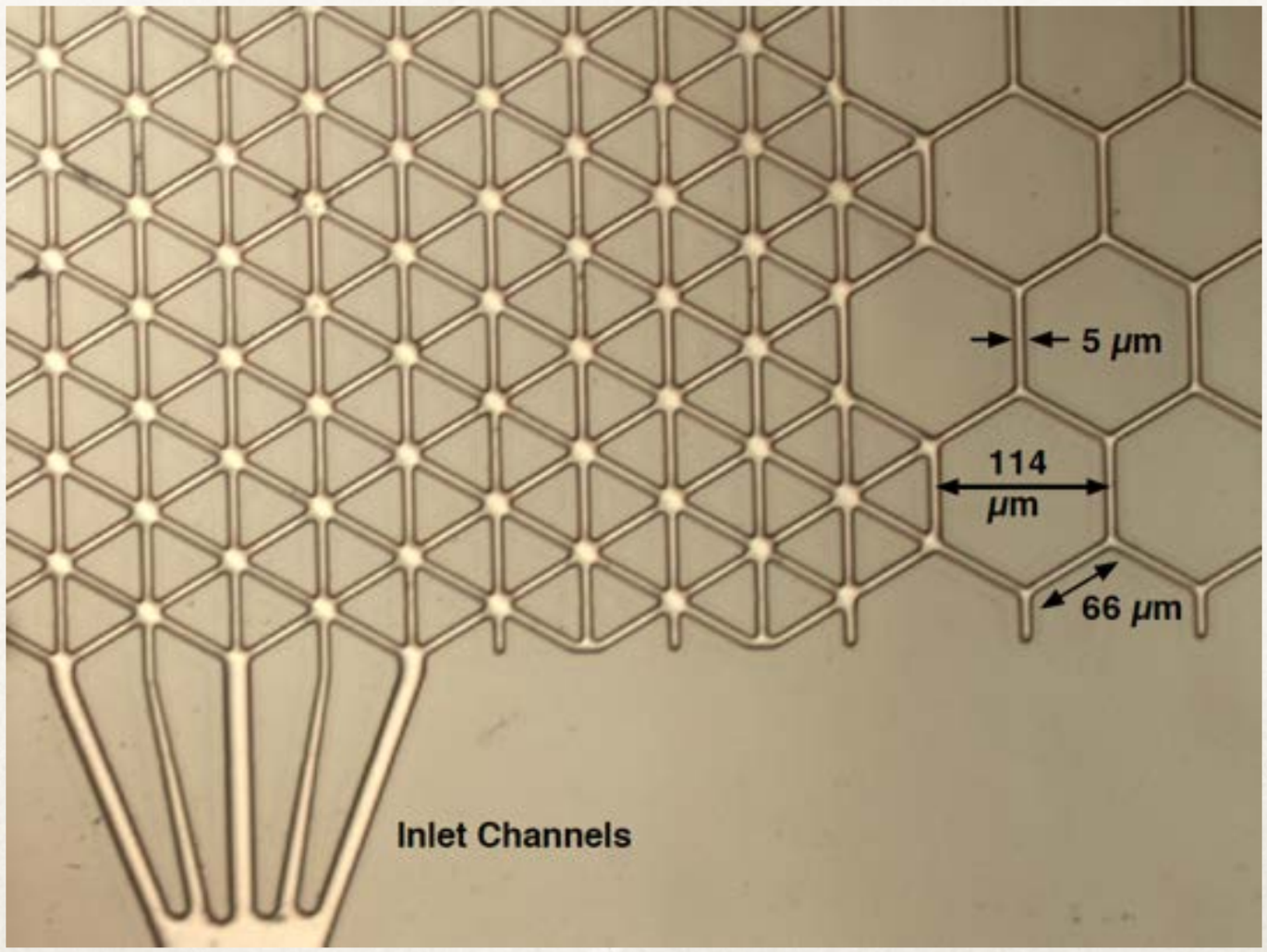
Test of Growth in Channels

- Channels 5 μm wide & deep etched into Si, covered with glass
- Channels filled with solution (3 molal Na_2SO_4)
- Cooled to induce supersaturation



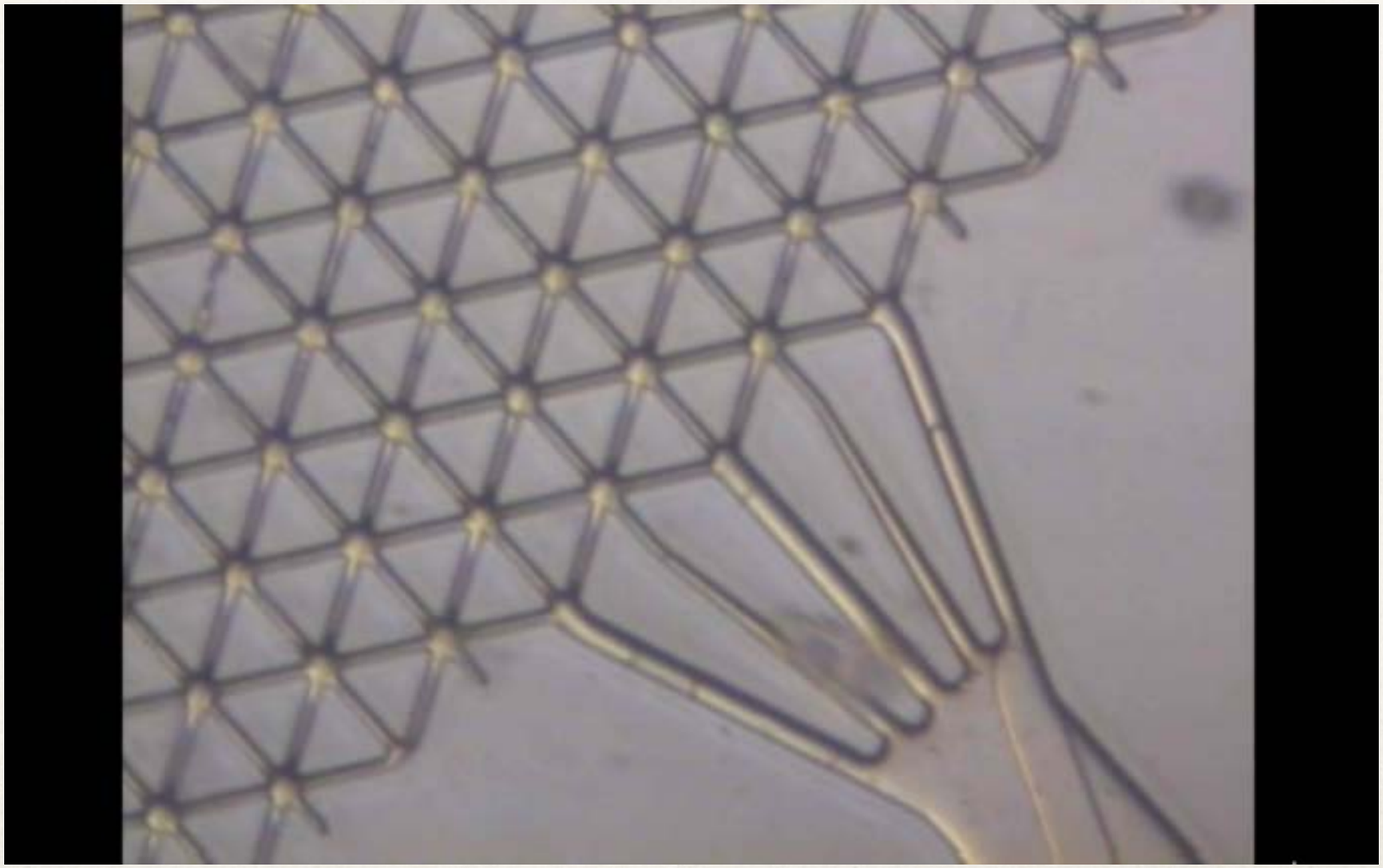
Channel structure

- Triangular pattern allows growth in straight line, but hexagonal pattern requires turn at every junction



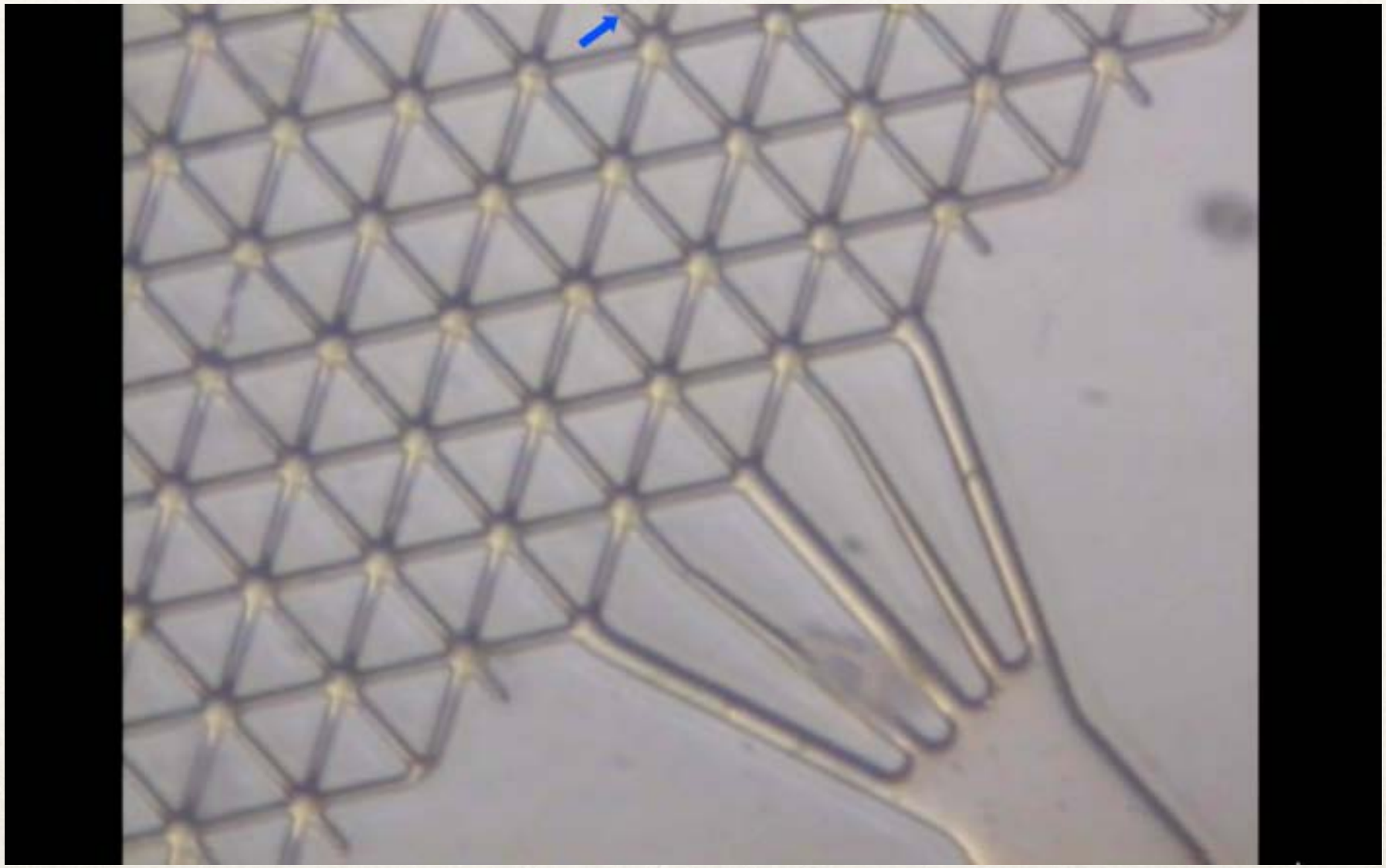
Growth in Channels

- 3 molal Sodium sulfate



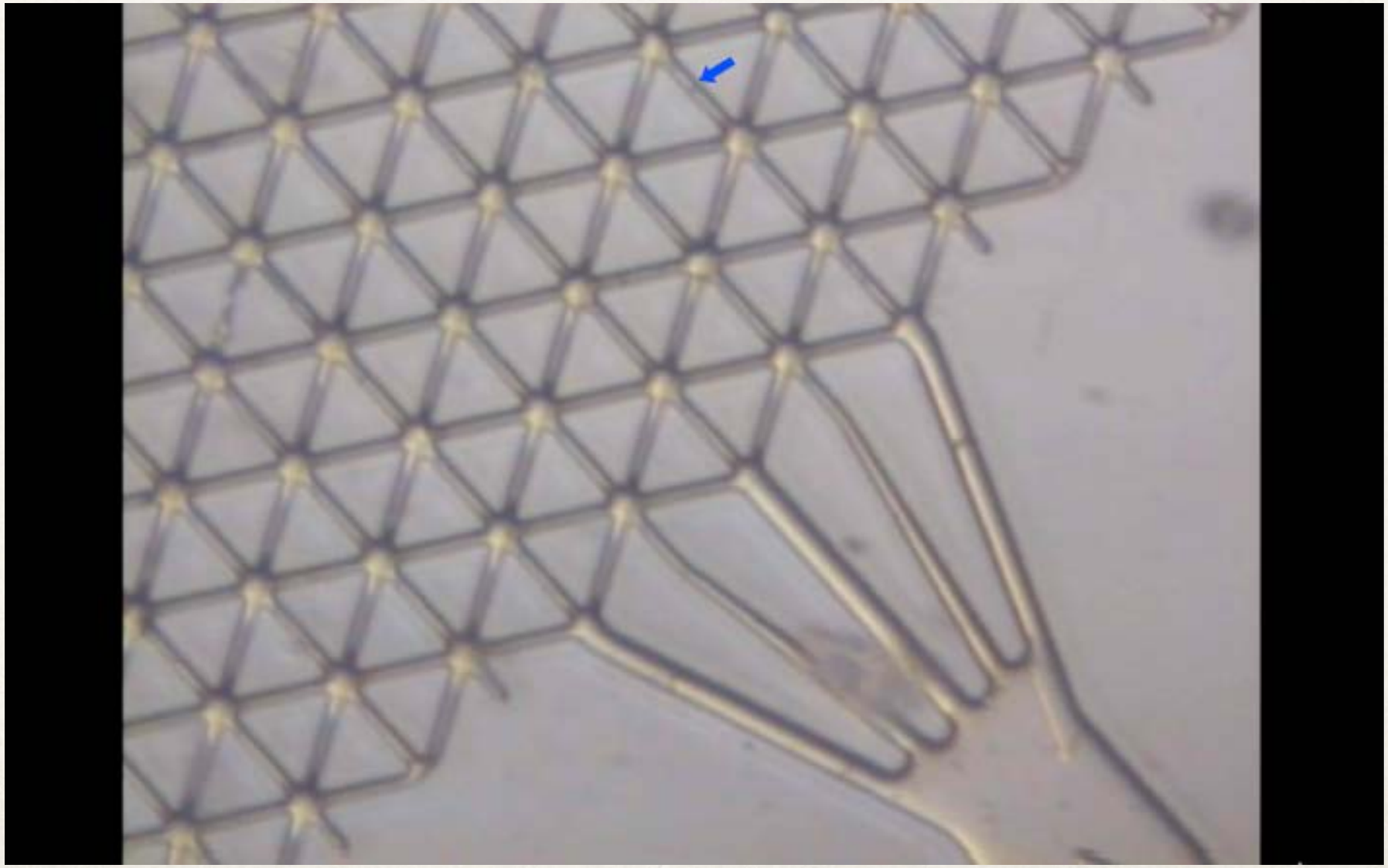
Branching

- Crystal enters



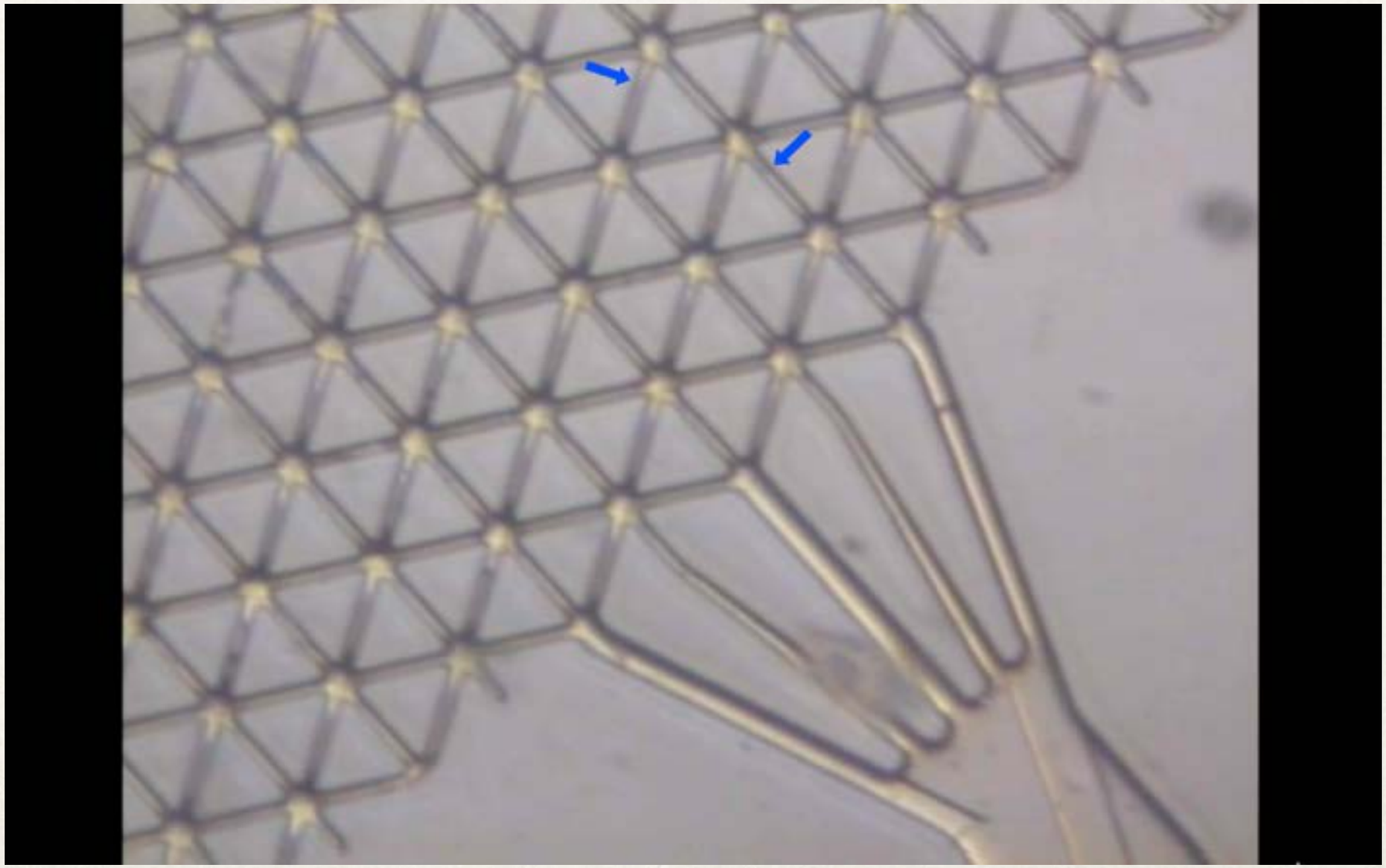
Branching

- Crystal passes junction, no branching



Branching

- Branch occurs



Conclusions

- Existence of crystallization pressure implies growth controlled by interface kinetics, not diffusion
  - If branching occurred freely, pores would fill quickly
- Slow transformations observed experimentally imply blocking at nodes in pore network
  - Blocked crystals probably grow intermittently at high supersaturation
- Images show delayed branching of sodium sulfate in lithographic channels
  - Need more control over nucleation, better images, numerical simulation of diffusion and growth kinetics

Acknowledgments

- Gilles Chanvillard
- Lafarge, for its support of Gilles at Princeton (2004)
- Dr Saurabh Vyawahare (pattern fabrication), John Bestoso (pattern design), Prof. Jim Sturm

PDMS Channels

- Pattern originally made in PDMS
- Channels distorted by crystallization pressure
- Therefore, created new pattern in silicon