ME-446: Liquid-gas interfacial heat and mass transfer

Bubbles from Electrochemical Reactions

Zhengmao Lu

Energy Transport Advances Laboratory

EPFL Mechanical Engineering

2024 Fall Semester

Photo Credit: Trougnouf

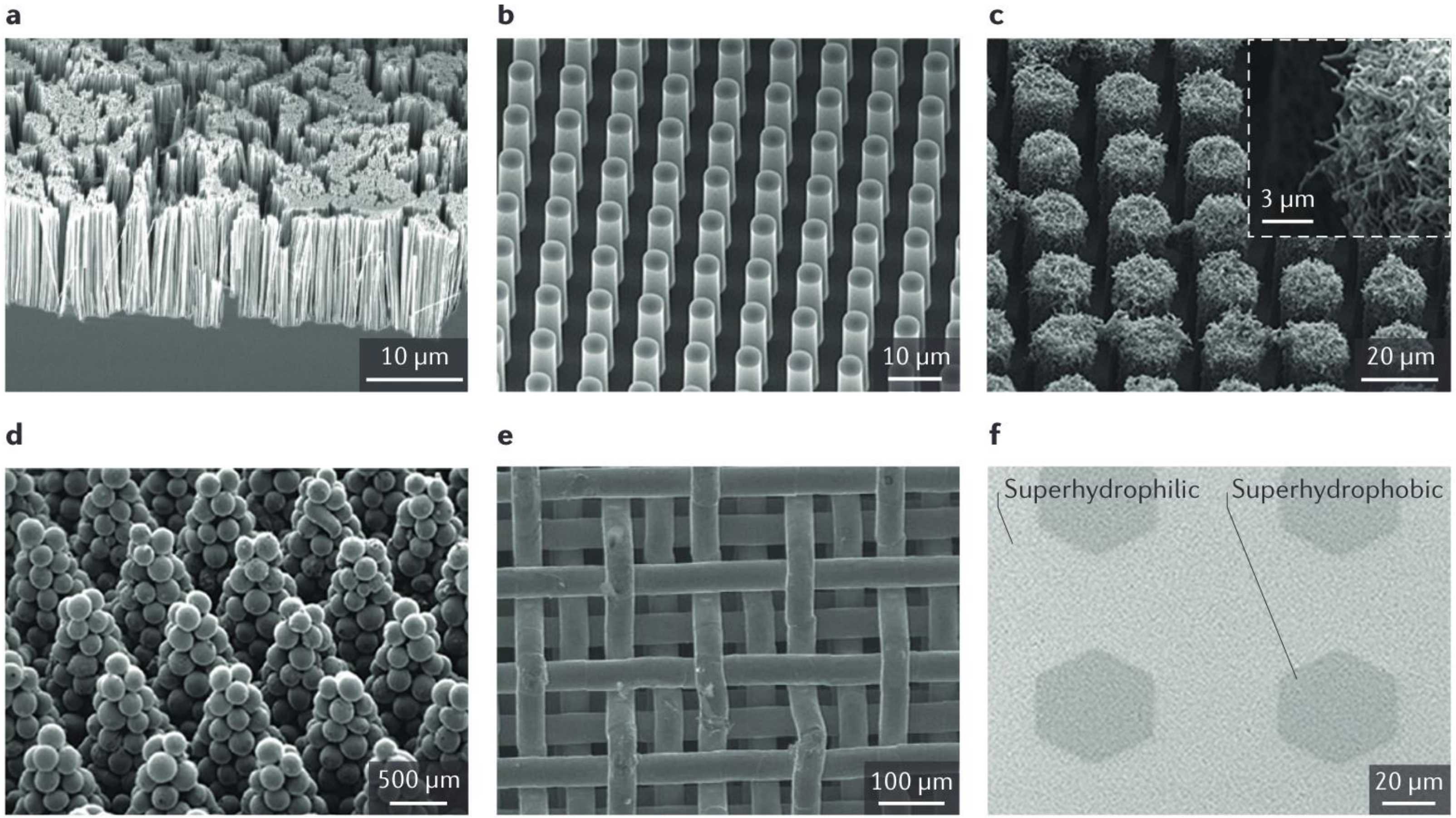
Last Time

- Force balance model for CHF
- Effect of surface parameters on CHF
- Statistical approach for CHF

Statistical Approach for CHF

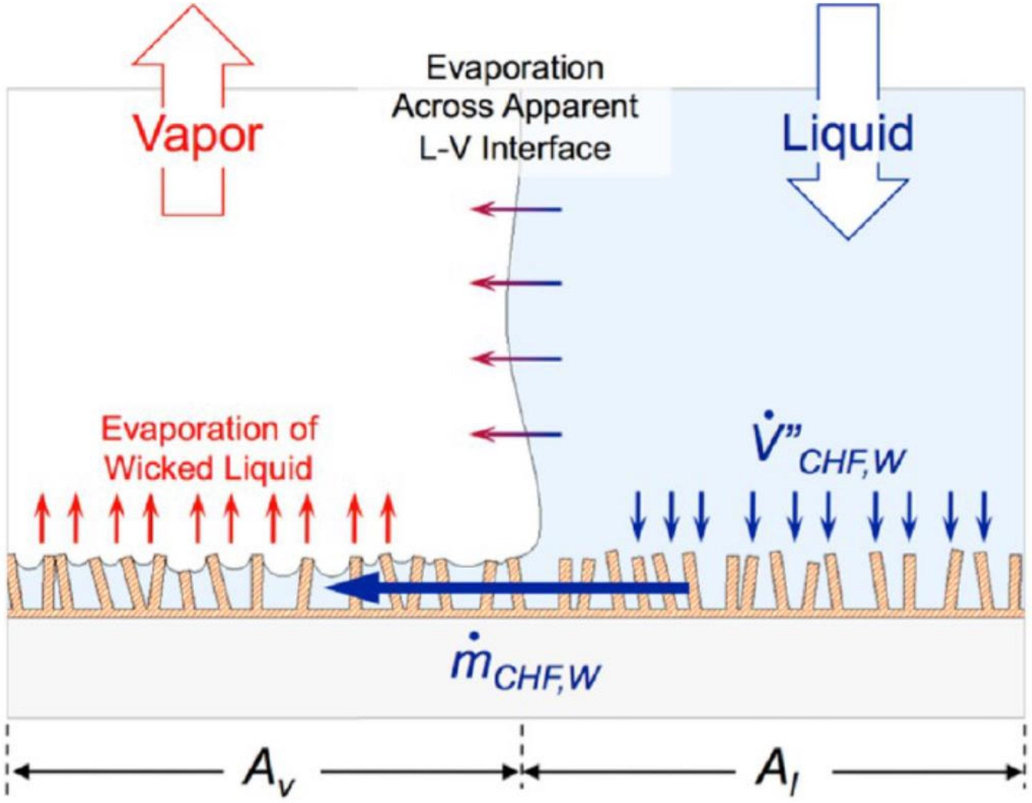
- Isolated bubbles dissipate heat better than merged bubbles
- With elevated temperature, more nucleation sites become activated while more bubbles are likely to merge into each other.
- We consider the probability of having N bubbles on the surface and the probability distribution of nearest neighbor distance
- **CHF is reached when you have the maximum number of isolated bubbles**

Surface Engineering for Boiling Enhancement



doi:10.1038/natrevmats.2016.92

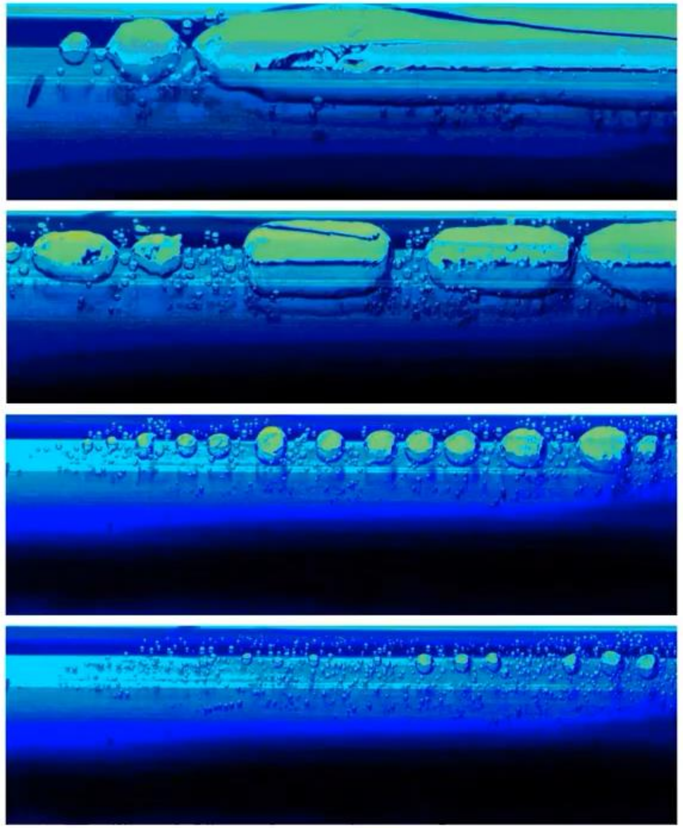
Wicking Helps Boiling



https://doi.org/10.1021/la5030923

https://doi.org/10.1021/acs.langmuir.7b01522

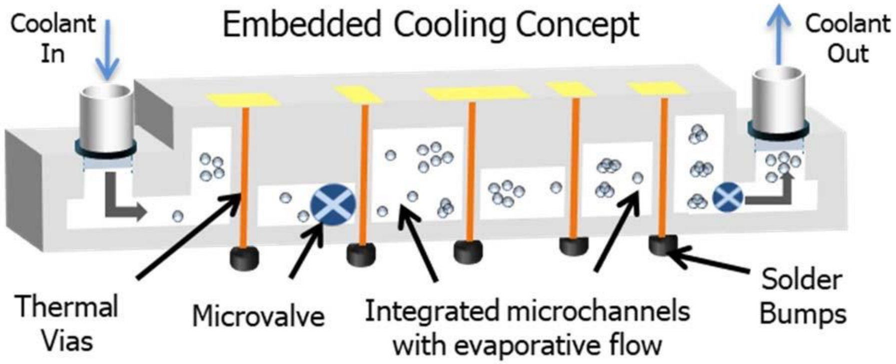
Intro to Flow Boiling



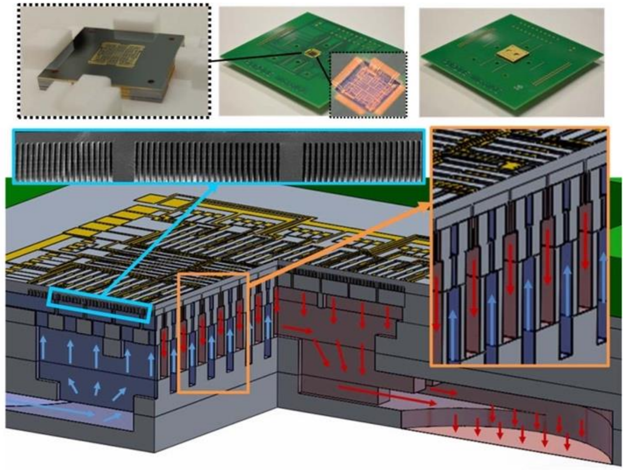
Different regimes in flow boiling
(slowed down 50 times)

https://www.youtube.com/shorts/HNcp7zDtwx8?feature=share

Primarily explored for high flux electronics cooling



DOI: 10.1109/TCPMT.2021.3111114



International Journal of
Heat and Mass Transfer
117 (2018) 319–330

Flow Regimes

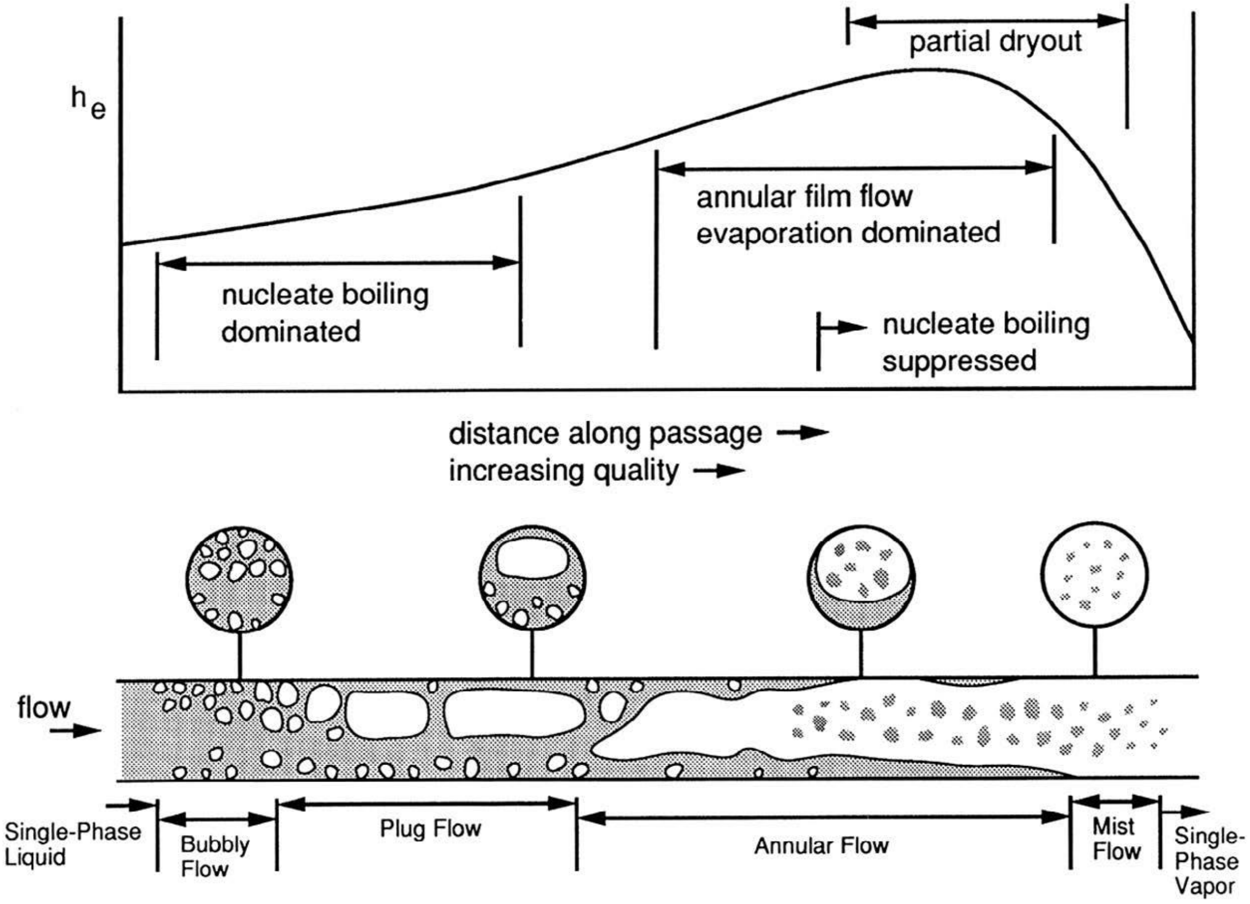


Figure 12.1 in Carey

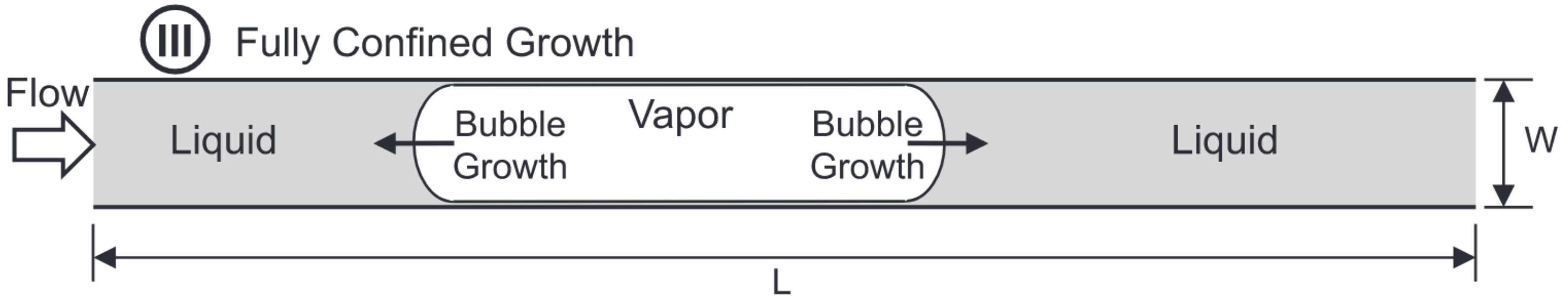
Bubbly flow: discrete bubbles dispersed in continuous liquid phase

Plug flow: coalescence of small bubbles produces large bubbles flowing in the upper portion

Annular flow: most liquid flowing along the wall and gas flowing in the central core

Mist flow: discrete droplets dispersed in continuous vapor phase

Oscillations in Microchannel Flow Boiling

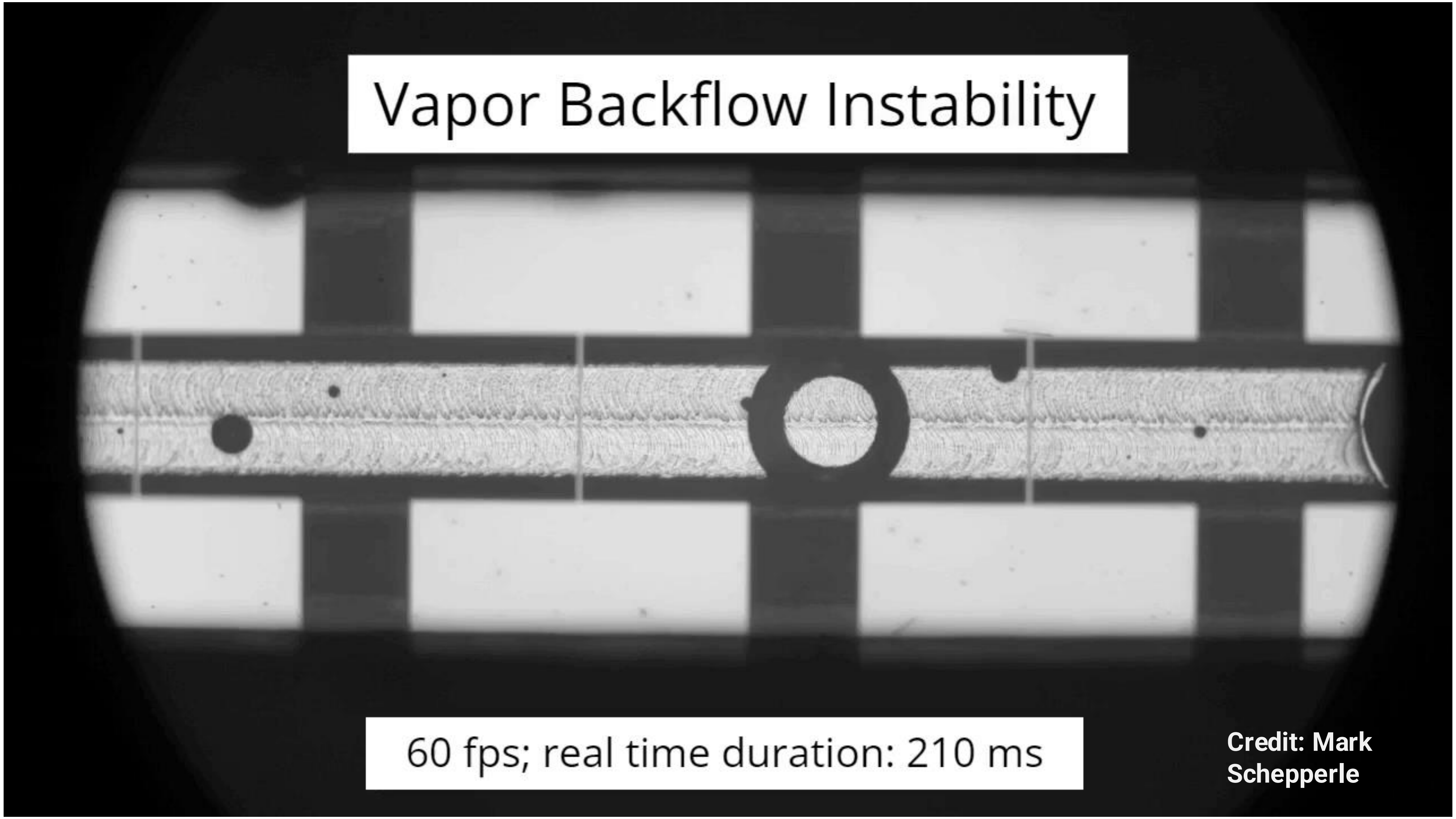


Bubble expansion toward the inlet causing density wave oscillation in microchannels

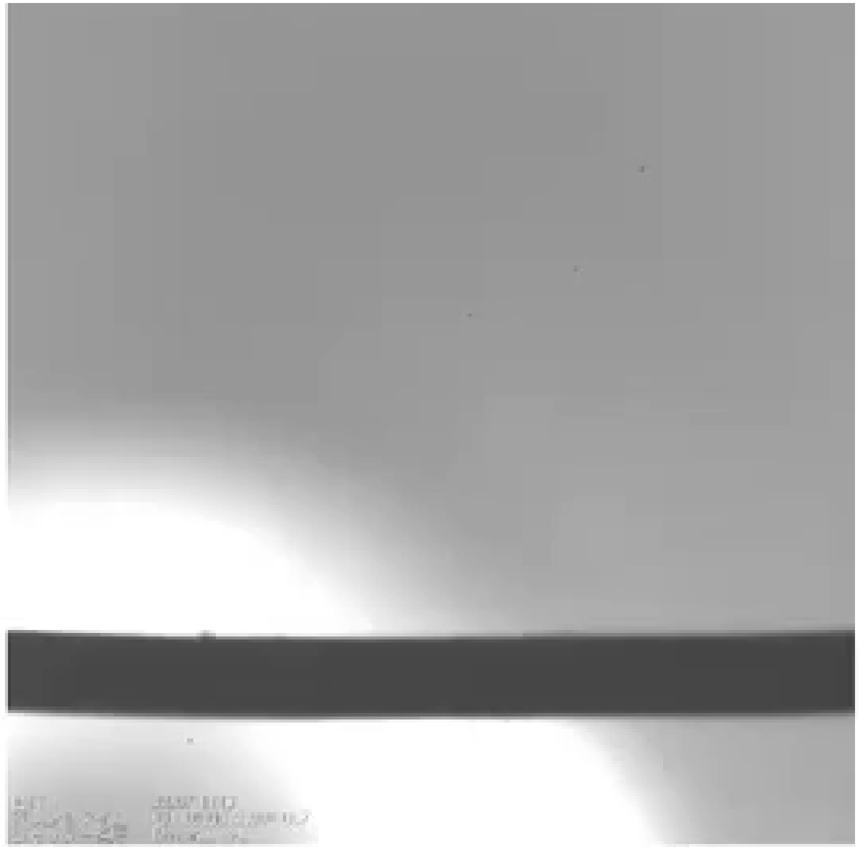
Flow rate reduced (potentially leading to backflow), which gives rise to further vapor expansion toward the inlet

Eventually, liquid rushes back into the channel when sufficient pressure is built up

Density Wave Oscillations in Microchannels



Gas Evolving Reaction



Industrial electrochemical processes that involves bubbles

Water splitting

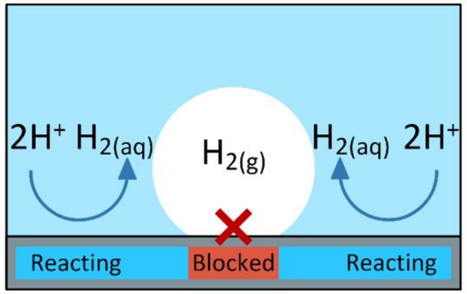
Aluminum production

Sodium chlorate production

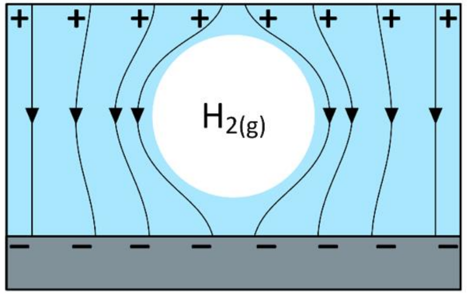
Chlorine and sodium hydroxide production

https://doi.org/10.1016/j.ijhydene.2022.01.166

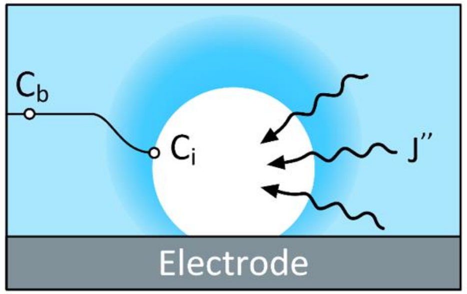
Effect of Bubbles on Electrochemical Reactions



Blocking reaction area



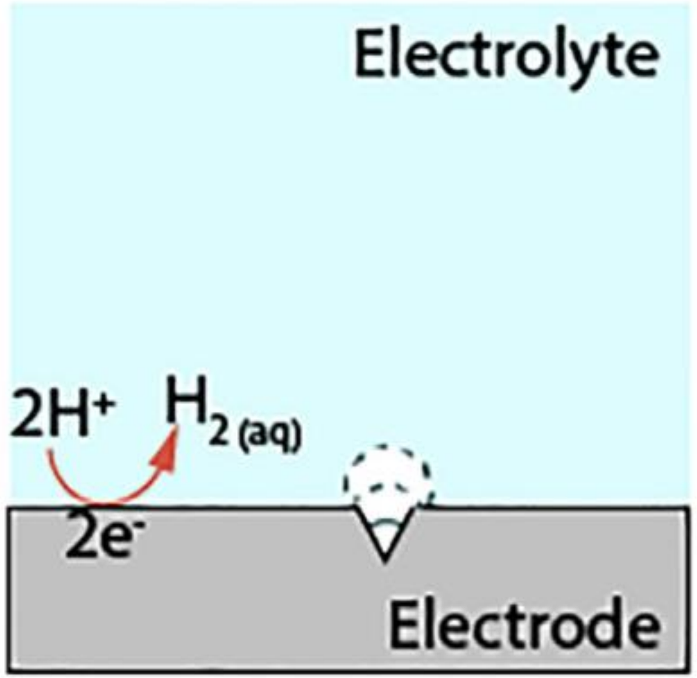
Additional resistance for ion transport



Additional diffusion resistance

Bubble-induced convection

Nucleation

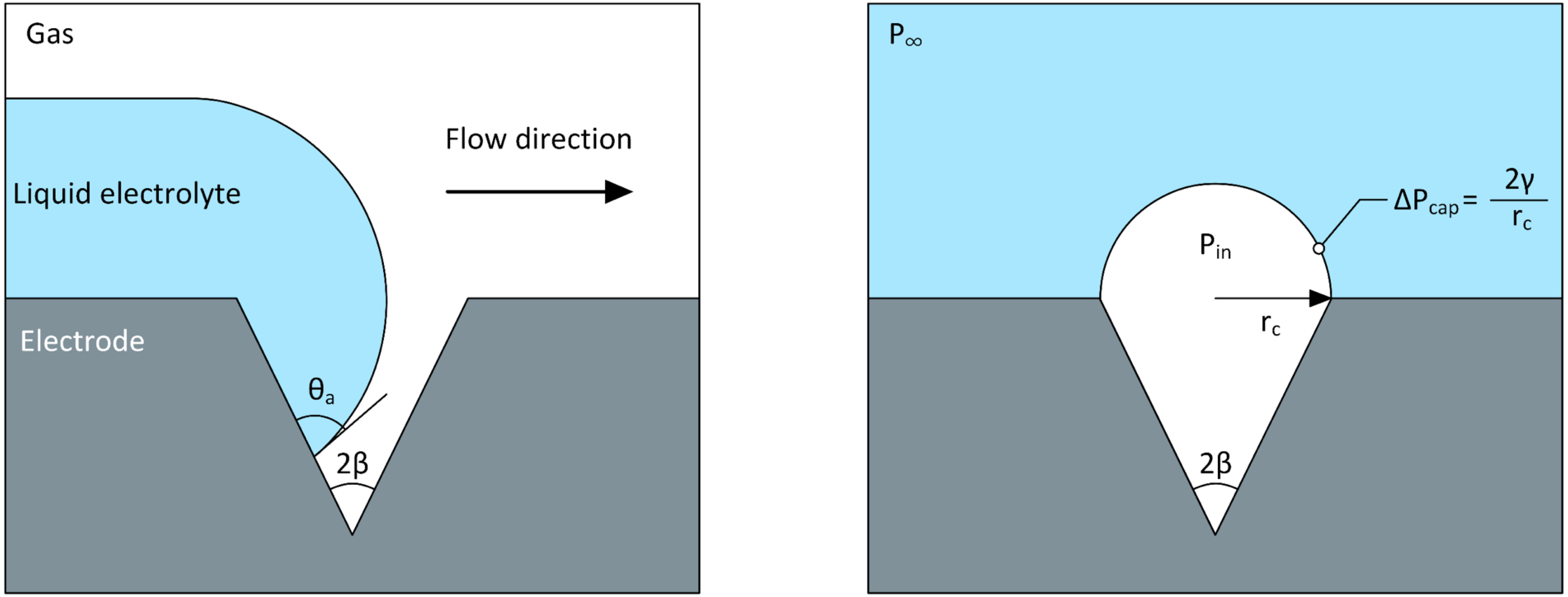


https://doi.org/10.1016/j.joule.2020.01.005

Equilibrium saturation concentration of dissolved gas in liquid is governed by Henry's law

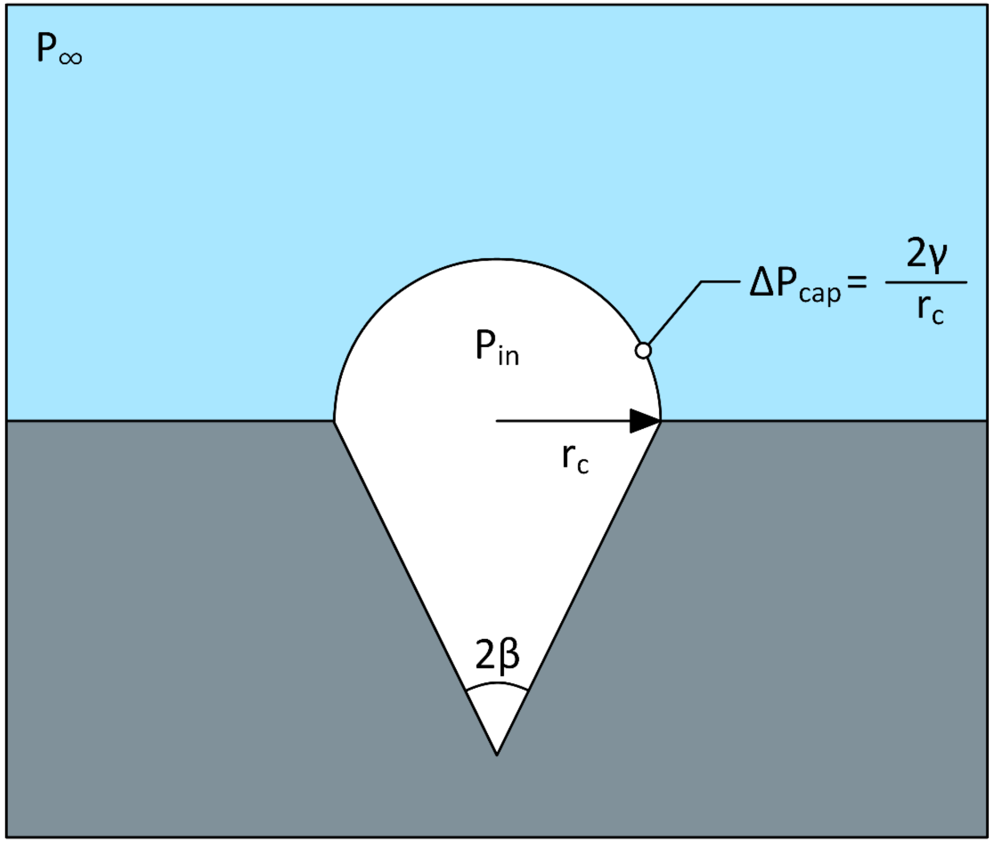
In electrochemical processes, nucleation takes place when concentration of dissolved gas becomes much larger than saturation values

Entrapped Gas Theory

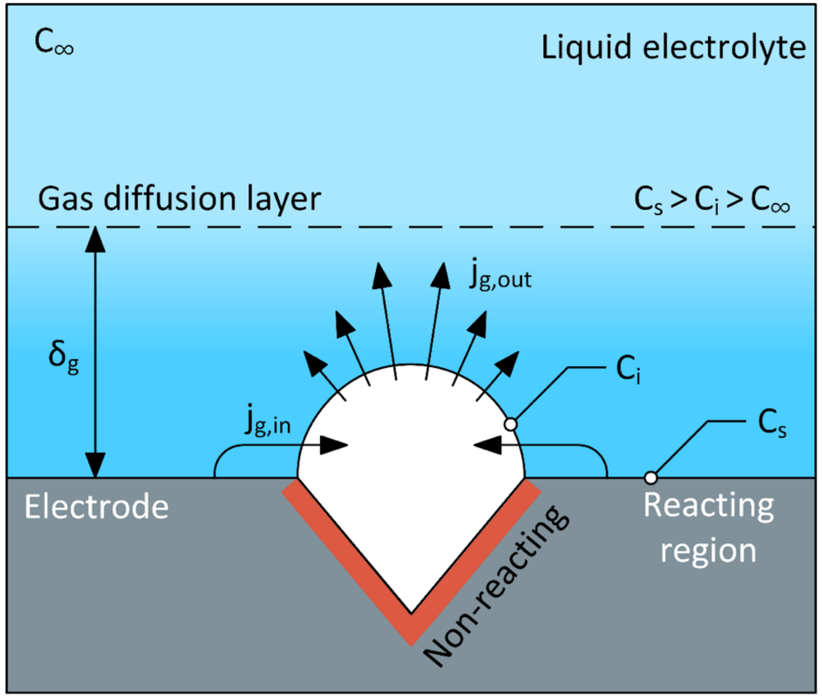


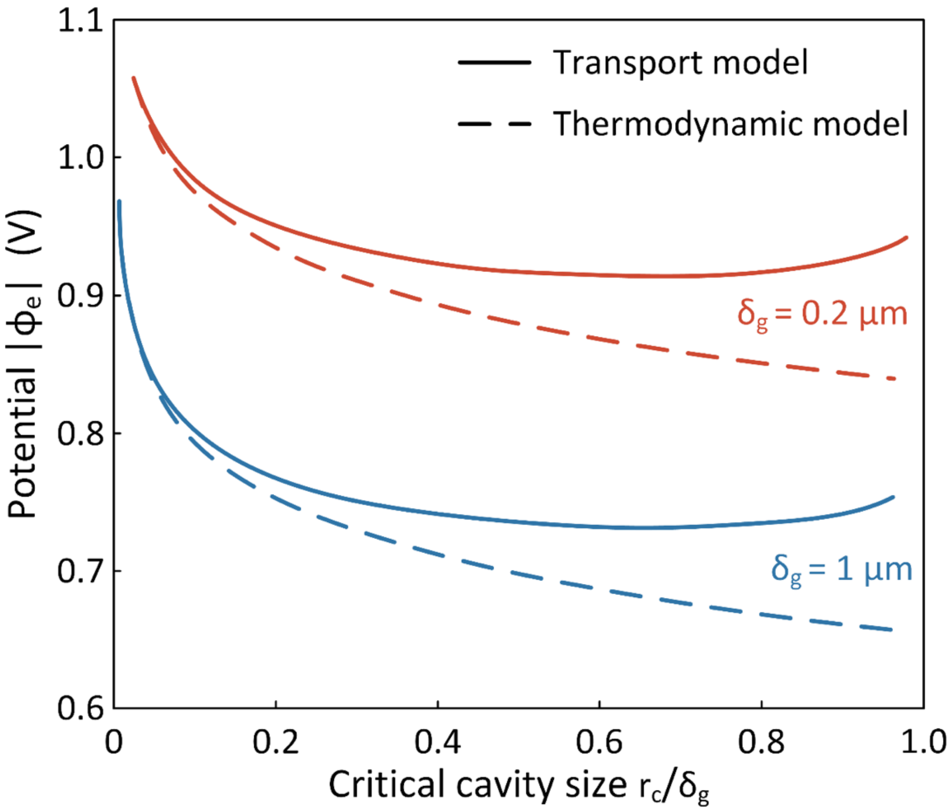
Surface cavity can cause gas-entrapping to facilitate nucleation

Critical Surface Gas Concentration



Transport Based Model





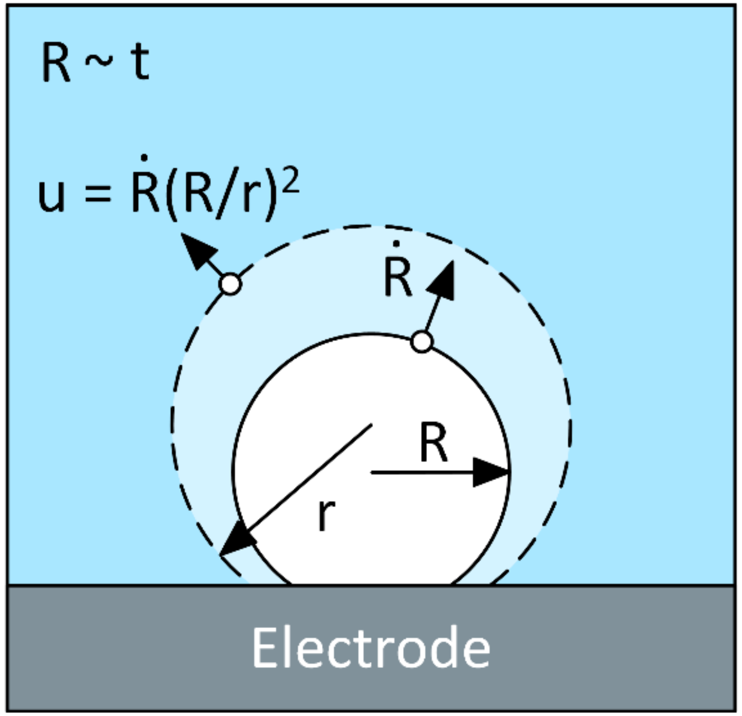
https://doi.org/10.1021/acs.langmuir.0c02690

The presence of bubble will impact how the gas is supplied to the bubble

When cavity is too large, the outgassing to the far field can collapse the bubble even when the gas is supersaturated at the electrode

Bubble Growth

- First stage: inertial-controlled growth



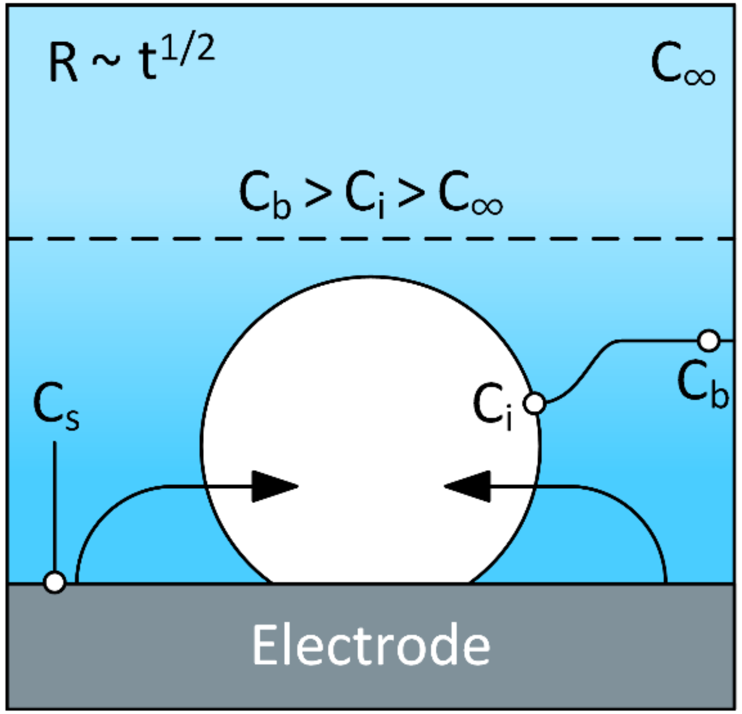
Balancing the kinetic energy of the flow field and the total work exerted from the pressure driven bubble expansion

$$R \sim t$$

Rayleigh–Plesset equation
(similar to the boiling case)

Bubble Growth

- Second stage: diffusion-controlled growth



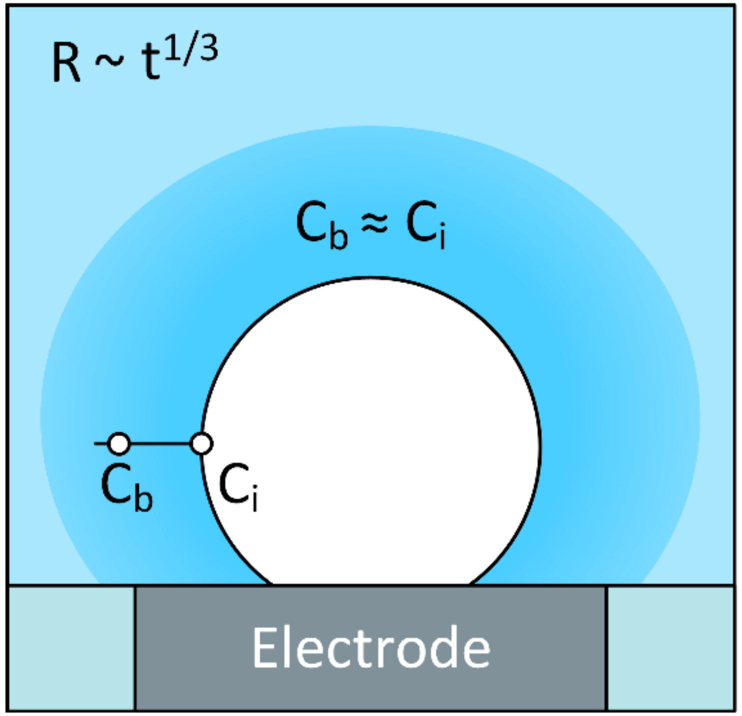
Bubble growth dictated by gas diffusion from the electrode to liquid-gas interface

$$R \sim \sqrt{t}$$

In boiling, this corresponds to thermal conduction from heated surface to liquid-vapor interface

Bubble Growth

- Third stage: reaction-controlled growth

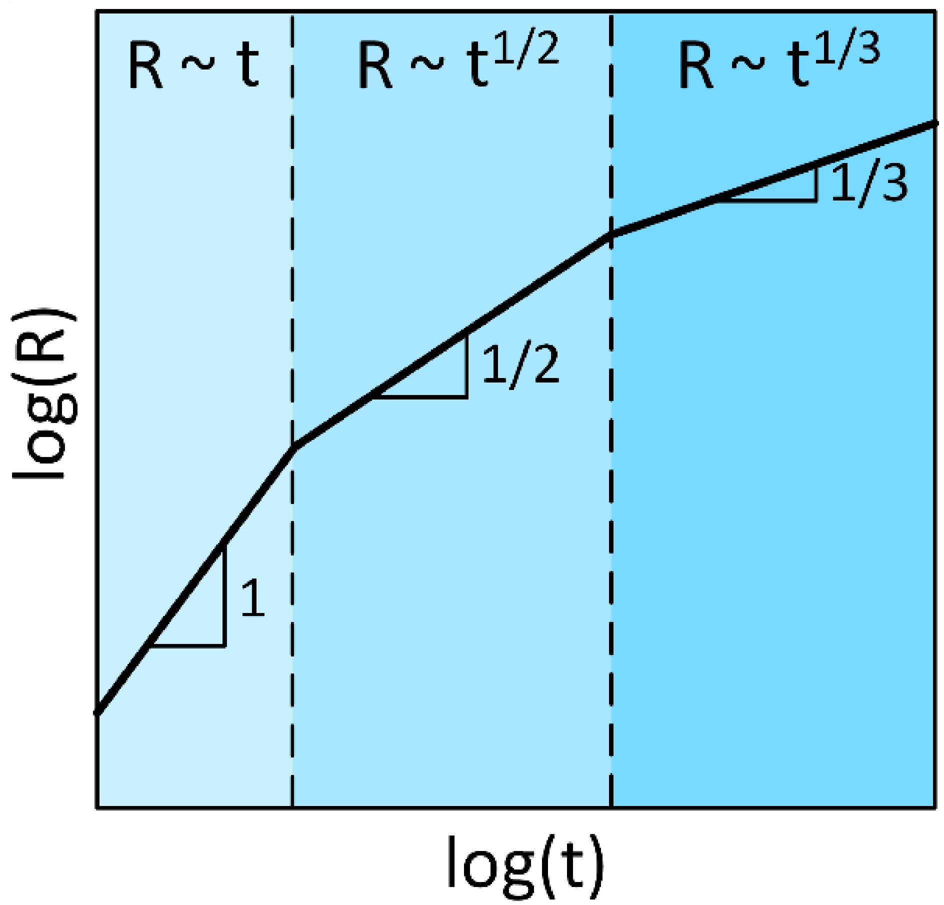


Rate of bubble volumetric increase is ultimately proportional to the total electrochemical reaction rate over the entire electrode surface

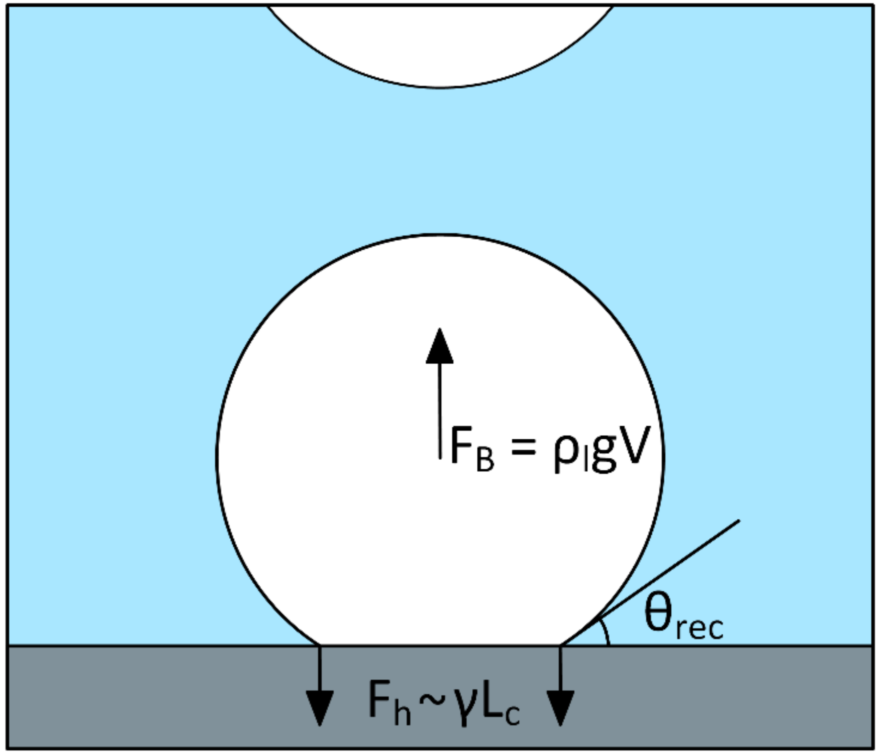
When bubble size is comparable to the electrode size,

$$R \sim t^{1/3}$$

Bubble Growth



Bubble Departure

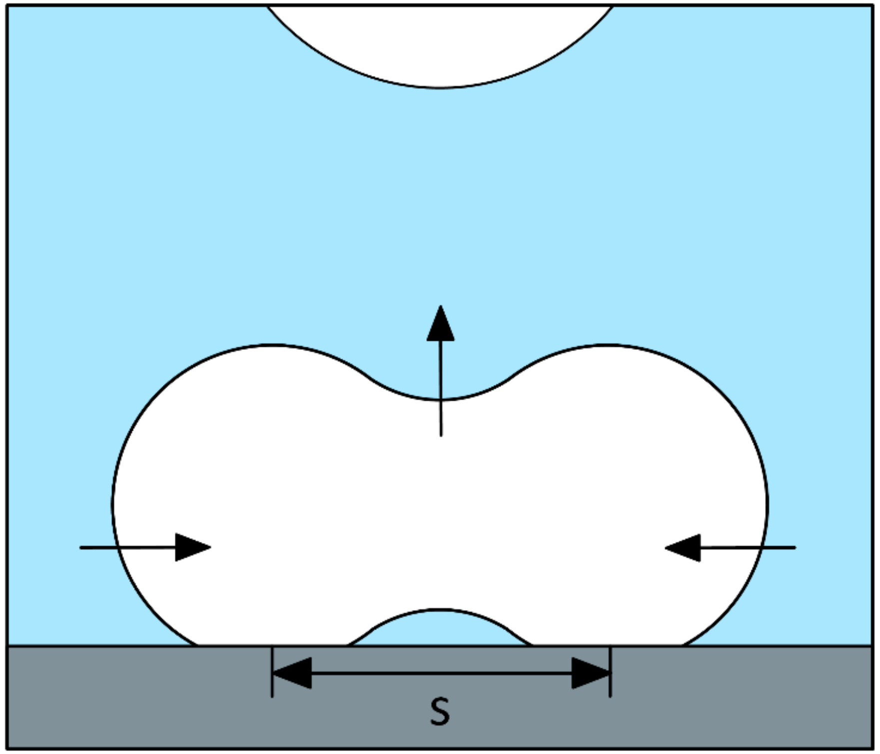


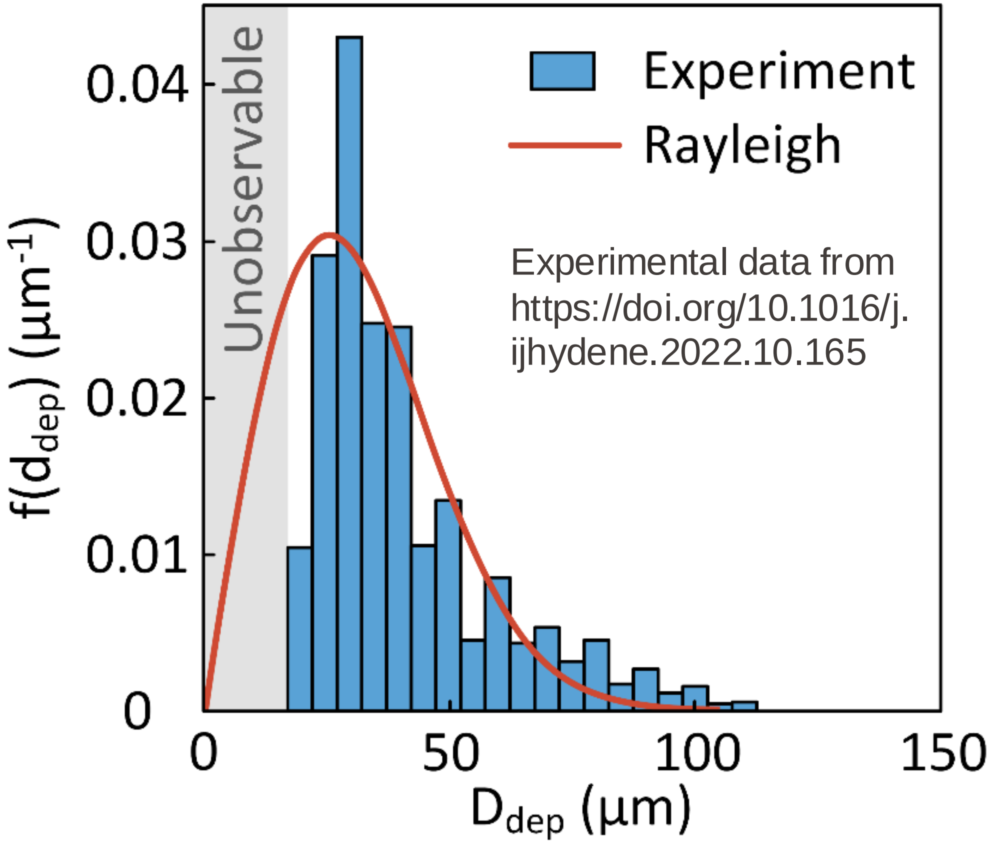
Fritz expression for bubble departure

$$\mathrm{Bo_d} = 0.0208\theta$$

$$\mathrm{Bo}_d = \frac{(\rho_l - \rho_v) d^2 g}{\sigma_{lv}}$$

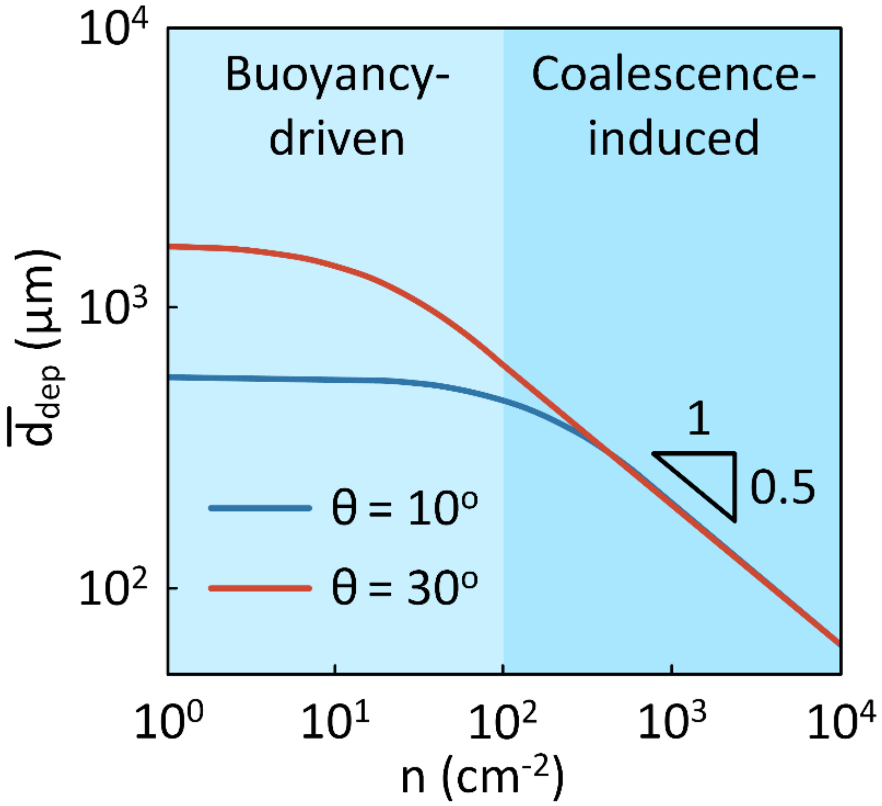
Coalescence-Driven Departure

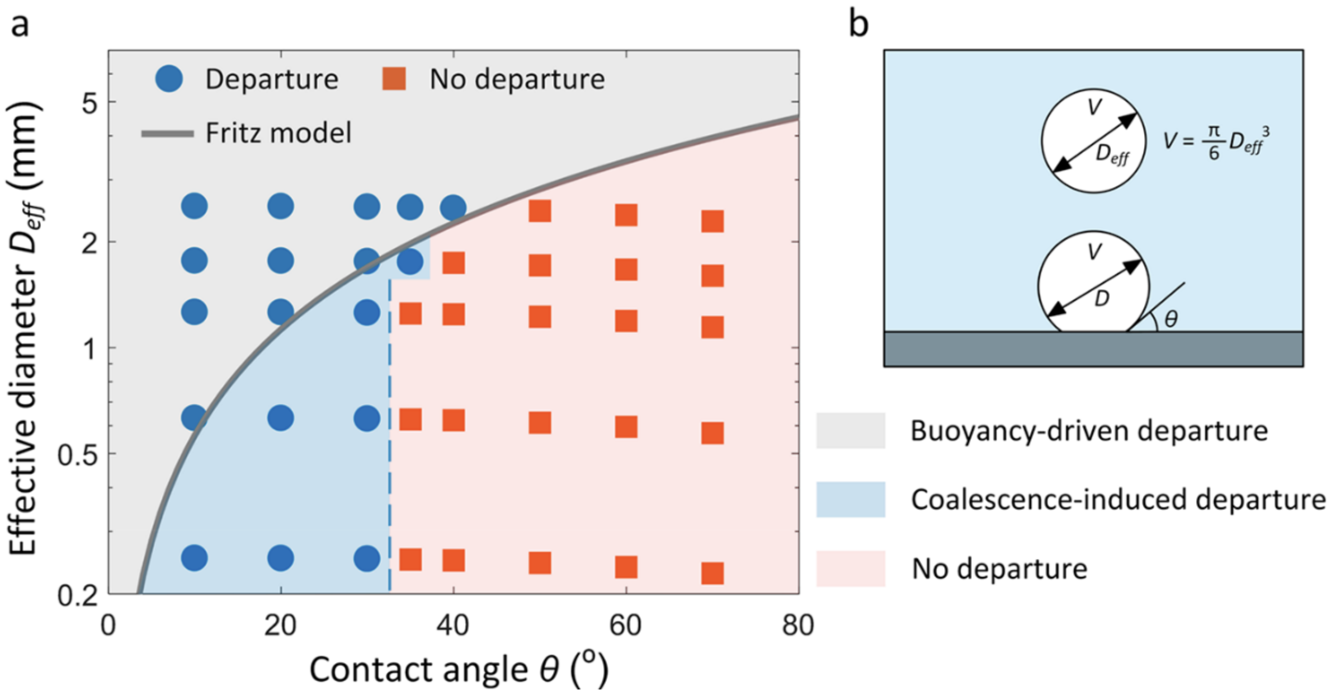




When two bubbles coalesce into one, volume is roughly consumed, but surface area becomes smaller. Excess surface energy needs to be released.

Different Departure Regime



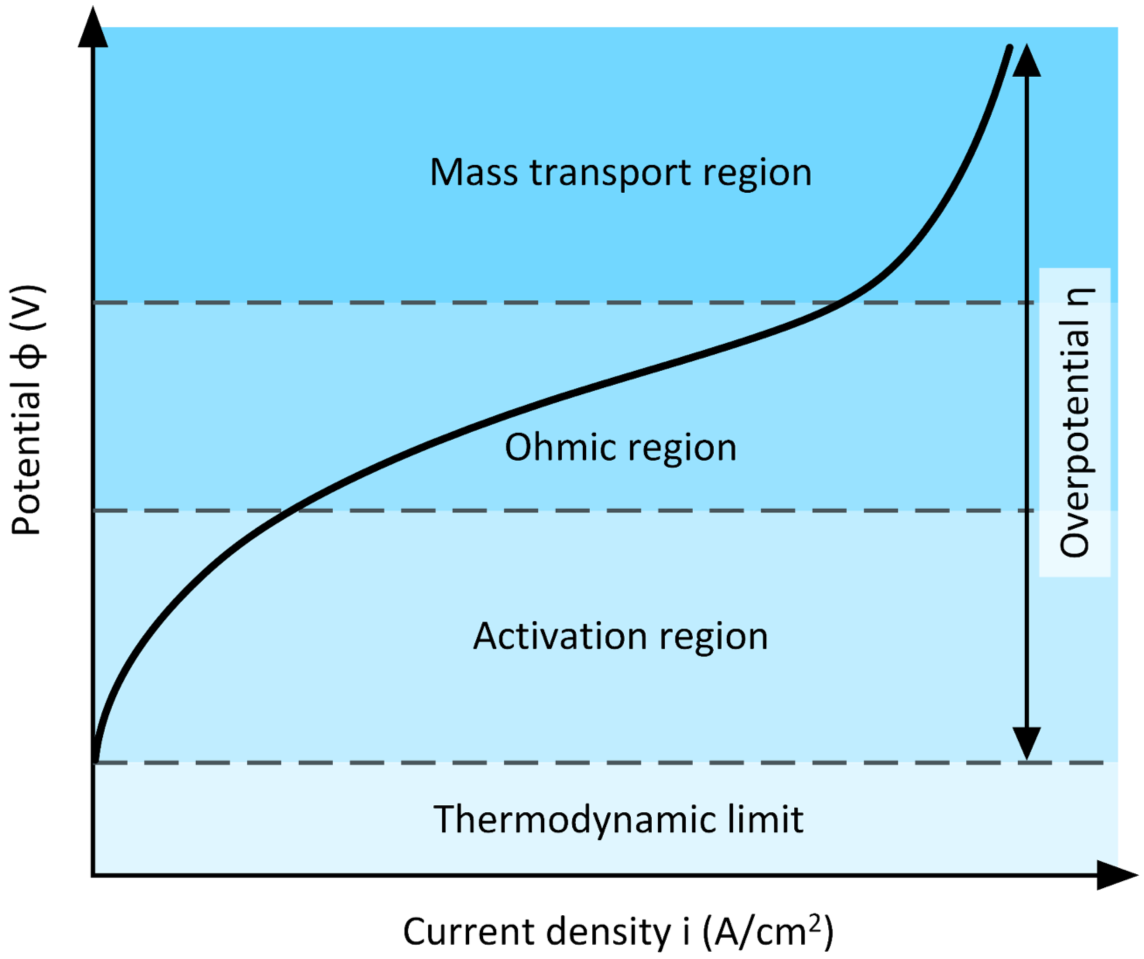


https://doi.org/10.1021/acs.langmuir.2c00118

Coalescence-induced departure is more likely when nucleation density is high

Coalescence-induced departure is unlikely when contact angle is above 30°

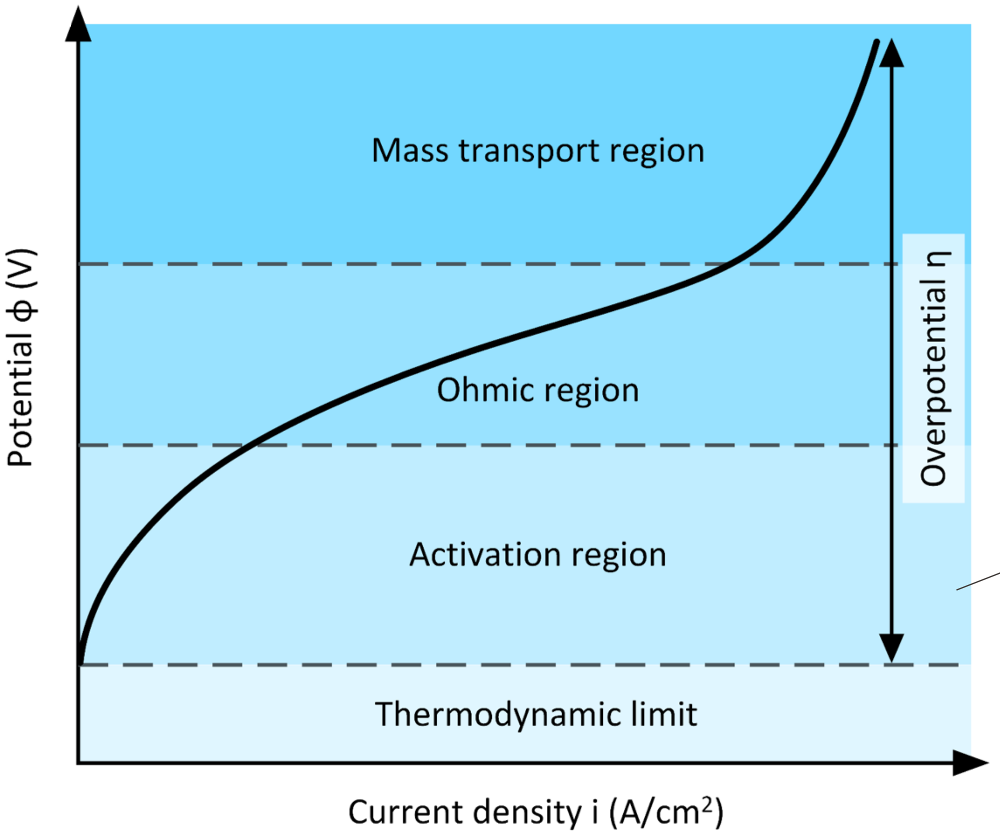
Impact on Electrochemical Overpotentials

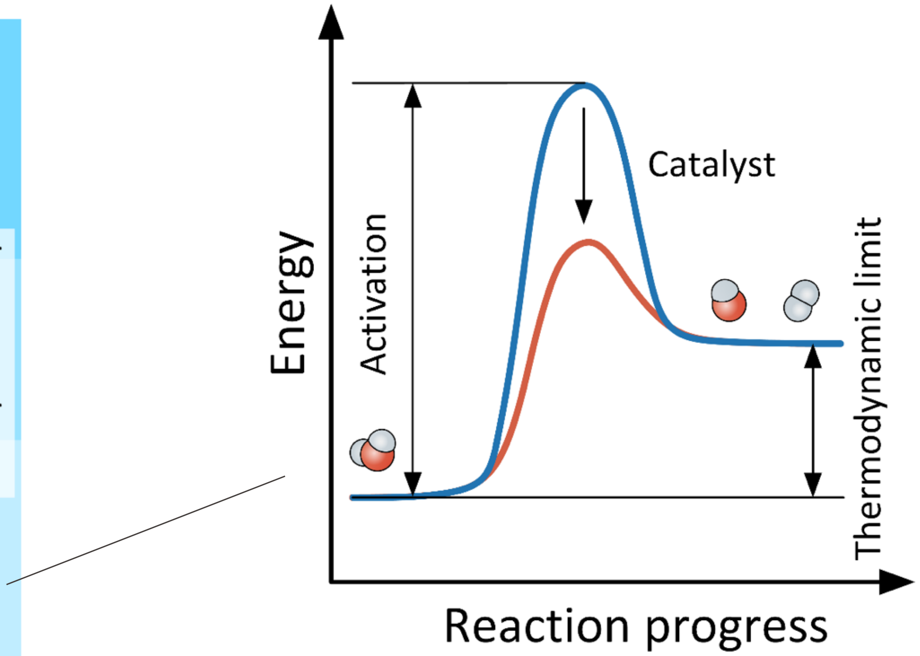


Overpotential (η) is the additional voltage required to drive the electrochemical process over the thermodynamic limit ϕ_{th}

Energy efficiency of an electrolytic cell

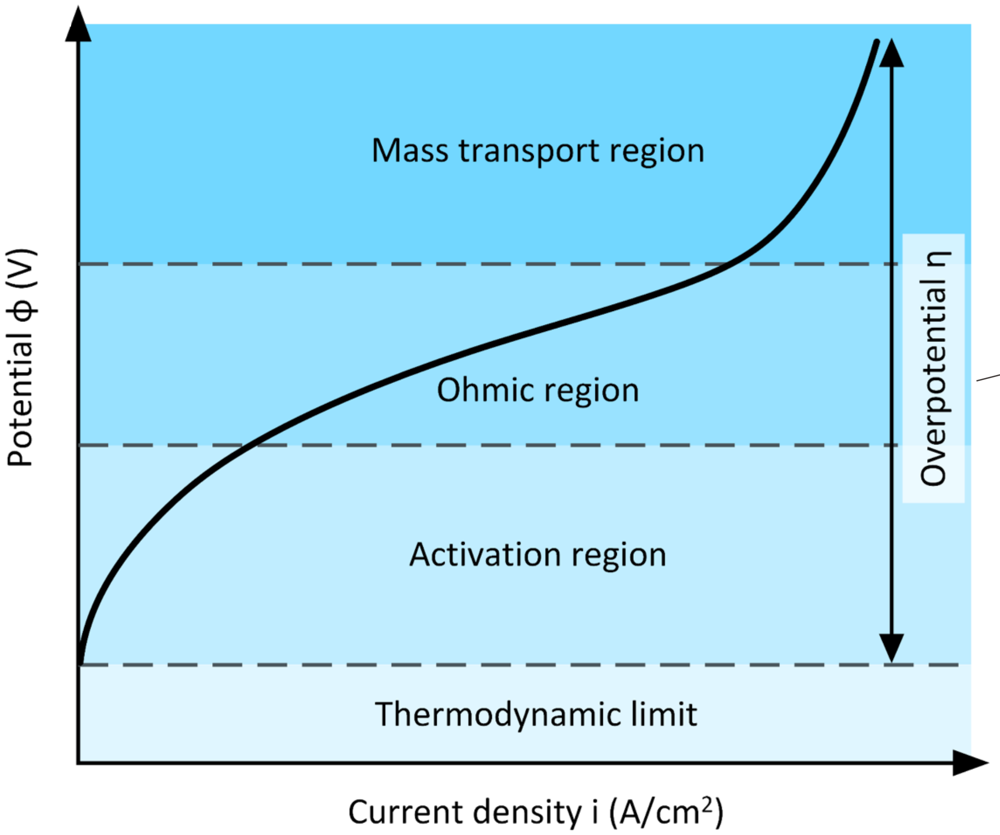
Activation Overpotentials

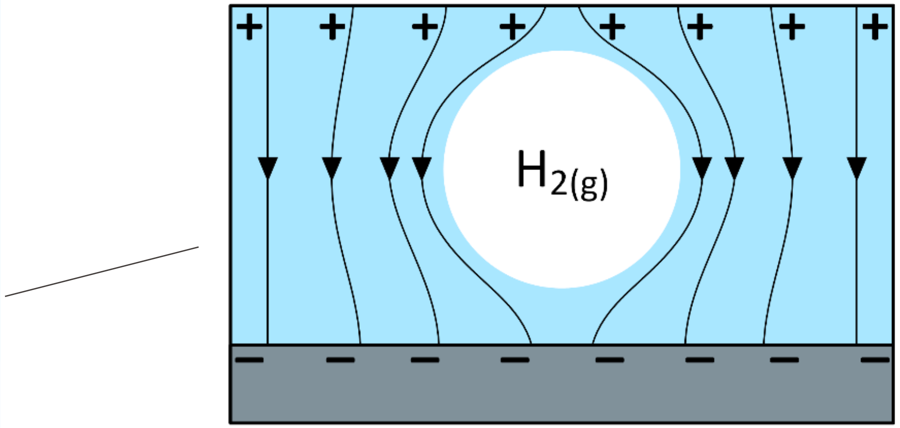




Activation overpotential η_{act} depends on the performance of the electrocatalyst

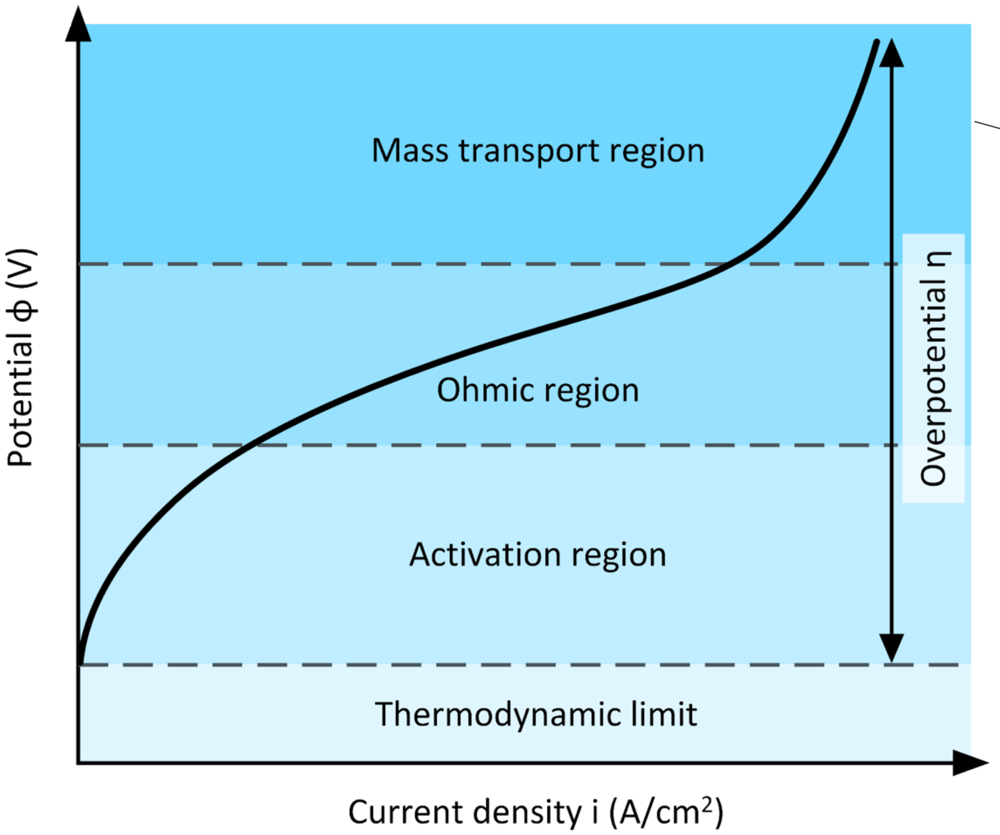
Ohmic Overpotentials

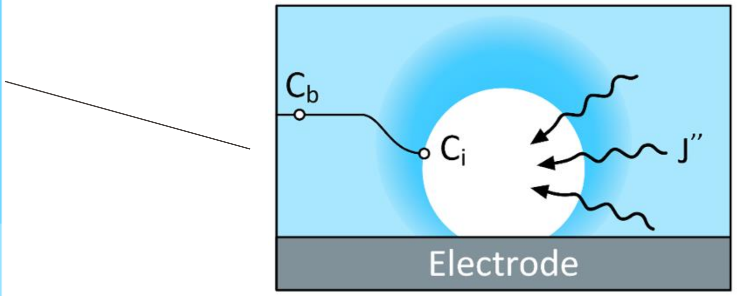




Gas bubbles are electrically insulating, which creates additional resistance for ion transport across the electrolyte

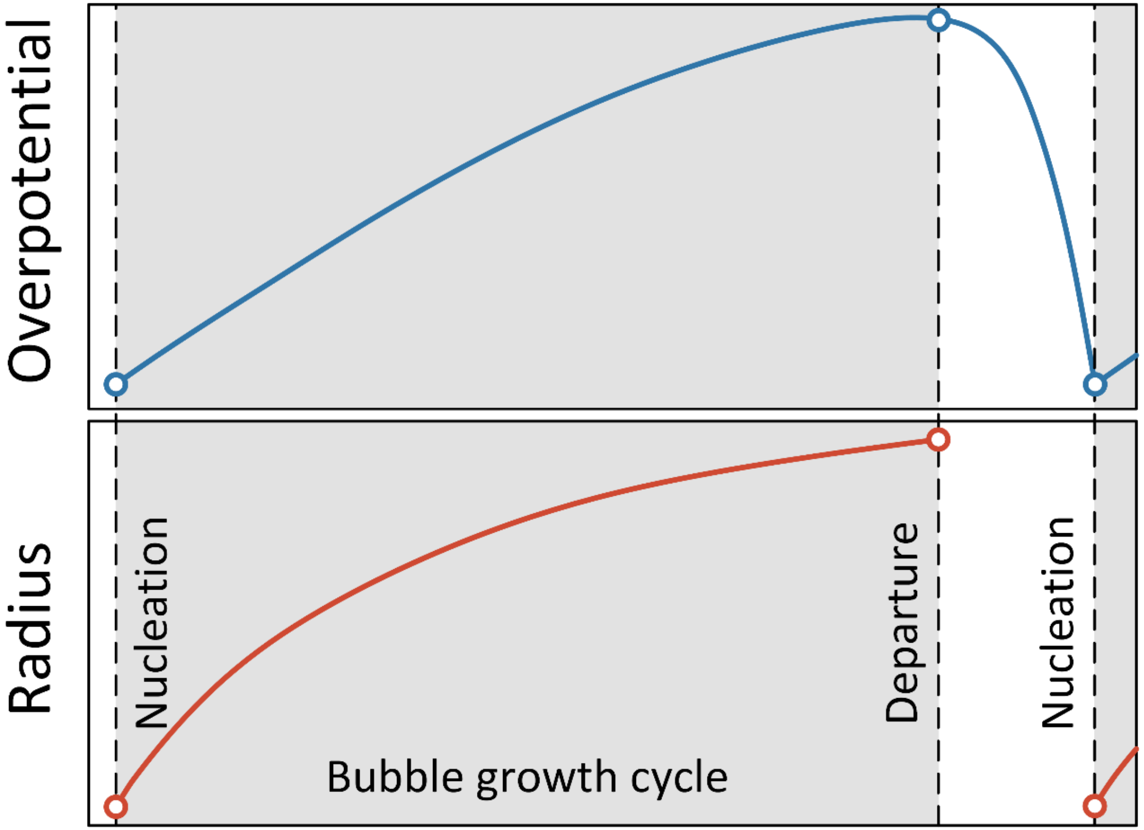
Concentration Overpotentials





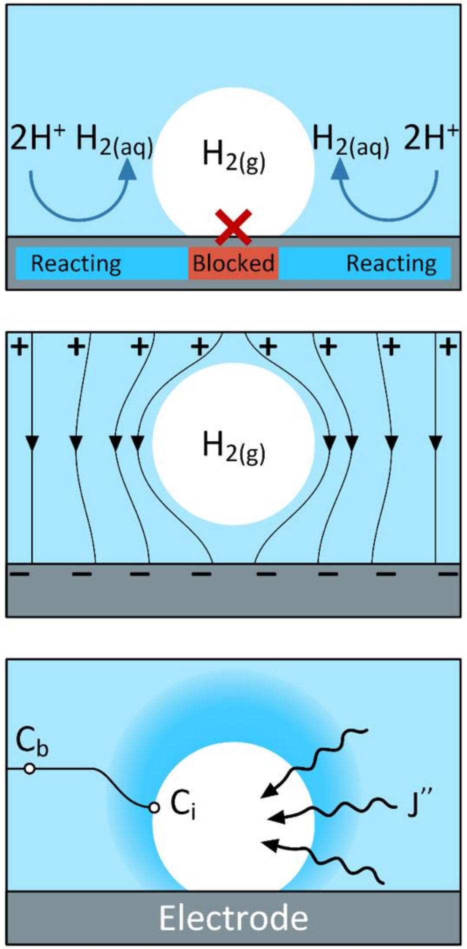
At higher current densities, the reaction may be limited how quickly the reactants and products are transferred to and away from the electrode (not driven by electrical field)

Impact on Electrochemical Overpotentials



Total overpotential typically increases with bubble radius and reaches the maximum value at the moment of bubble departure.

Impact on Electrochemical Overpotentials



Blocking reaction area

Additional resistance for ion transport

Additional diffusion resistance

Bubble-induced convection