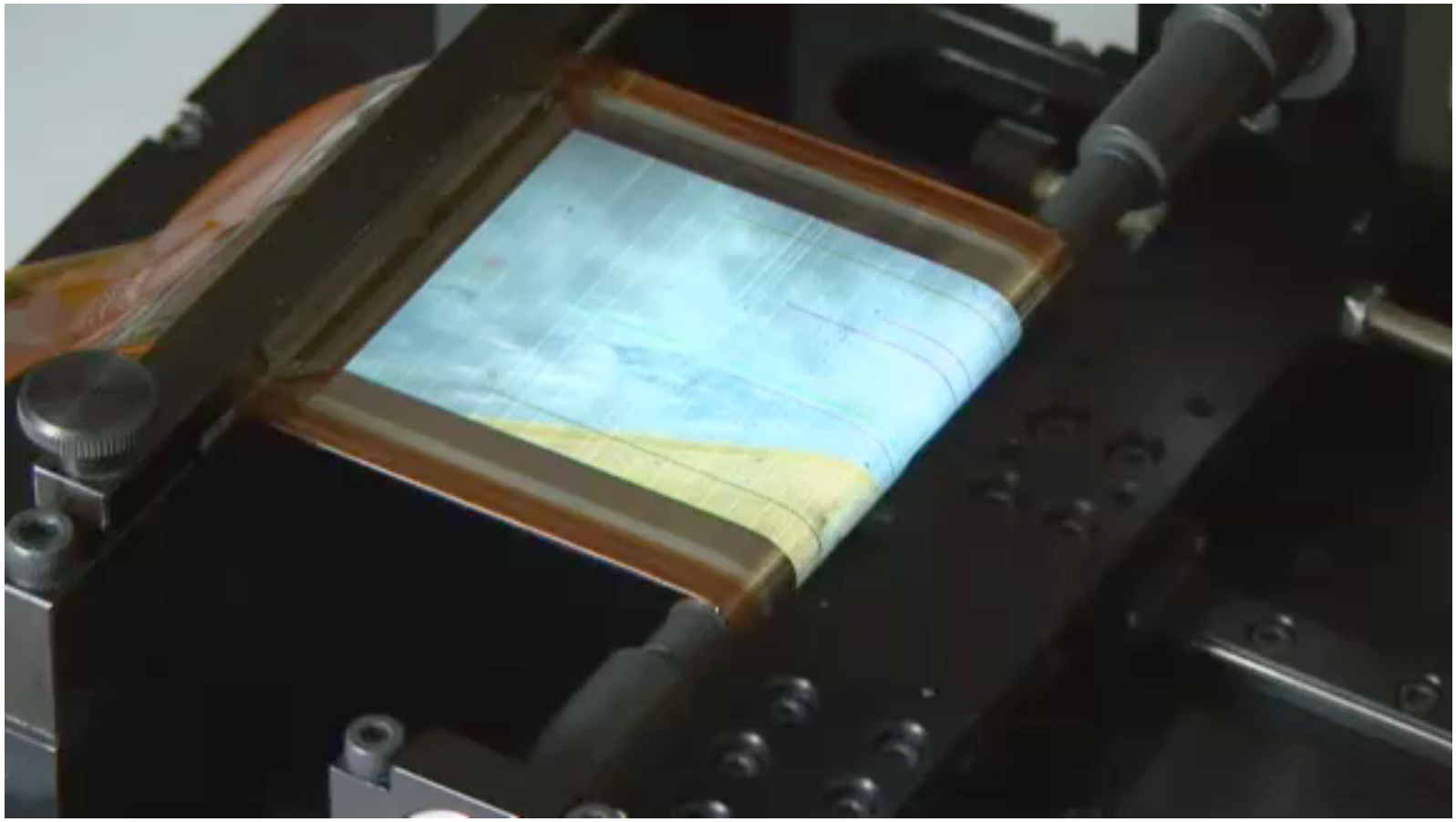
Low Temperature Solvent Annealing in Organic Thin Films

A. E. Hosoi
with Tony Yu and Vladimir Bulovic

Battelle
The Business of Innovation

Organic electronics

Flexible Devices



Sony OTFT-driven OLED

Organic Electronics

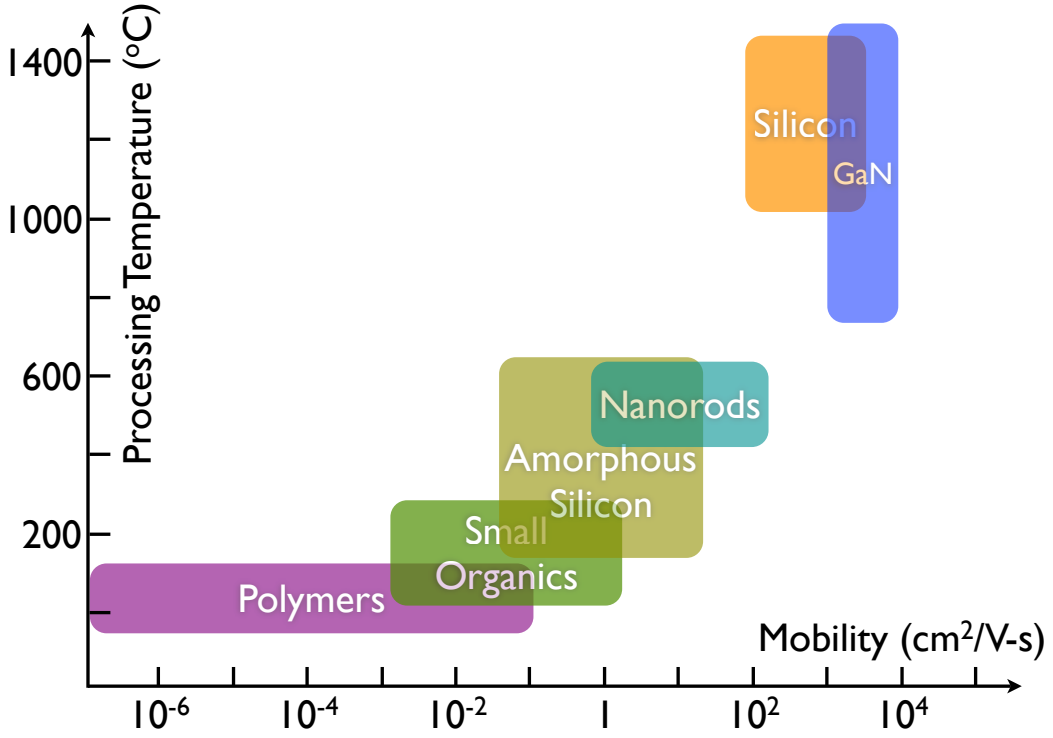
Advantages

- Flexibility
- Transparency
- Low temperature manufacturing (Low cost)

Challenges

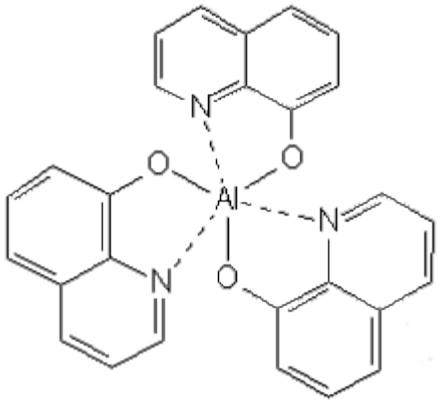
- Low mobility (slow)

Goal: Make crystalline films and structures out of organic semiconductors

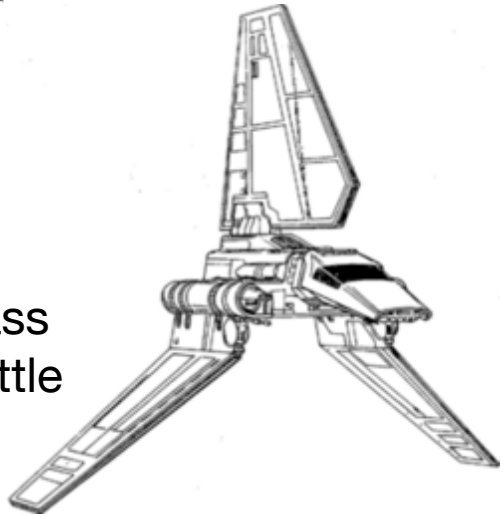


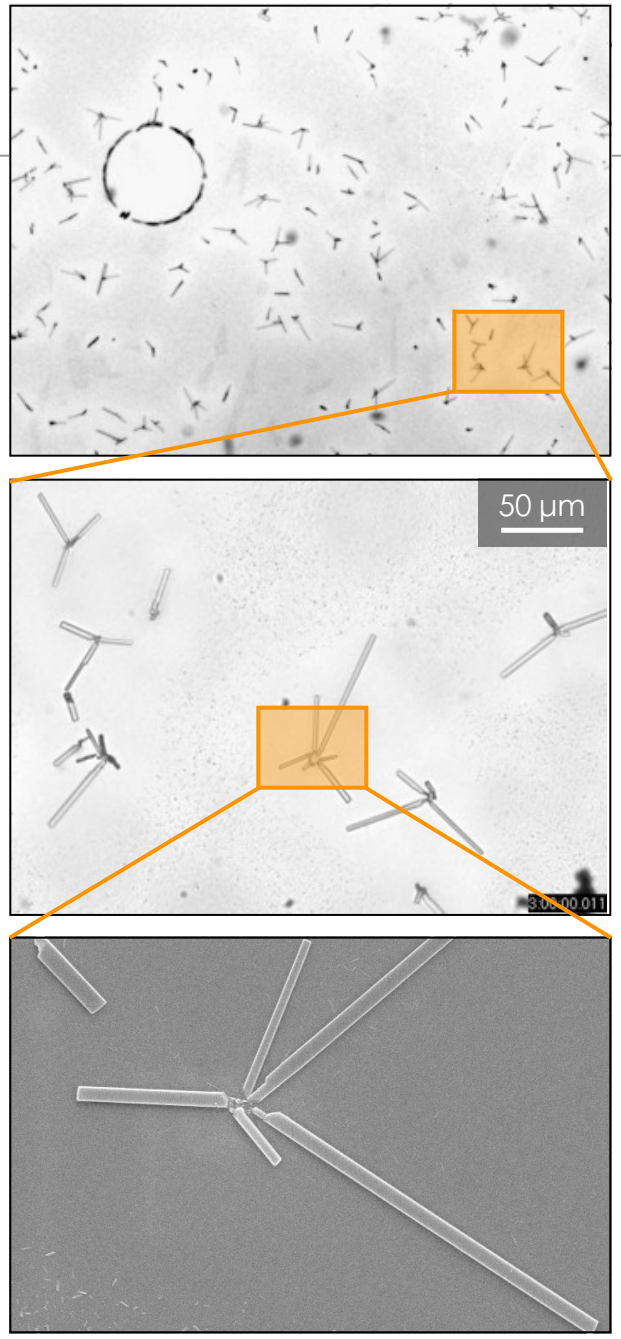
Our Molecule

Tris(8-hydroxyquinoline)aluminium (Alq3)

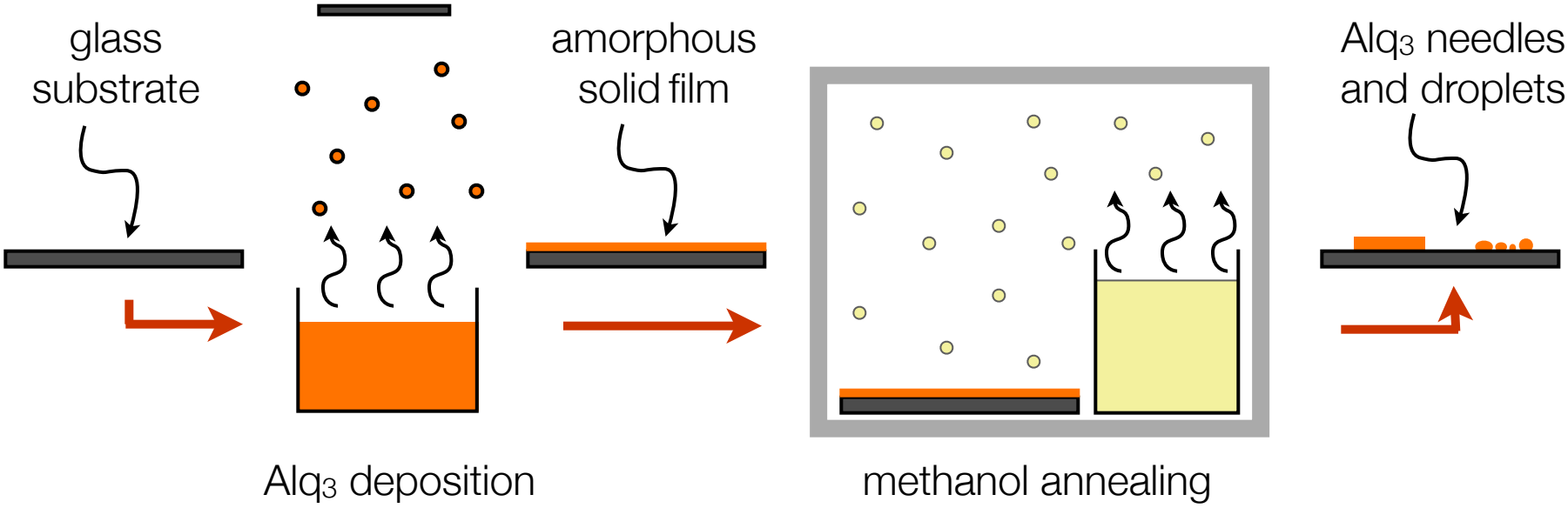


Lambda Class
Imperial Shuttle

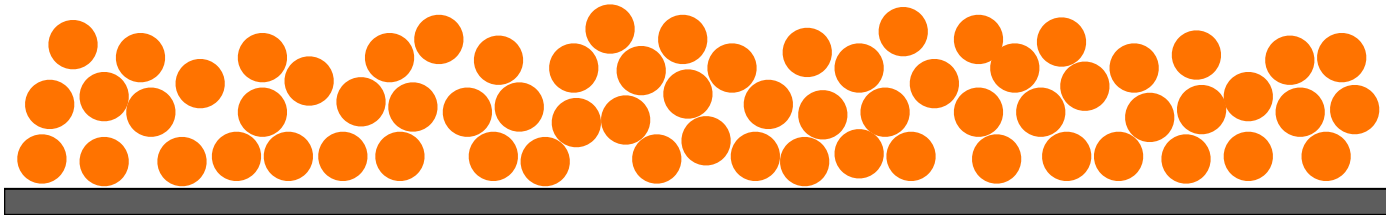




Producing Alq_3 needles on glass



Physical Picture



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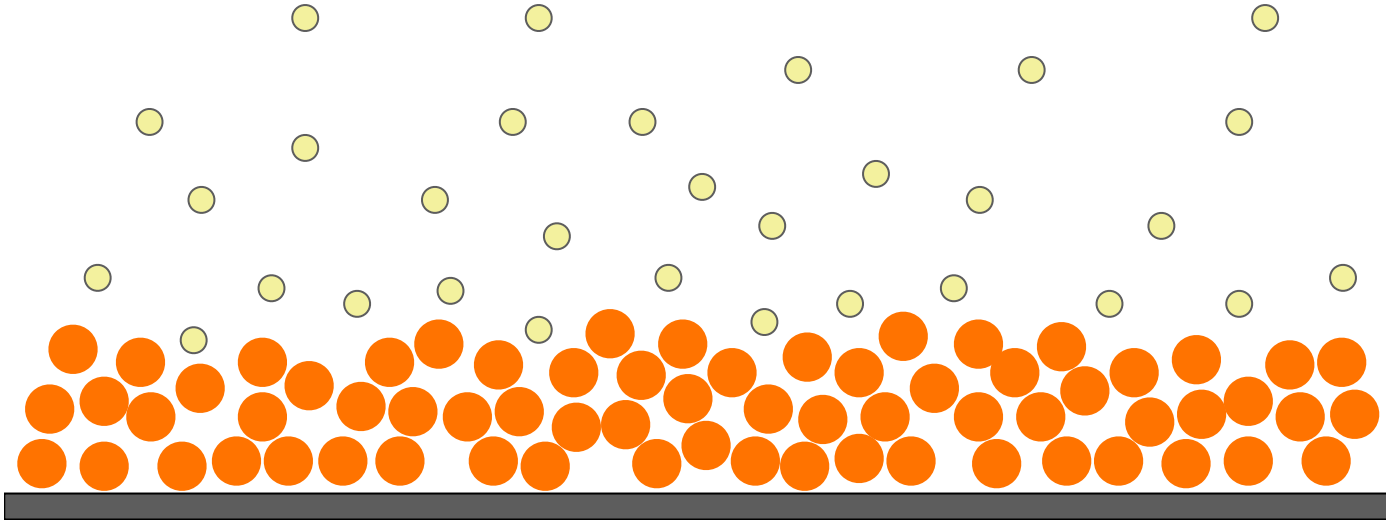

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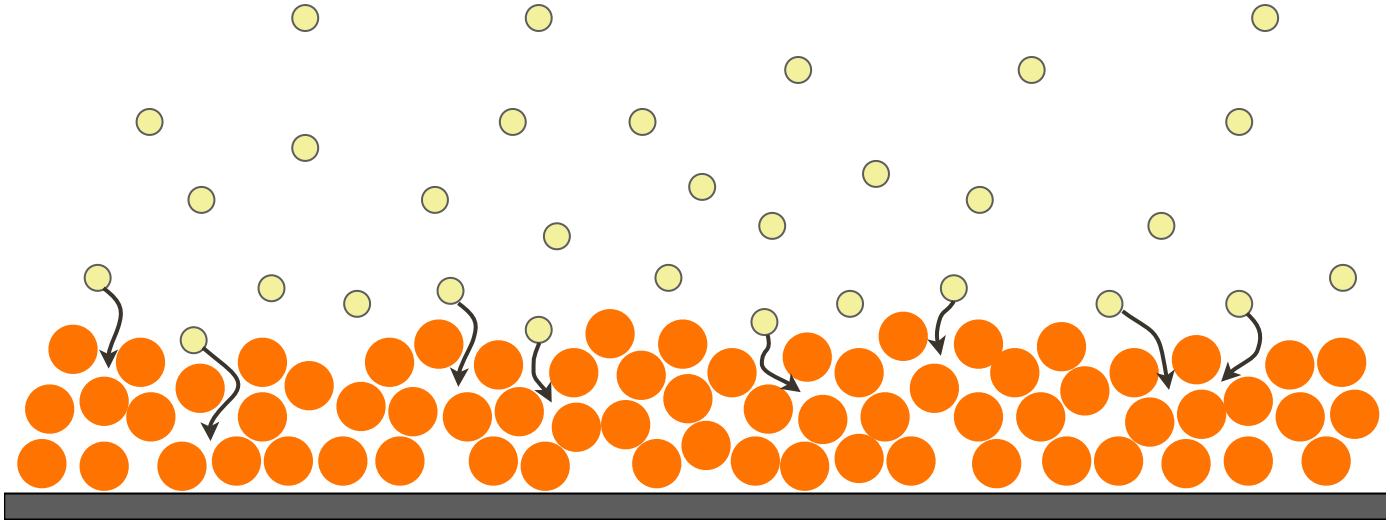

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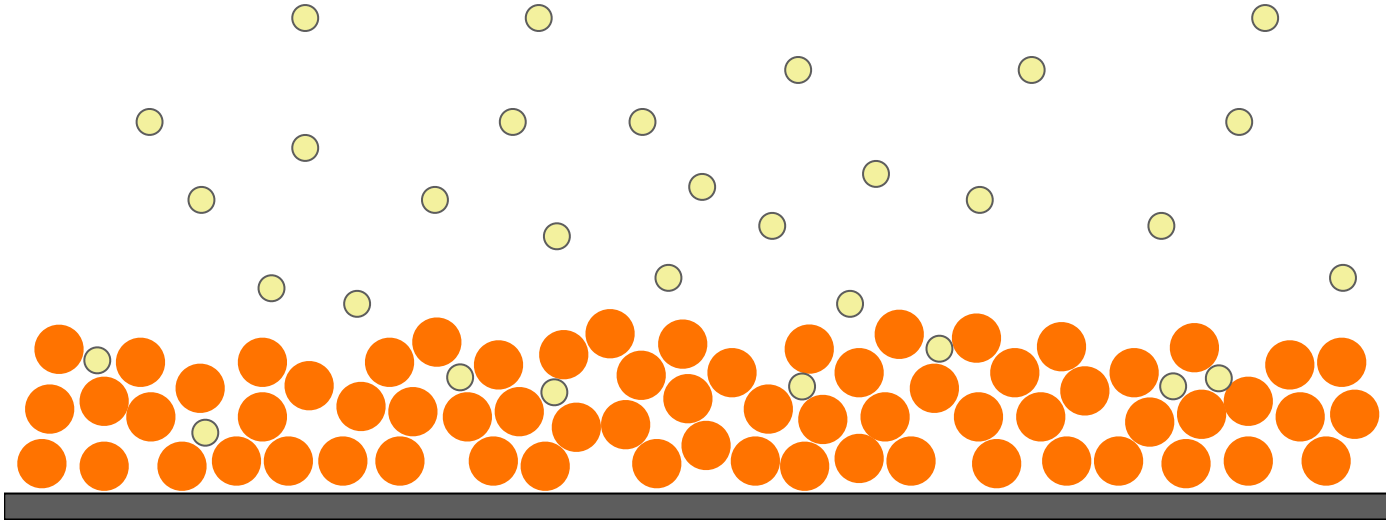

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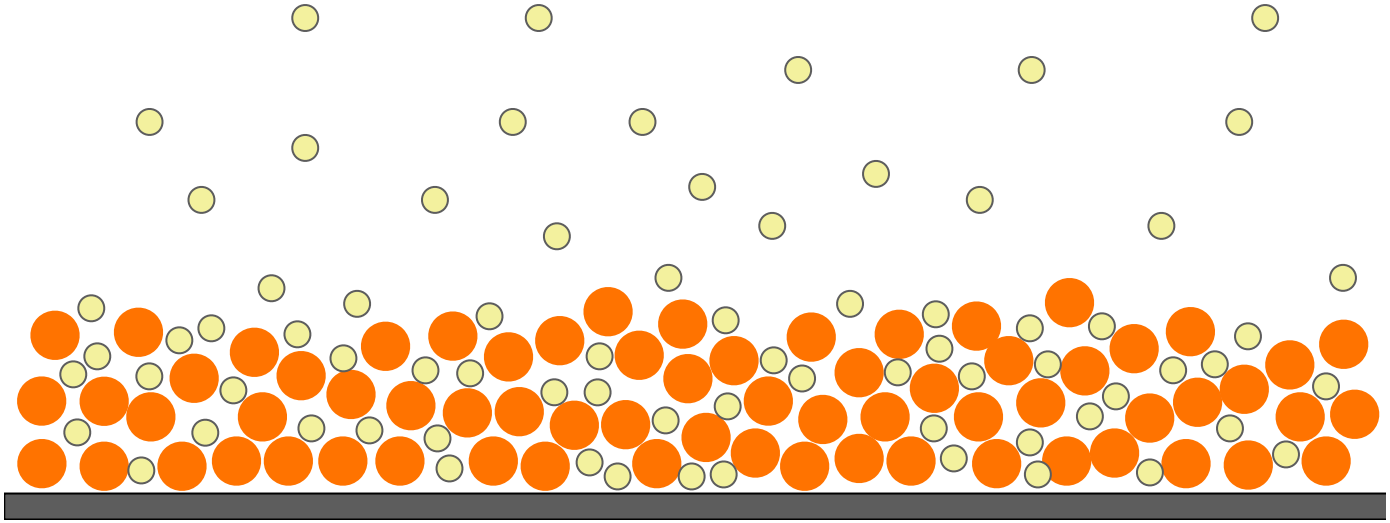
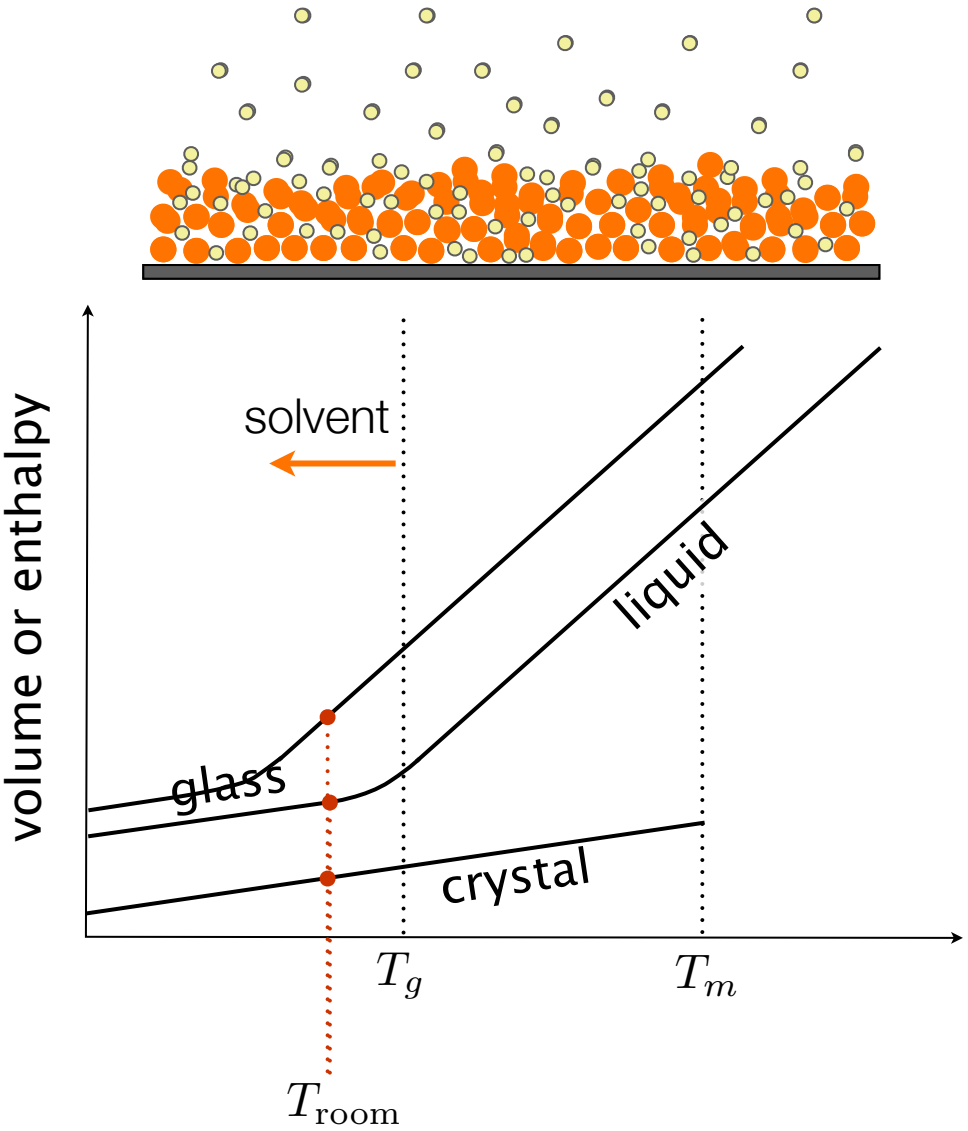
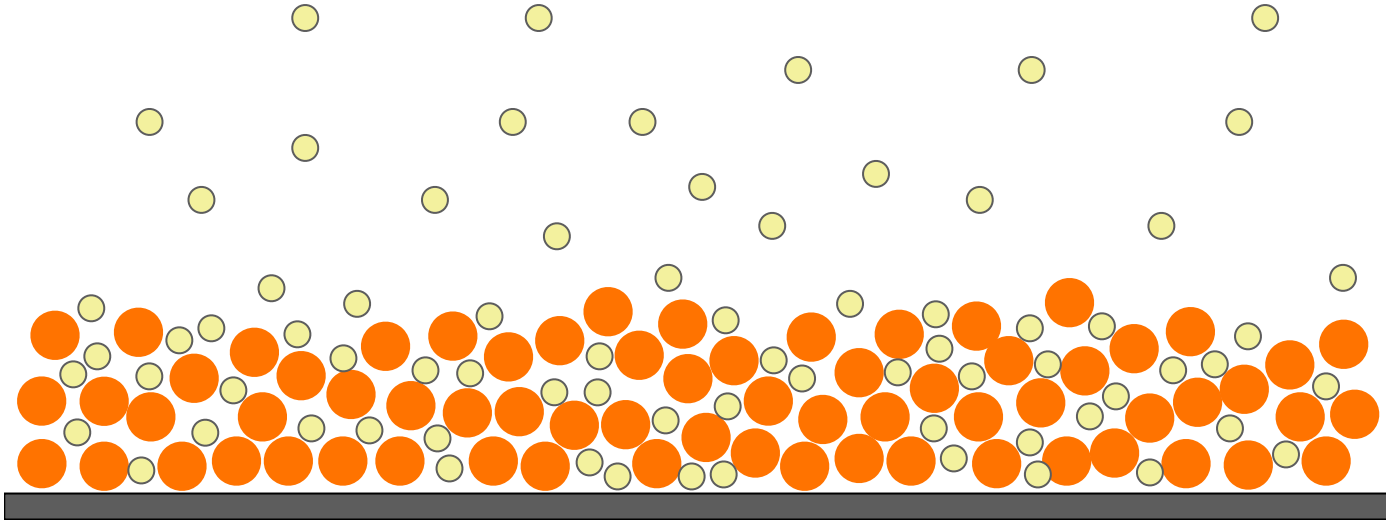


Solvent annealing: plasticization



Debenedetti and Stillinger (2001)

Physical Picture



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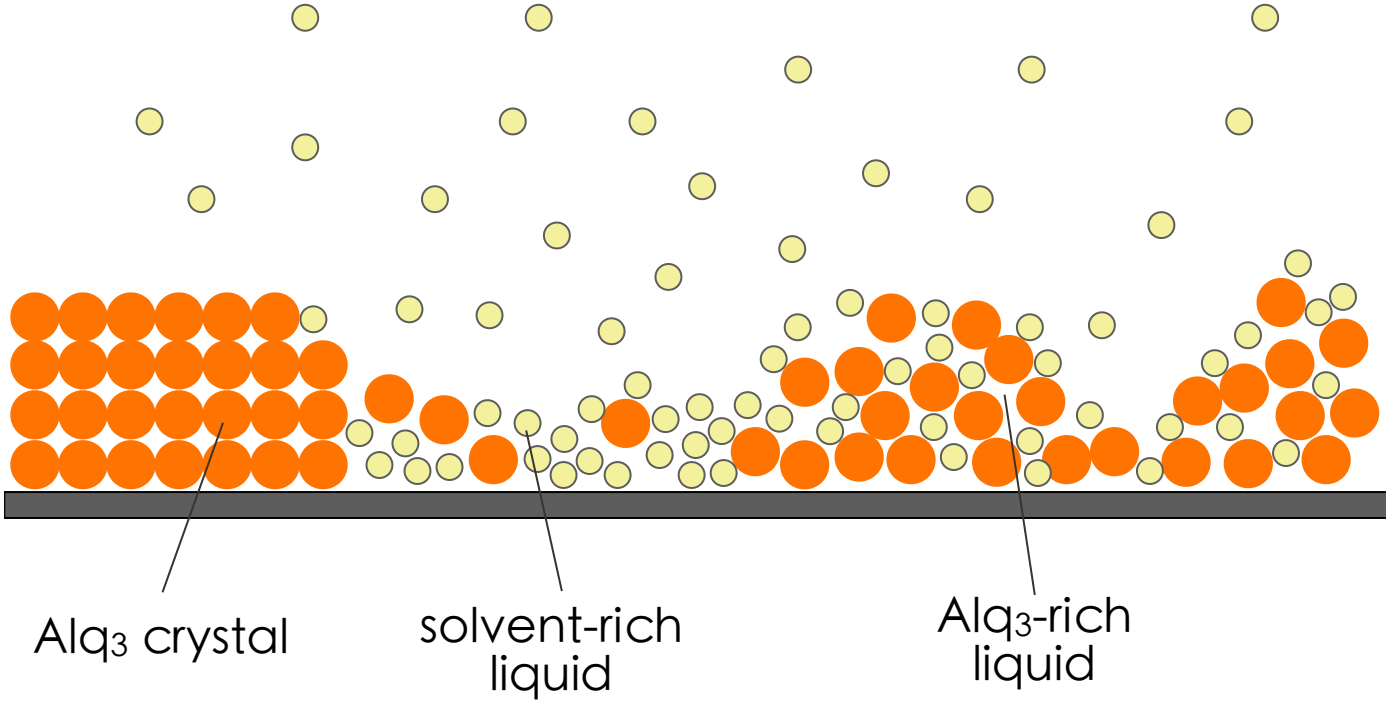

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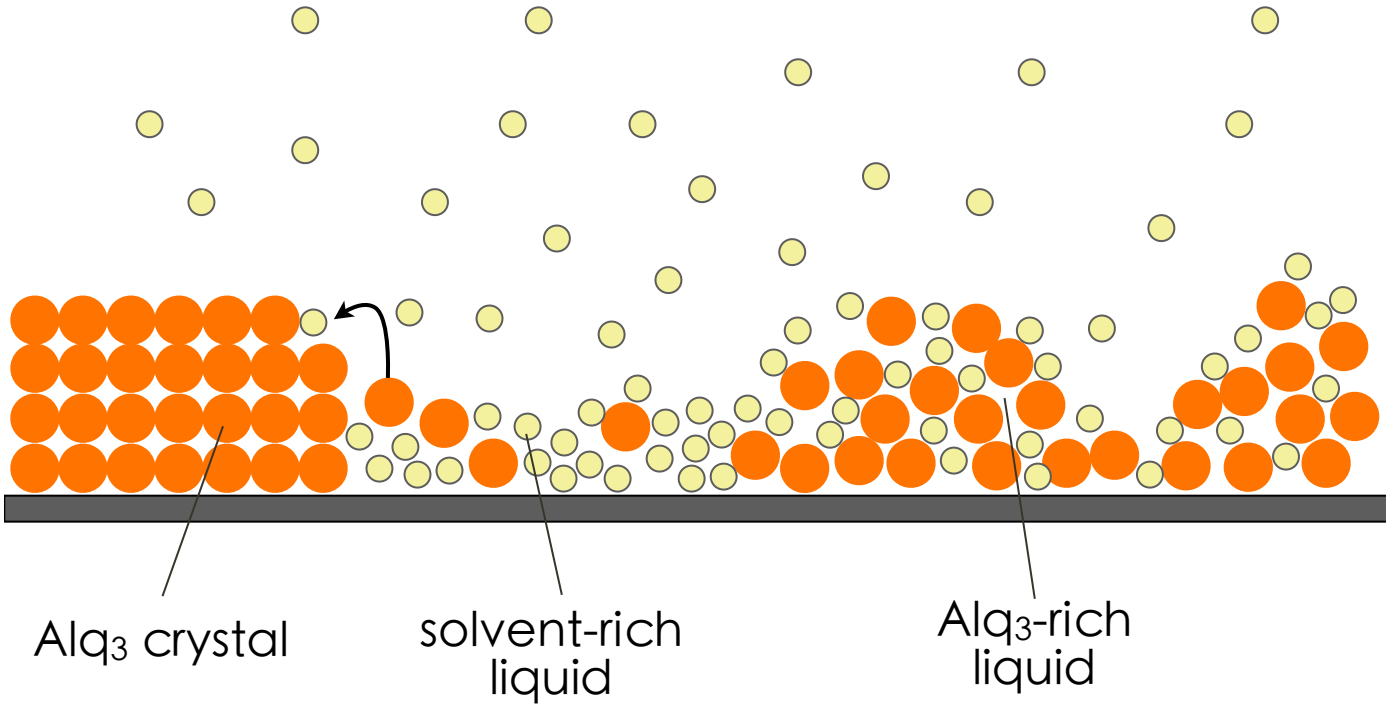

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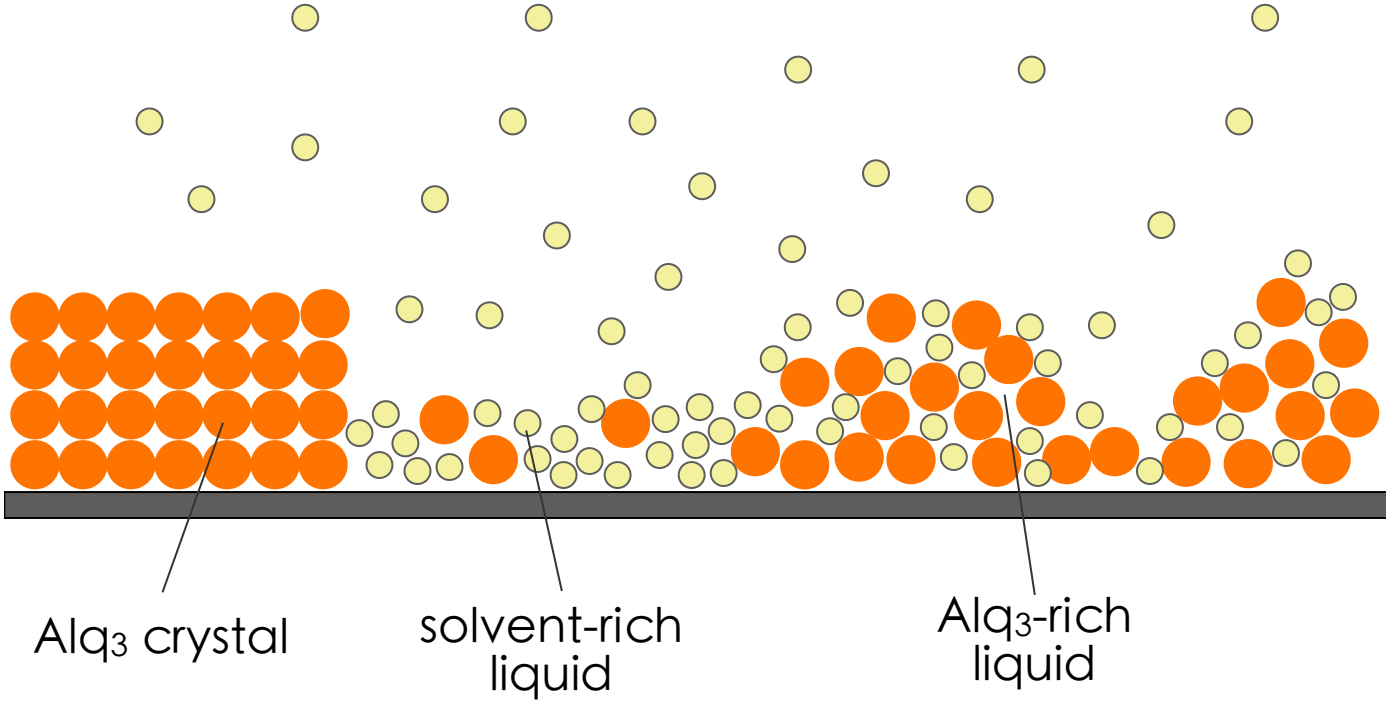

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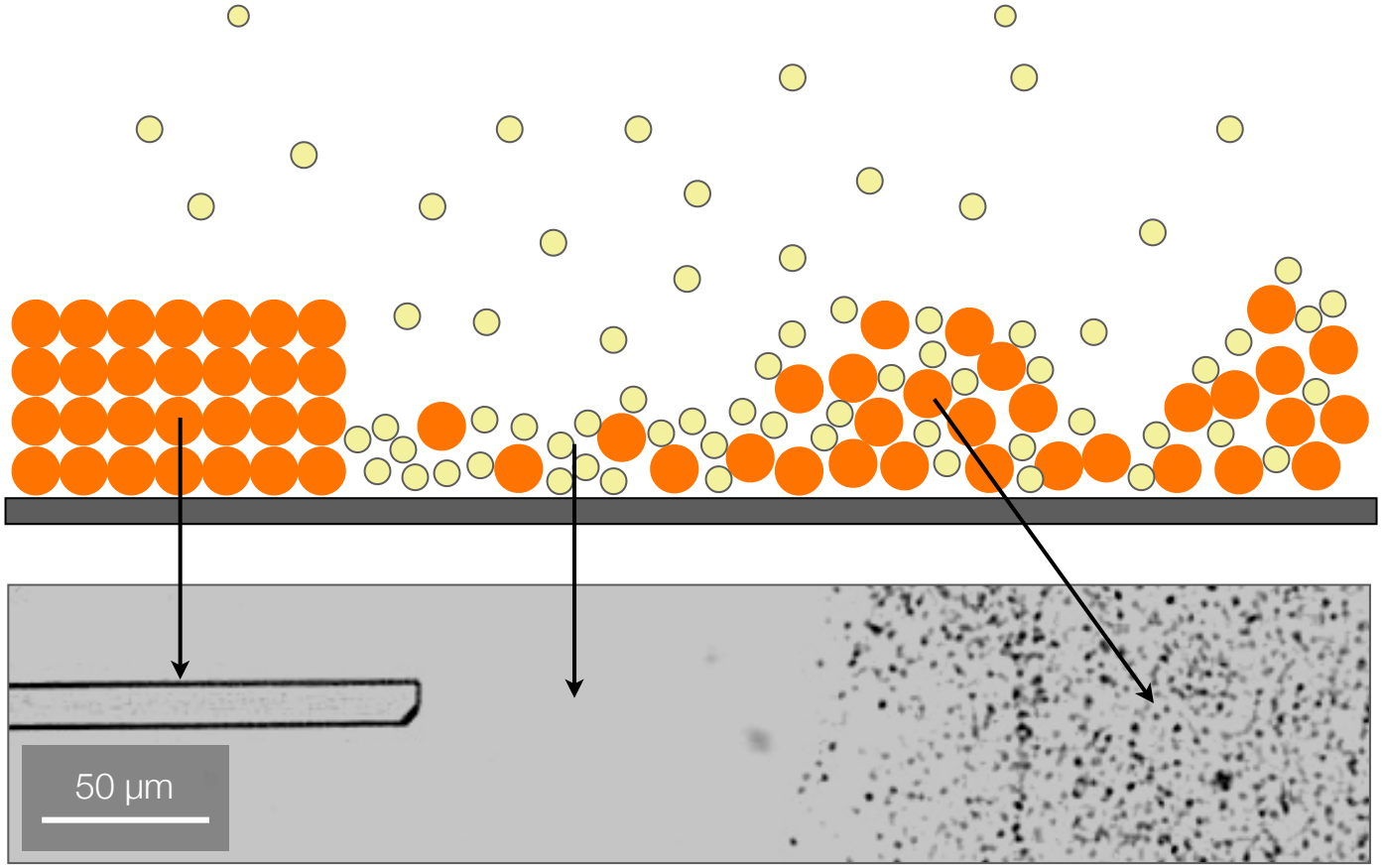
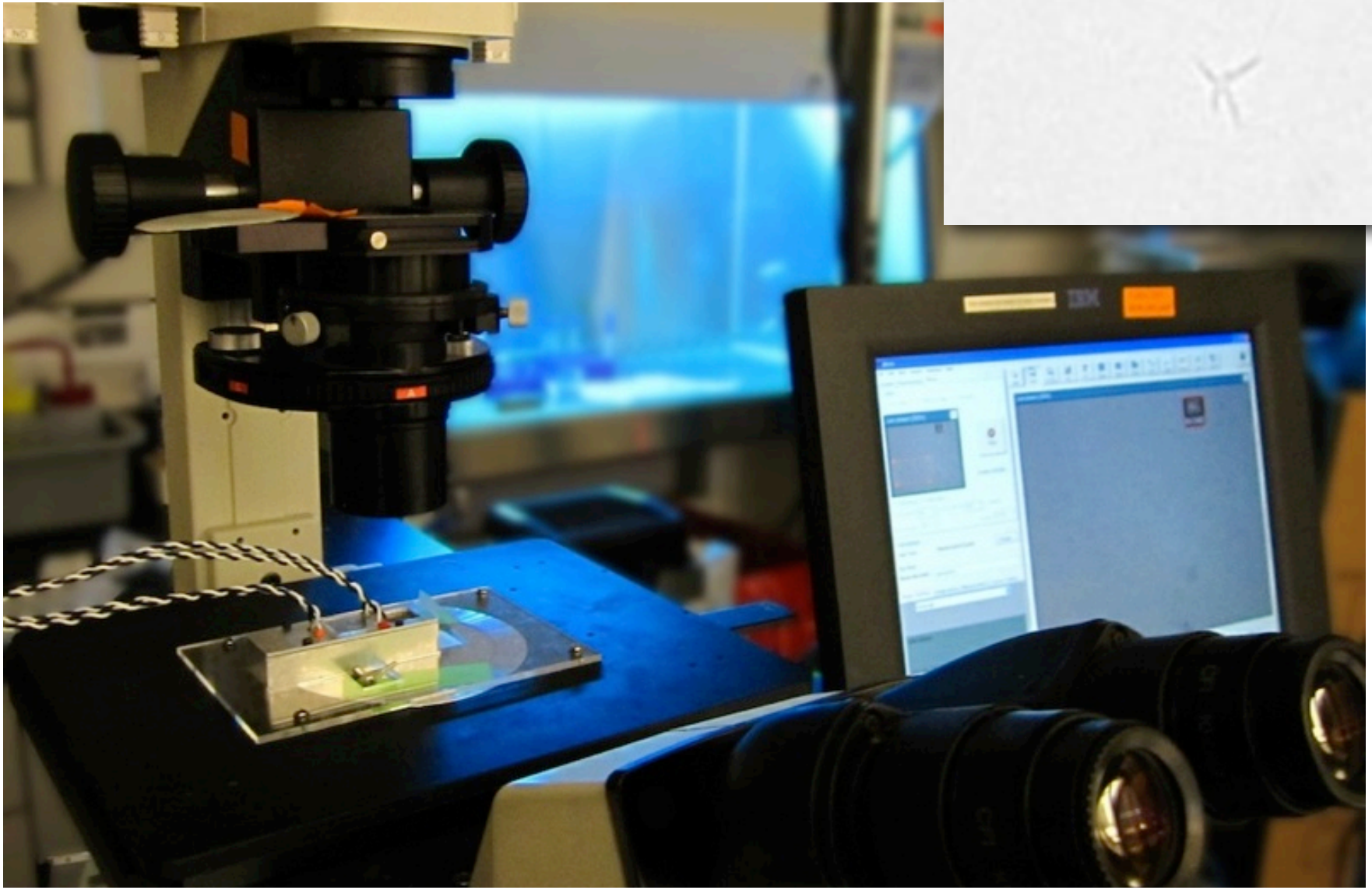
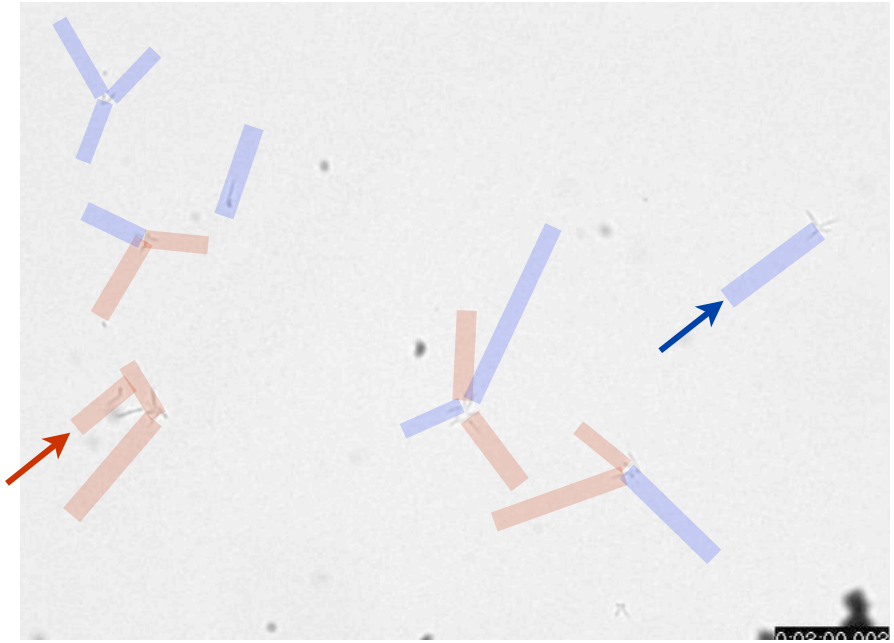


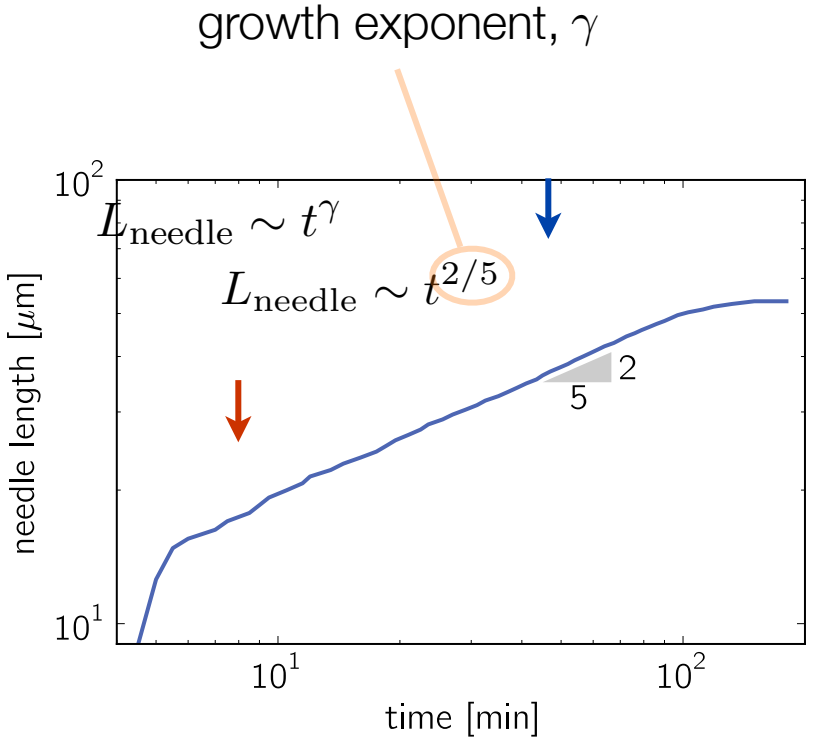
Experiments



Needle growth rates

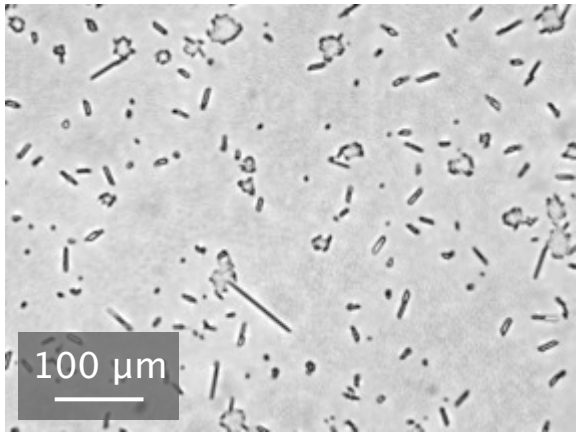


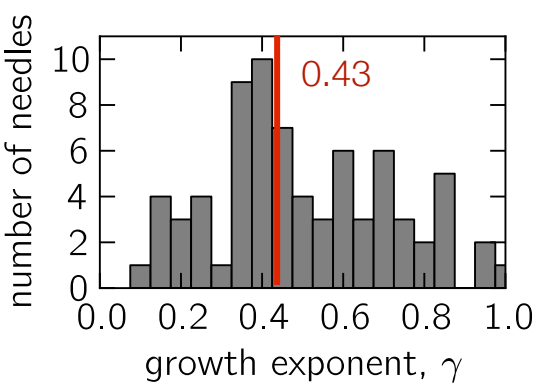
unobstructed
obstructed



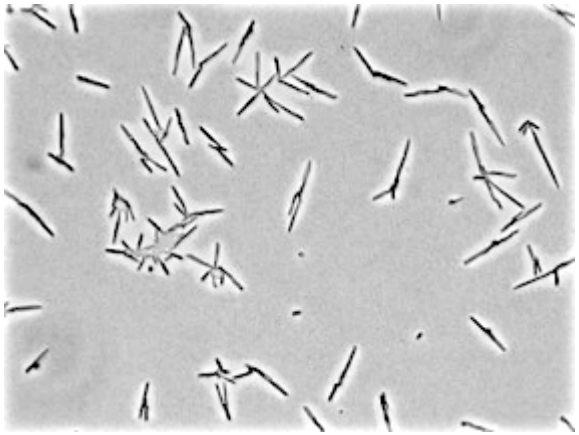
Needle growth and film thickness

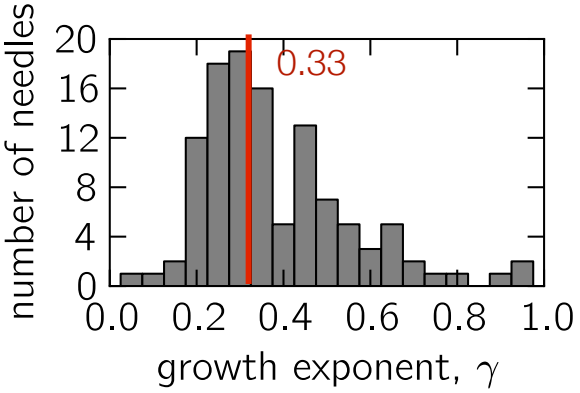
$h_{\mathrm{Alq_3}} = 15\,\mathrm{nm}$



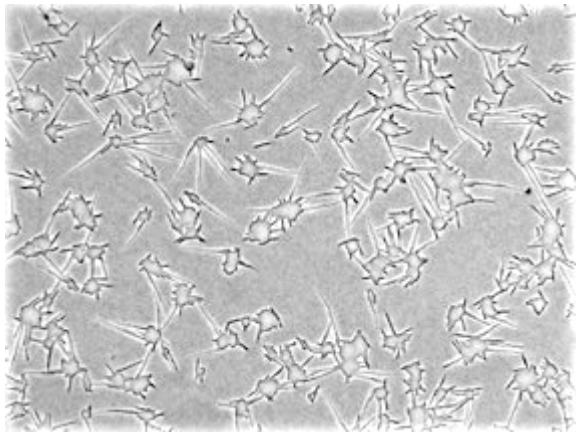


$h_{\mathrm{Alq_3}} = 30\,\mathrm{nm}$

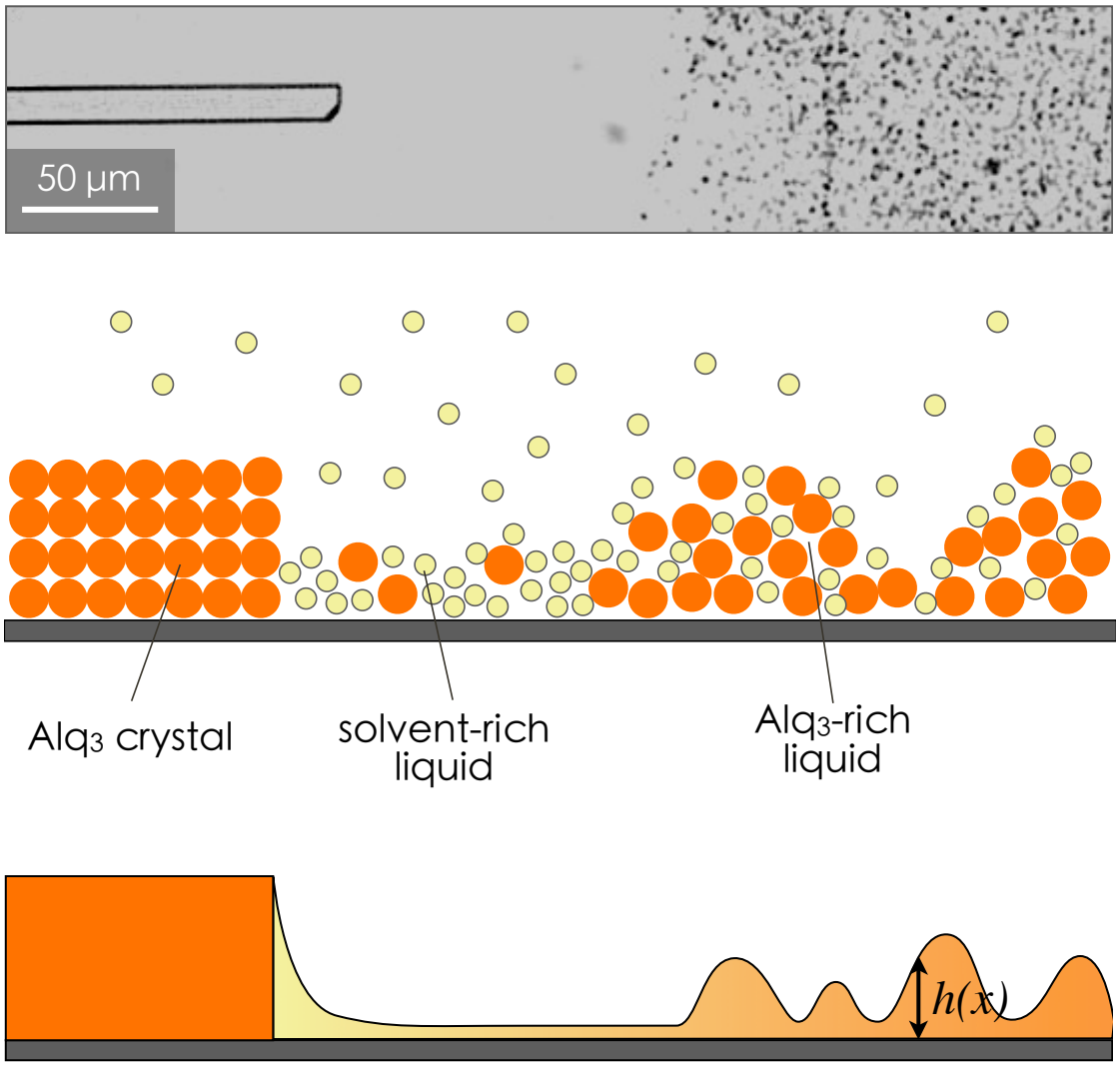




$h_{\mathrm{Alq_3}} = 60\,\mathrm{nm}$



Mathematical Model



Thin Film Model

fluid:
(mixture)

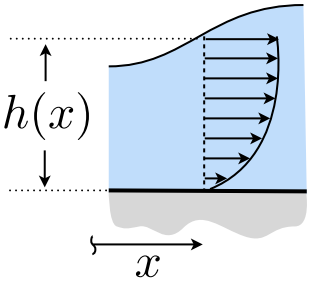
$$\frac{\partial h}{\partial t} = -\frac{\partial Q}{\partial x}$$

solvent:

$$\frac{\partial \phi h}{\partial t} = -\frac{\partial J}{\partial x}$$

net flux

$$Q = -\frac{h^3}{3\mu}\frac{\partial p}{\partial x}$$



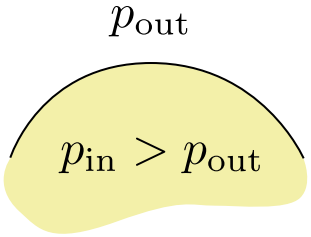
$$J = -Dh\frac{\partial \phi}{\partial x} + \phi Q$$

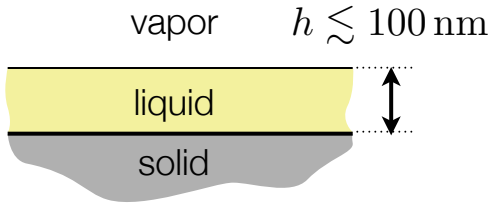
diffusion convection

$$p = -\sigma\frac{\partial^2 h}{\partial x^2} + \frac{A_{slv}}{6\pi\varepsilon^3}\left[\left(\frac{\varepsilon}{h}\right)^3 - \left(\frac{\varepsilon}{h}\right)^4\right]$$

capillary pressure disjoining pressure

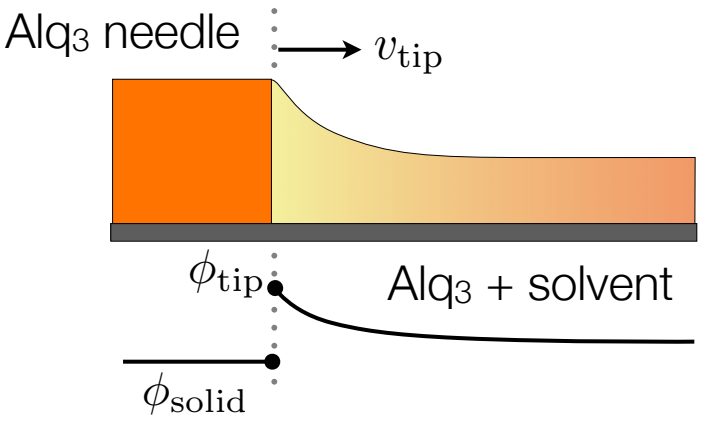
Aside: 6-12 potential give 3-9 exponents however experimental data indicates than many materials can be modeled with 3-4.





capillary pressure intermolecular pressure

Dimensionless evolution equations



thin film: $$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x}\left[\frac{\partial p}{\partial x}h^3\right]$$

solvent: $$\frac{\partial \phi h}{\partial t} = \frac{\partial}{\partial x}\left[\alpha h\frac{\partial \phi}{\partial x} + \phi\frac{\partial p}{\partial x}h^3\right]$$

pressure: $$p = -\frac{\partial^2 h}{\partial x^2} + \left[\left(\frac{\varepsilon}{h}\right)^3 - \left(\frac{\varepsilon}{h}\right)^4\right]$$

$$v_{\text{tip}} = -\alpha \left.\frac{\partial \phi}{\partial x}\right|_{\text{tip}}$$

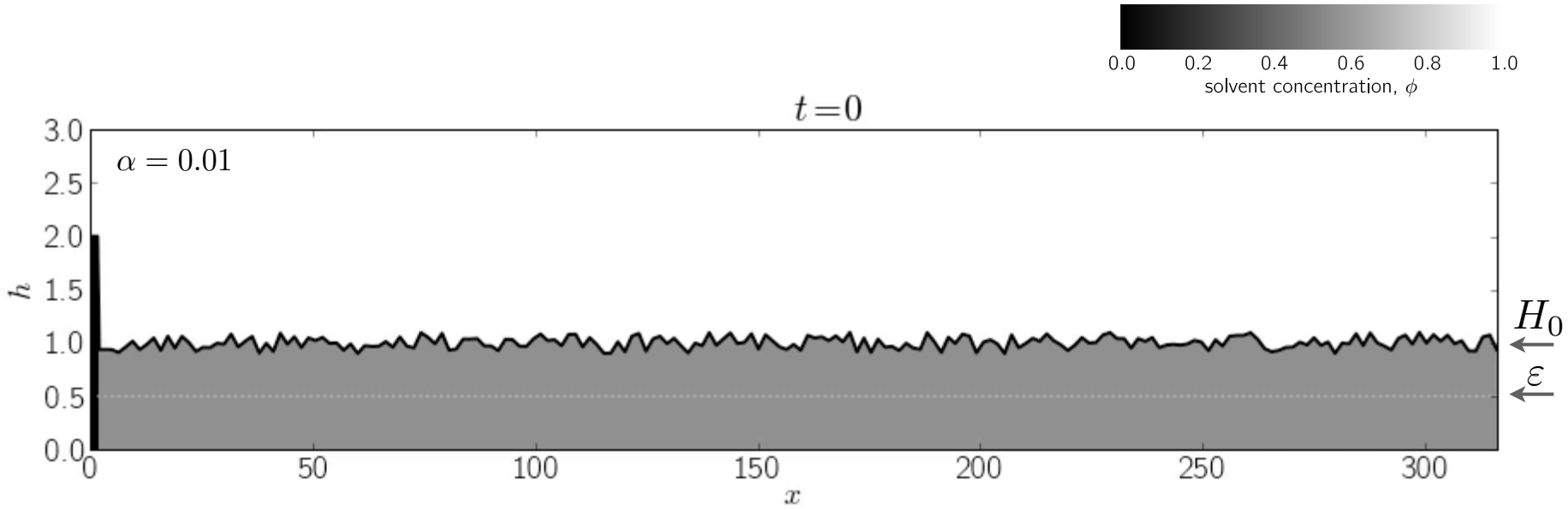
Boundary condition at the crystal given by conservation of mass (interface velocity set by flux into the crystal)

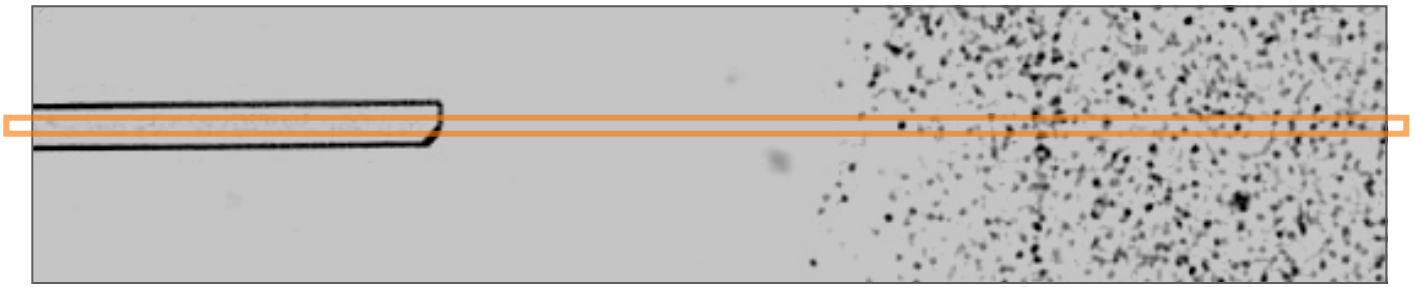
$$x = \sqrt{\frac{A_{slv}}{6\pi\sigma\tilde{\varepsilon}^3 H_0}}\,\frac{\tilde{x}}{L}$$

$$t = \frac{A_{slv}^2 H_0}{108\pi^2\mu\sigma\tilde{\varepsilon}^6}\,\frac{\tilde{t}}{\rho H_0 L/\mu}$$

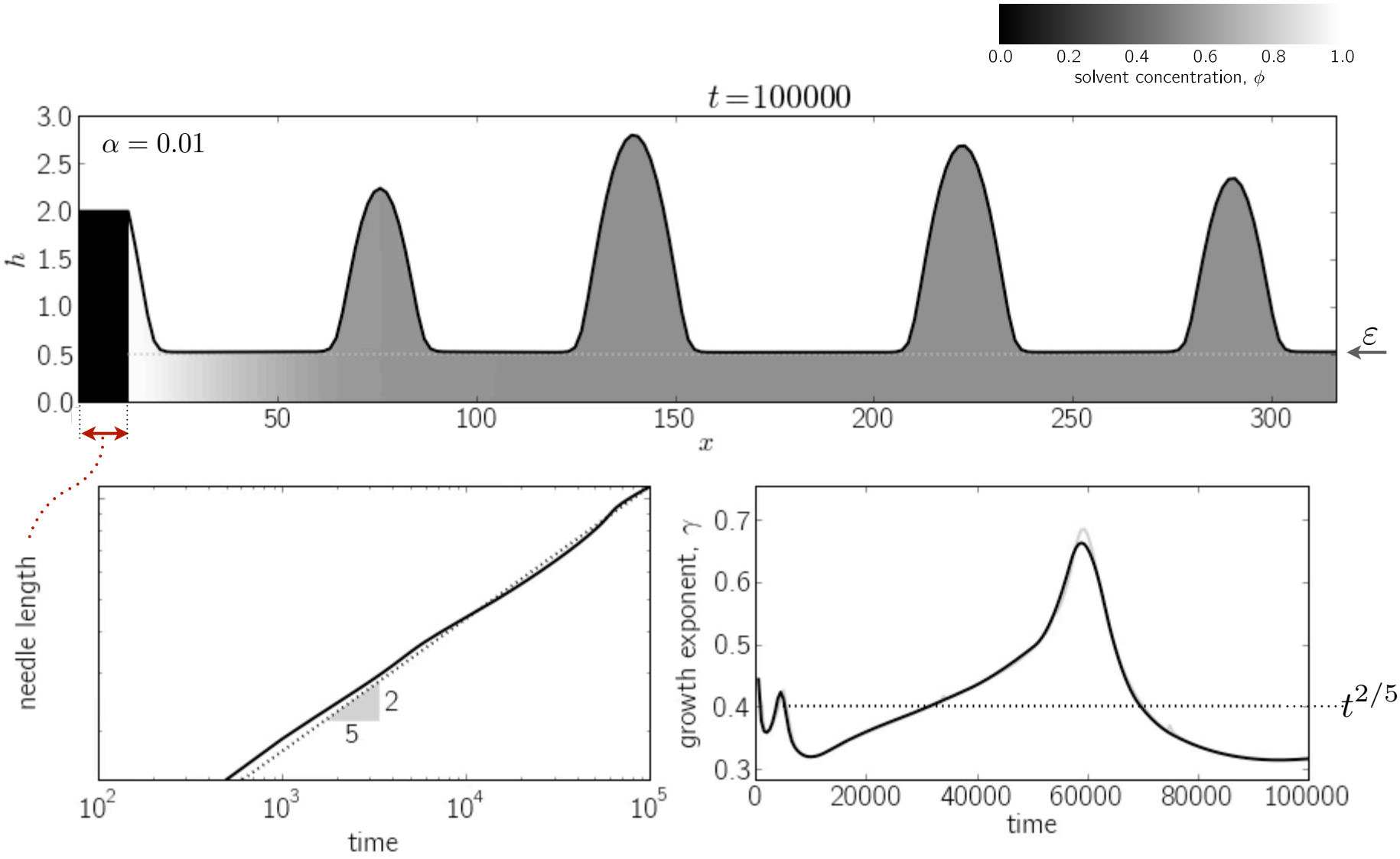
coarsening dominated ← small α — $\alpha = \dfrac{\text{diffusion}}{\text{coarsening}}$ — large α → diffusion dominated

Needle growth and thin-film evolution

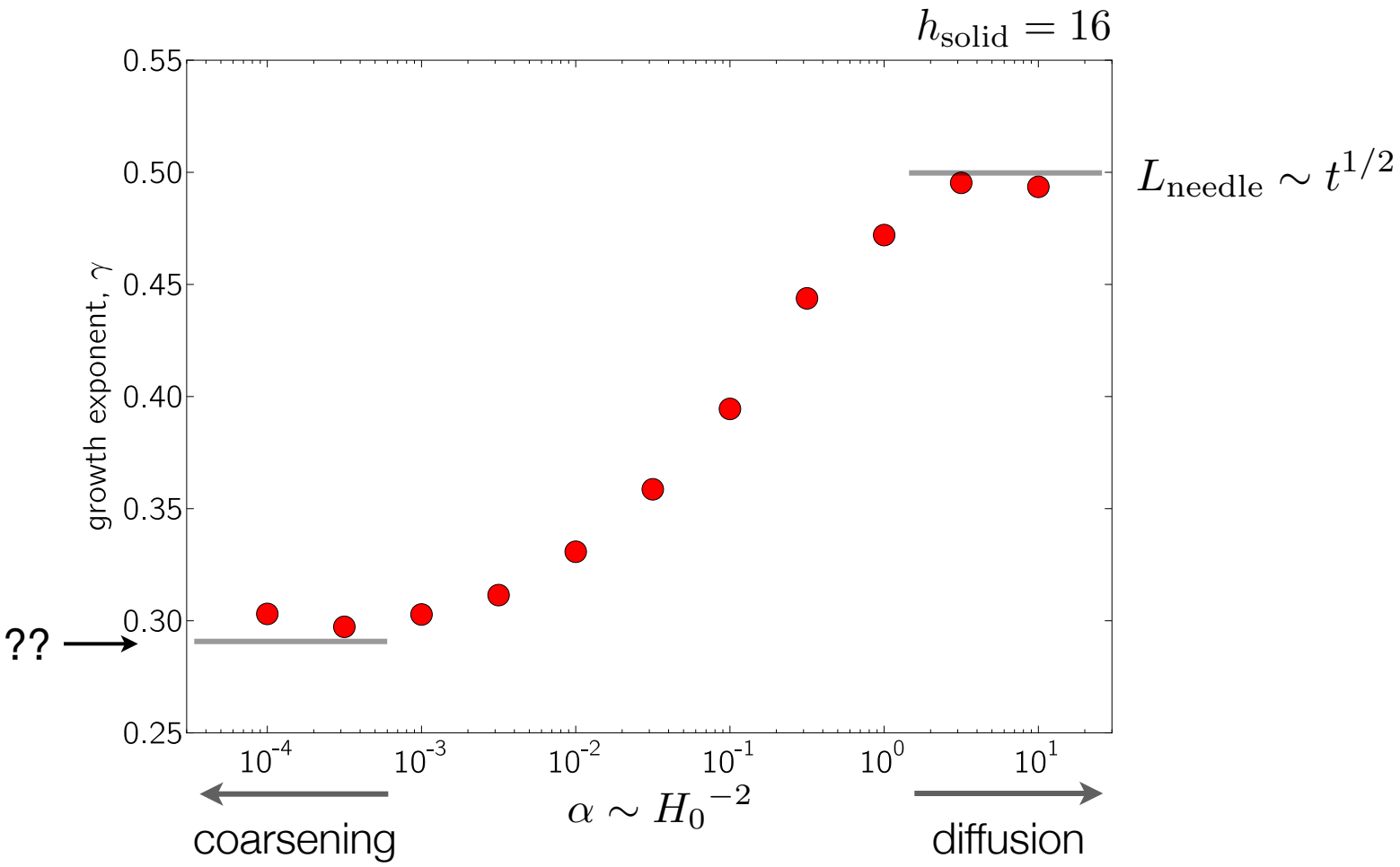




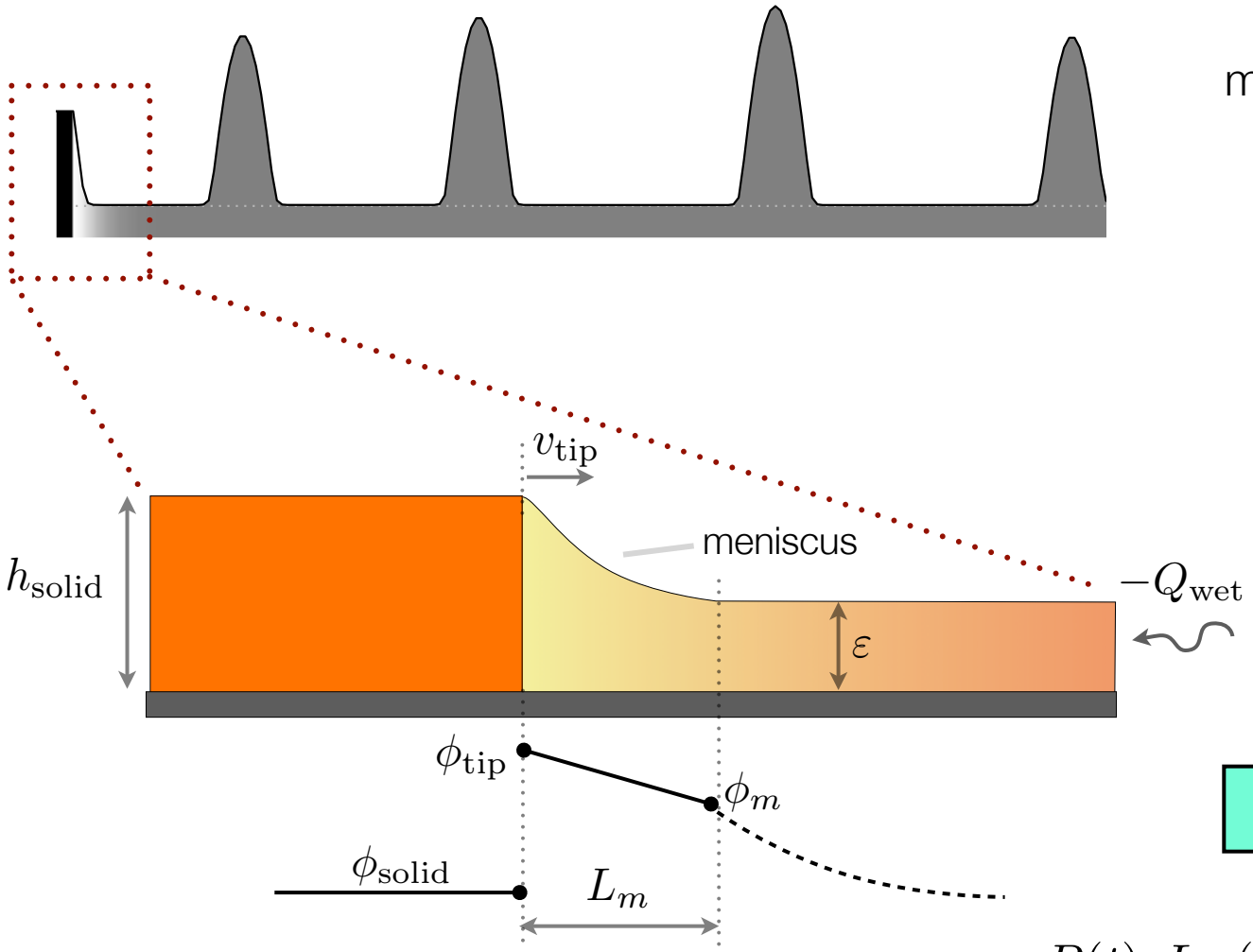
Needle growth and thin-film evolution



Needle growth: α = diffusion vs. coarsening



Low-α limit: coarsening-dominated



mass conservation:

$$v_{\text{tip}} h_{\text{solid}} + \dot{\forall}_m = -Q_{\text{wet}}$$

Flux in:

$$Q_{\text{wet}} \sim -\varepsilon^3 \frac{\partial p}{\partial x}$$

Rate of change of volume of meniscus:

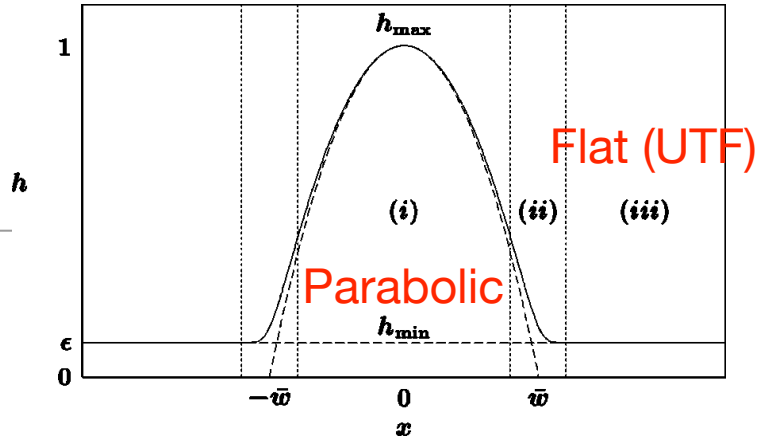
$$\dot{\forall}_m \sim h_{\text{solid}} \dot{L}_m$$

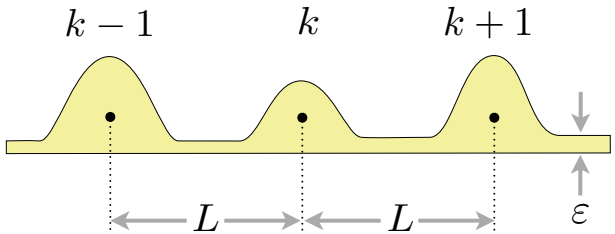
Crystal growth

$$P(t), L_m(t) \Rightarrow v_{\text{tip}}(t) \Rightarrow L_{\text{needle}}(t)$$

Droplet coarsening

$$\cancel{\frac{\partial h}{\partial t}} = \frac{\partial}{\partial x}\left[\frac{\partial p}{\partial x}h^3\right] \qquad p = -\frac{\partial^2 h}{\partial x^2} + \left[\left(\frac{\varepsilon}{h}\right)^3 - \left(\frac{\varepsilon}{h}\right)^4\right]$$

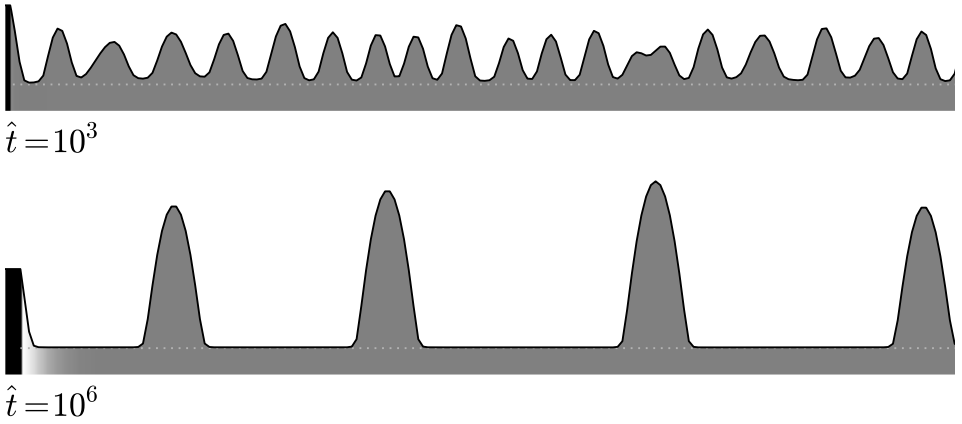


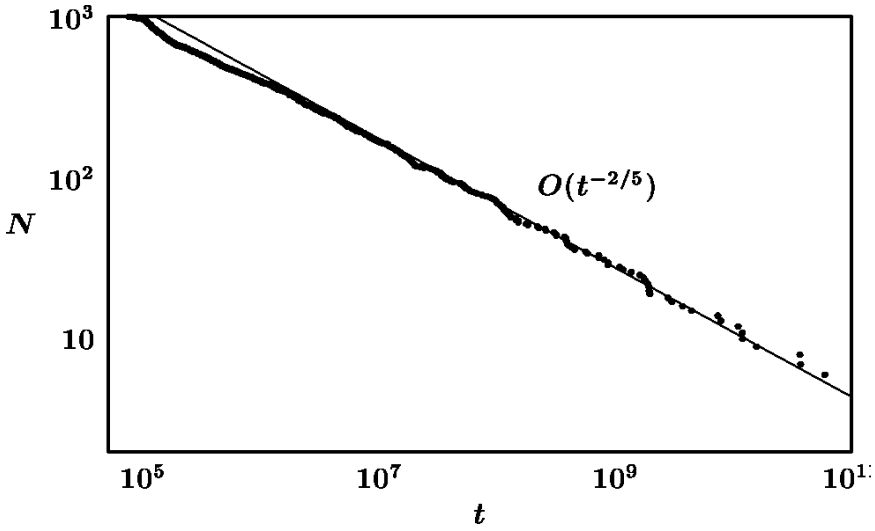


$$\frac{\mathrm{d}P_k}{\mathrm{d}t} \sim \frac{\varepsilon^3}{L}{P_k}^3(P_{k+1} - 2P_k + P_{k-1})$$

$$P_k \gg P_{k\pm1} \quad \Rightarrow \quad \frac{\mathrm{d}P_k}{\mathrm{d}t} \sim -\frac{1}{L}{P_k}^4$$

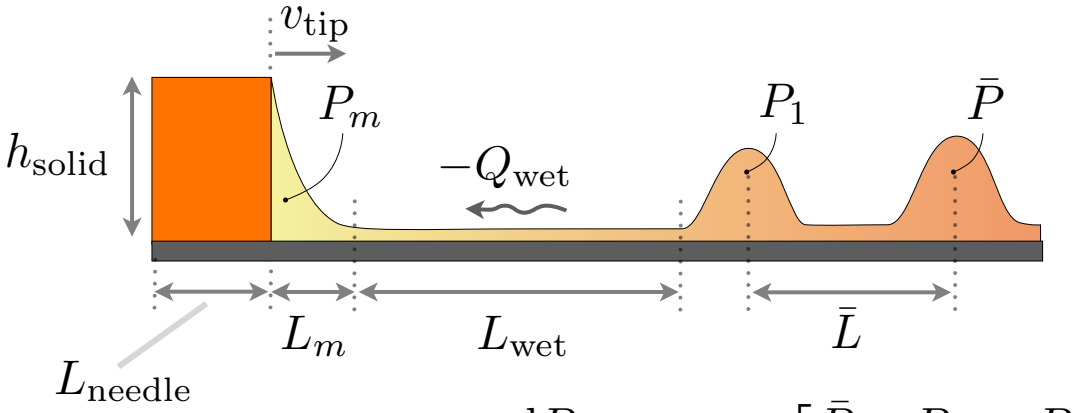
$$\bar{L} \sim t^{2/5}$$
$$\bar{P} \sim t^{-1/5}$$
$$N_{\mathrm{drop}} \sim t^{-2/5}$$

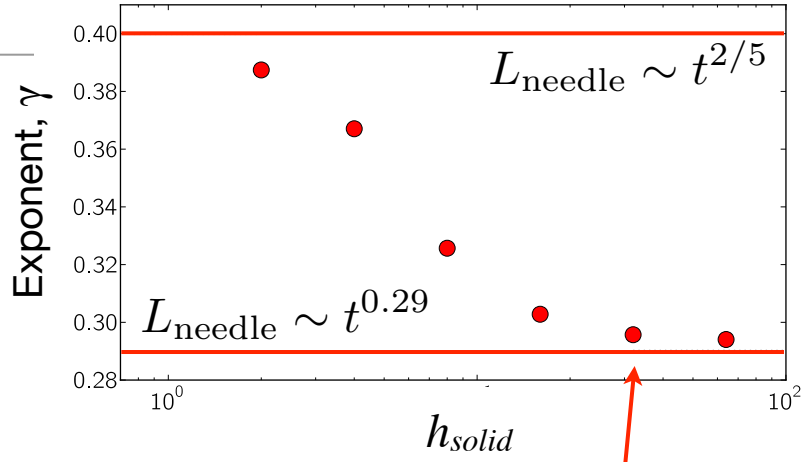




Glasner and Witelski "Coarsening dynamics of dewetting films," *PRE* **67** (2003)

Low-α limit: height dependence





$$\frac{\mathrm{d}P_1}{\mathrm{d}t} \sim \varepsilon^3 {P_1}^3 \left[\frac{\bar{P} - P_1}{\bar{L}} + \frac{P_m - P_1}{L_{\text{wet}}} \right]$$

$P_1 \sim t^{-1/5}$

$L_{\text{wet}} \sim t^{2/5}$

$$Q_{\text{wet}} \sim -\frac{P_1}{L_{\text{wet}}} \sim -t^{-3/5}$$

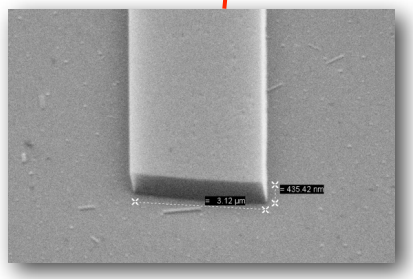
$v_{\text{tip}} \sim t^{-3/5}$ → $L_{\text{needle}} \sim t^{2/5}$

$P_m \sim -t^{-2a}$

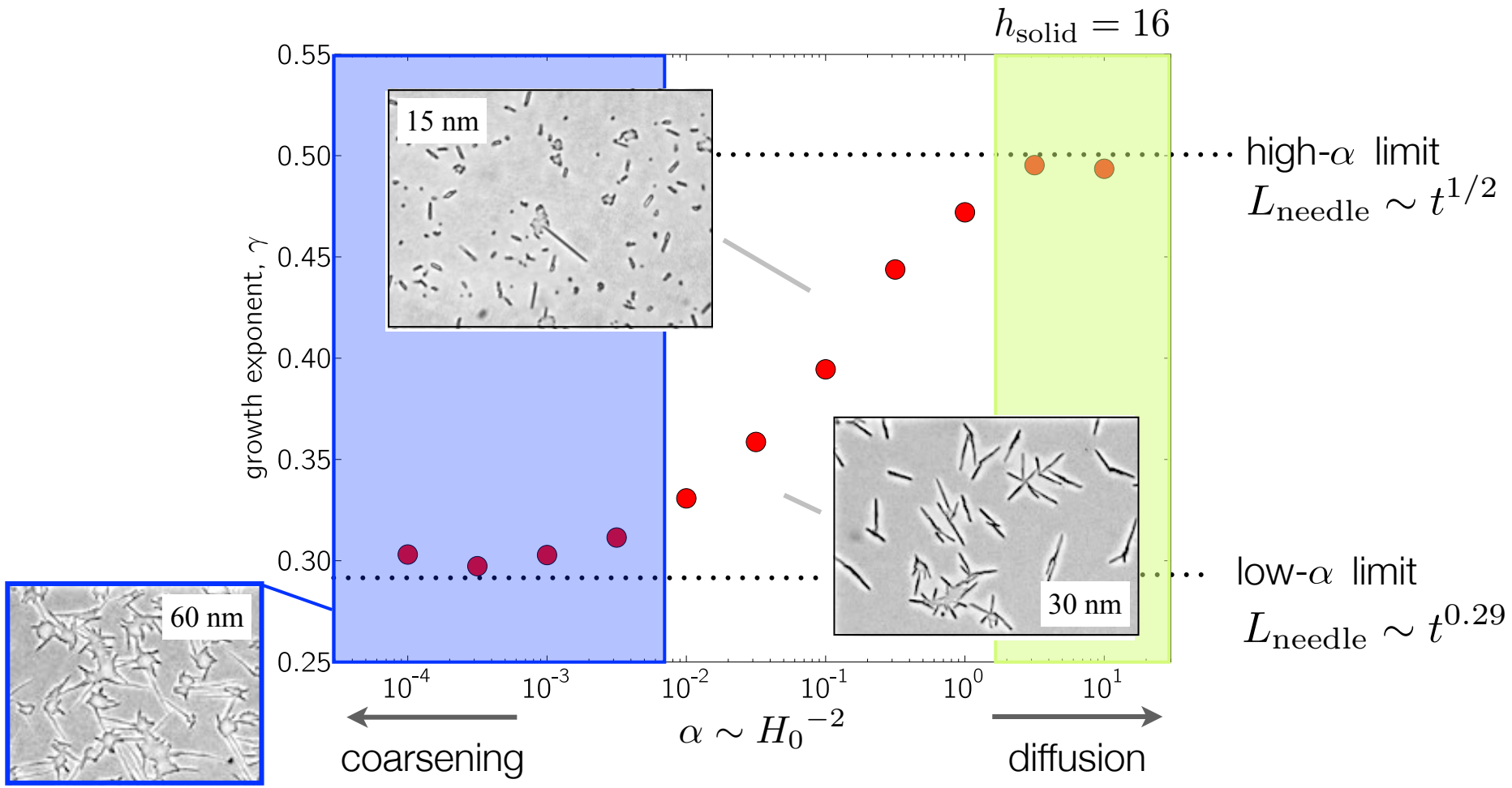
$L_{\text{wet}} \sim t^{(5-14a)/(10-10a)}$

$$Q_{\text{wet}} \sim \frac{P_m}{L_{\text{wet}}} \sim -t^{-(5+6a-20a^2)/(10-10a)}$$

$v_{\text{tip}} \sim t^{-0.71}$ → $L_{\text{needle}} \sim t^{0.29}$



Needle growth: α = diffusion vs. coarsening



Tony Yu