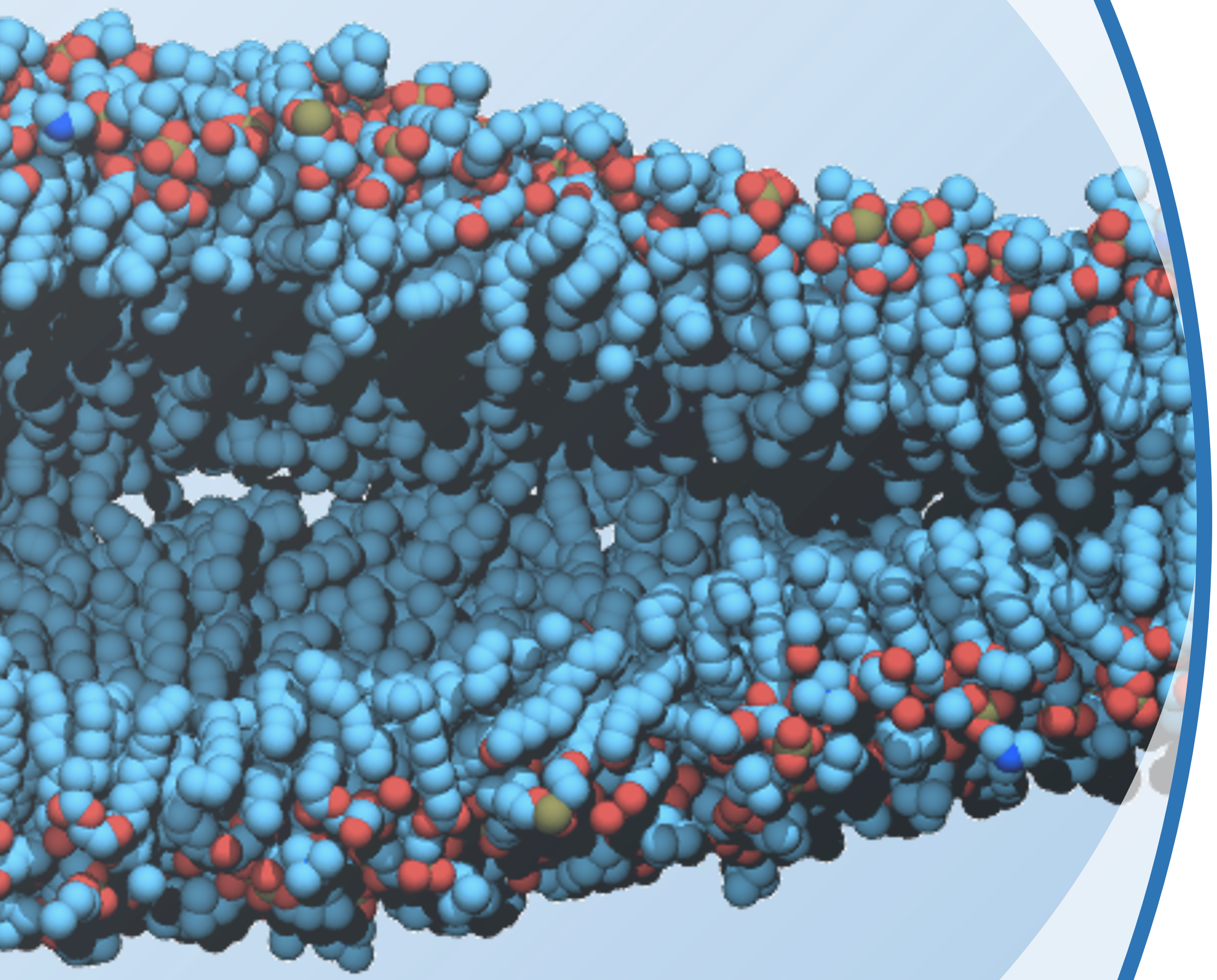
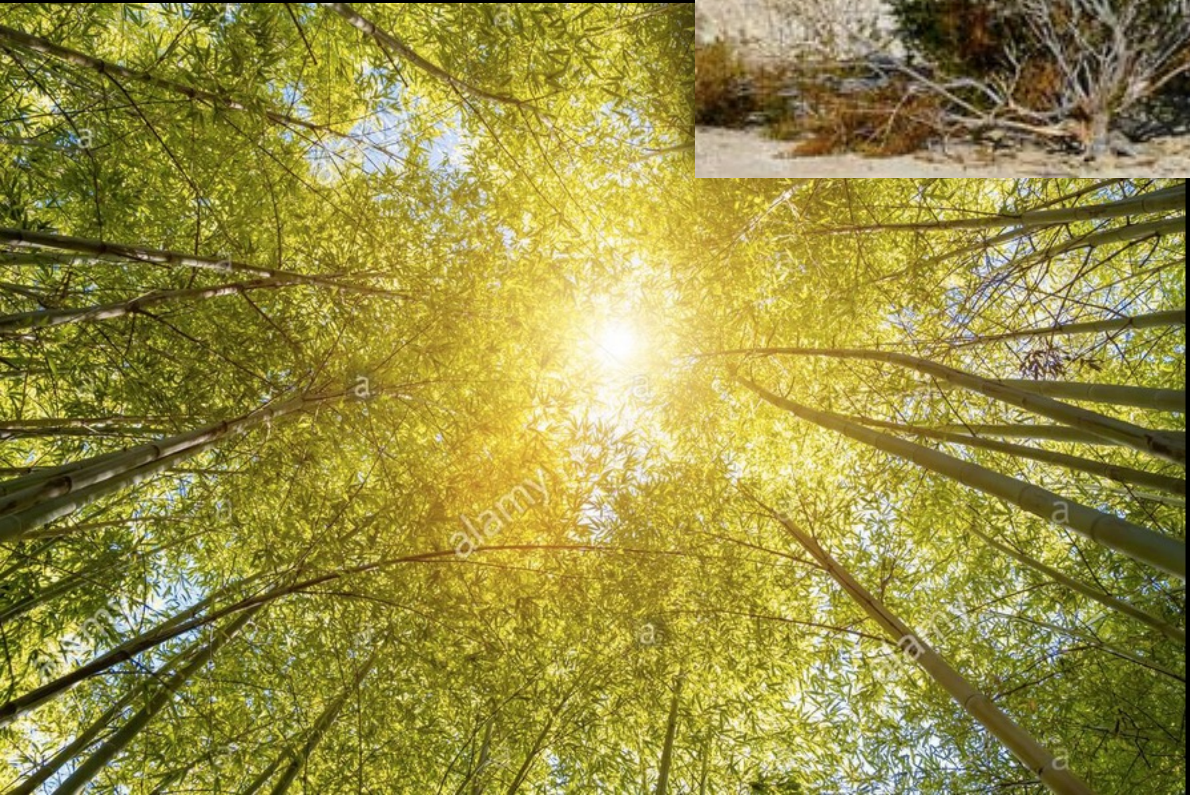


Cavitation in lipid bilayers poses strict negative pressure stability limit in biological liquids

Matej Kanduč
Jožef Stefan Institute, Ljubljana

What limits the suction intensity of plants?



In collaboration with:

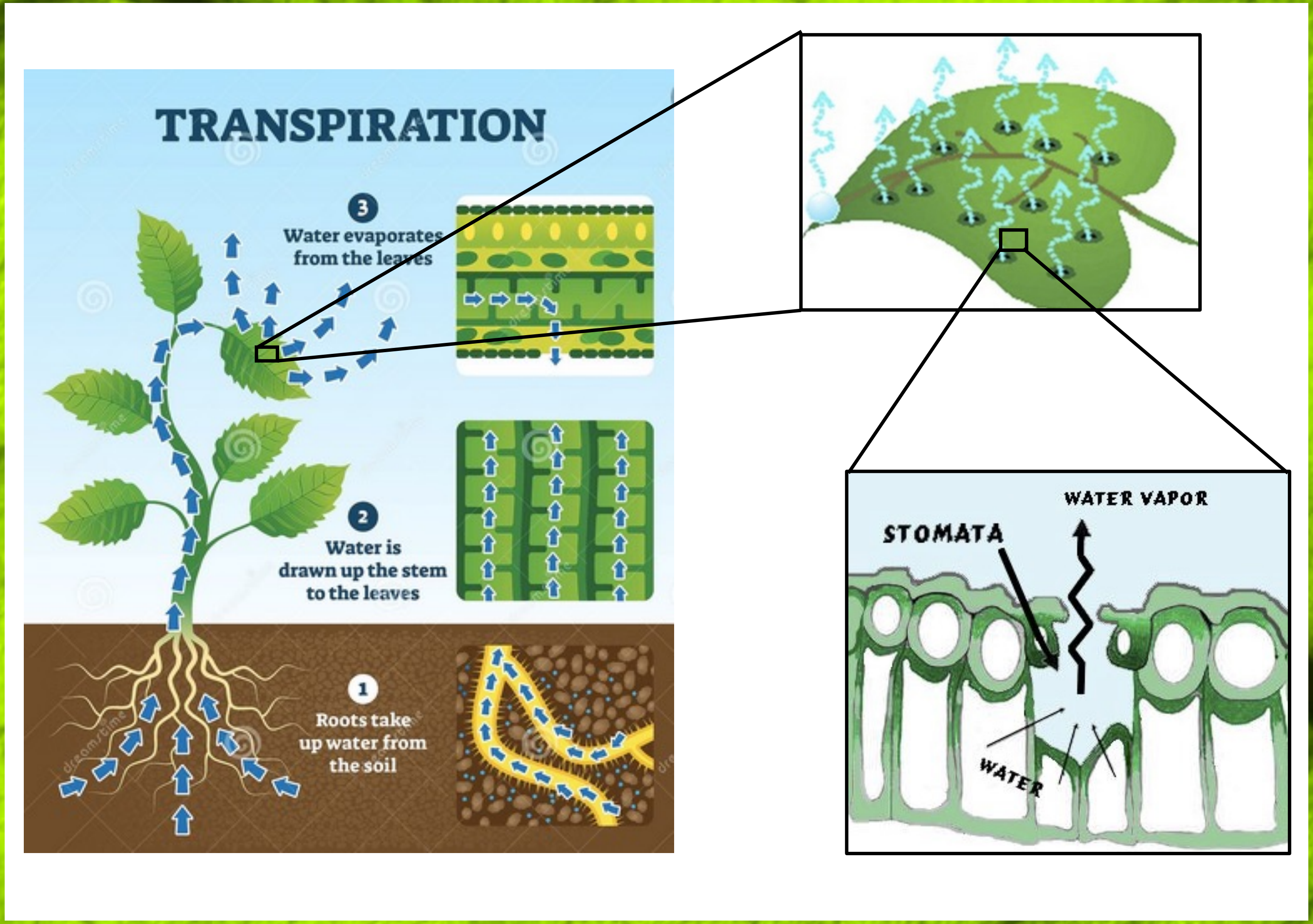
Physics

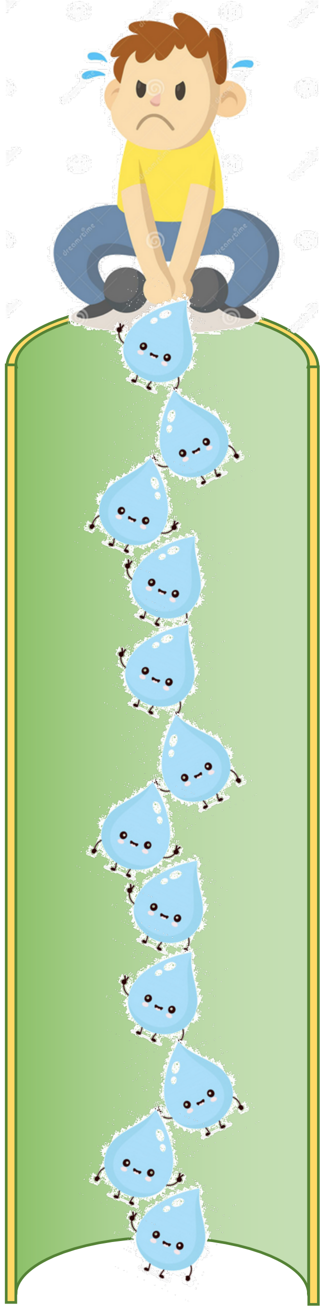
- Roland R. Netz, FU Berlin
- Emanuel Schneck, TU Darmstadt
- Philip Loche, FU Berlin

Botany

- Jochen Schenk, Cal State Fullerton
- Steven Jansen, Ulm University

Hydraulic systems in plants

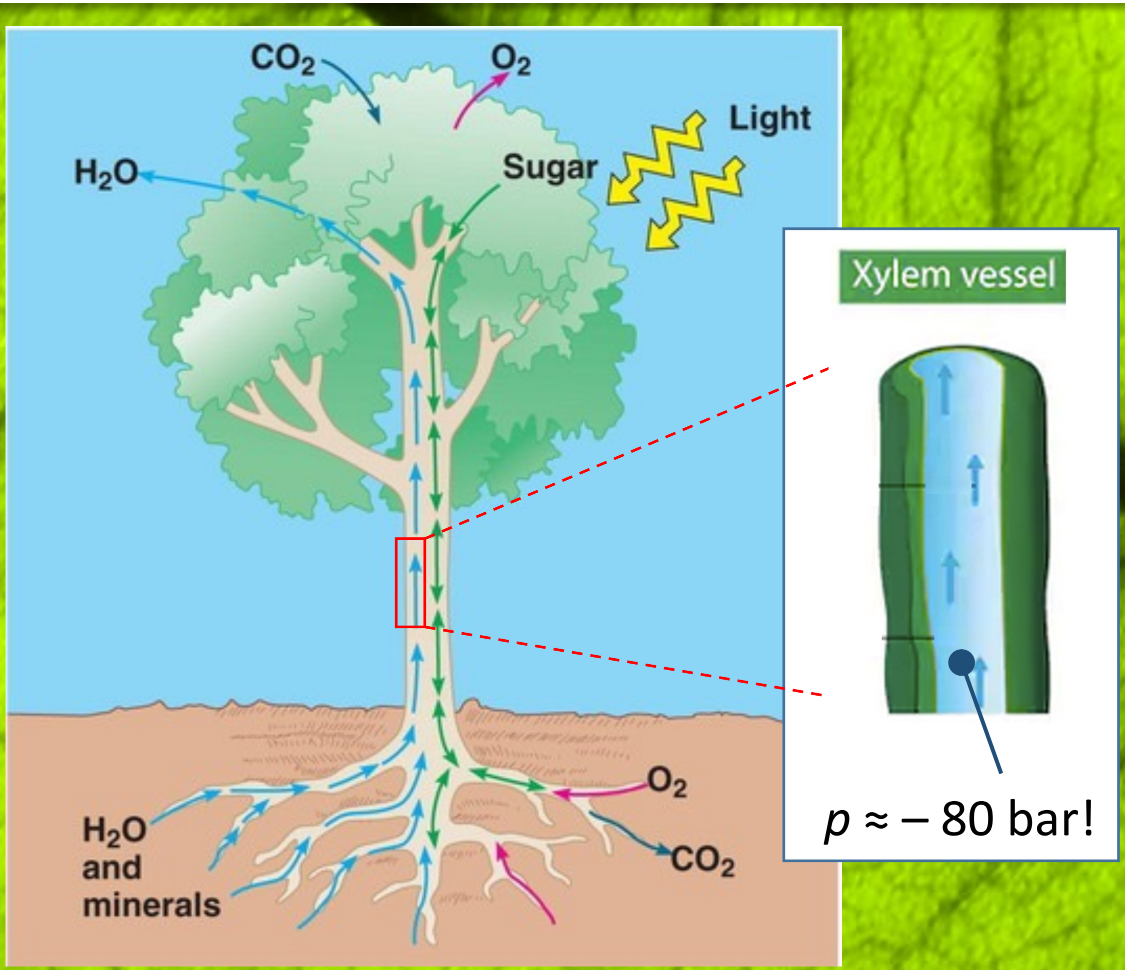




Hydraulic systems in plants

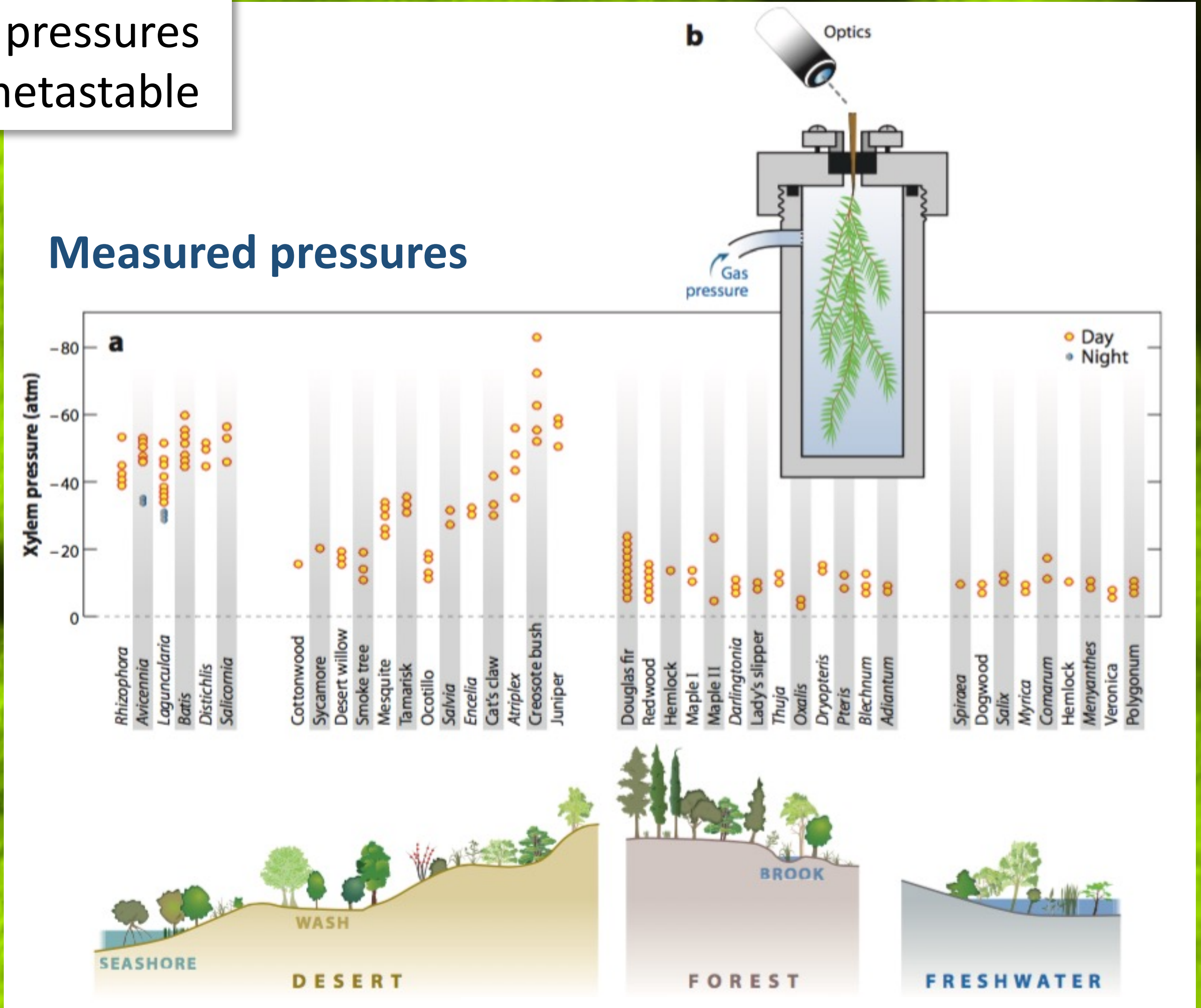
Plants transport water from the roots under negative pressures

Problem: Water and the surrounding structures are metastable



$p \approx -80$ bar!

Measured pressures



Stroock et al., Annu. Rev. Fluid Mech. 2014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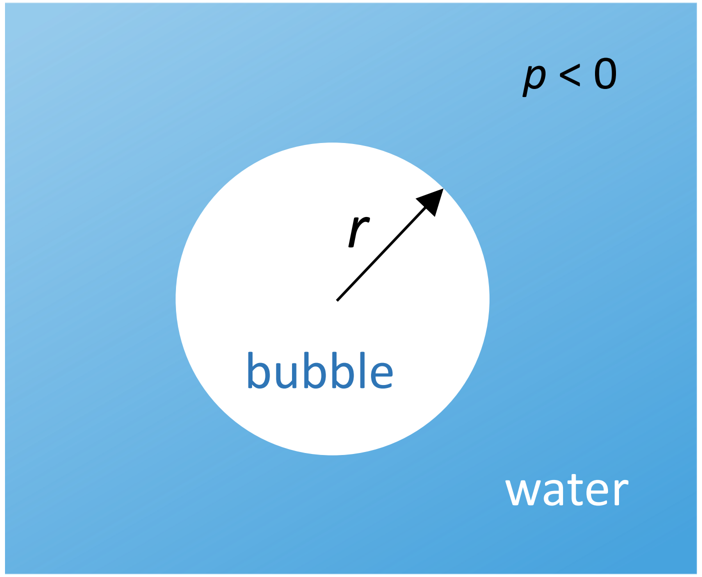
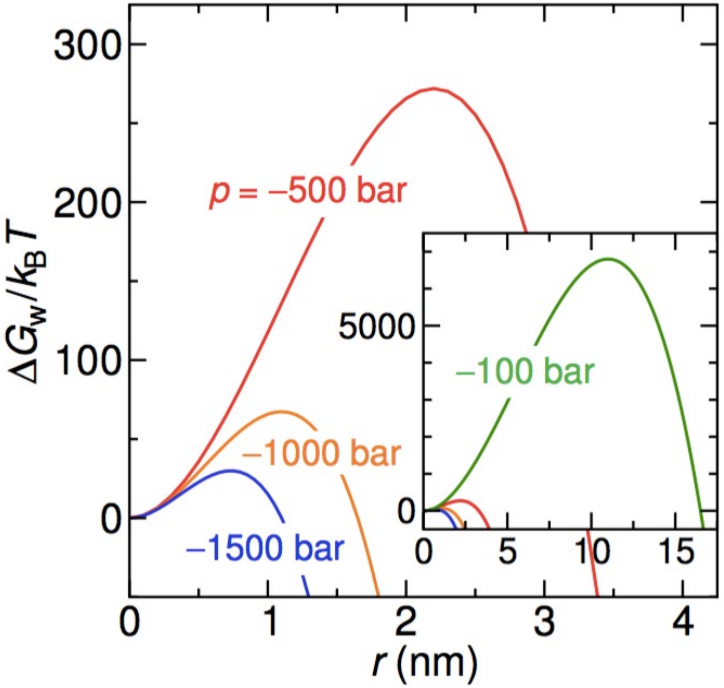
Free energy of a bubble formation

Cavitation barrier





Free energy of the bubble:

$$\Delta G_\mathrm{w} = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 p$$

Free energy barrier:

$$\Delta G_\mathrm{w}^* = \frac{16\pi}{3}\frac{\gamma_0^3}{p^2}$$

Transition rate theory

- Arrhenius description of the transition rate over the barrier

$$k = k_0\, \mathrm{e}^{-\beta \Delta G_\mathrm{w}^*}$$

where

$$k_0 = \kappa_0 V$$

- cavitation rate:

$$\frac{\mathrm{d}f}{\mathrm{d}t} = -kf$$

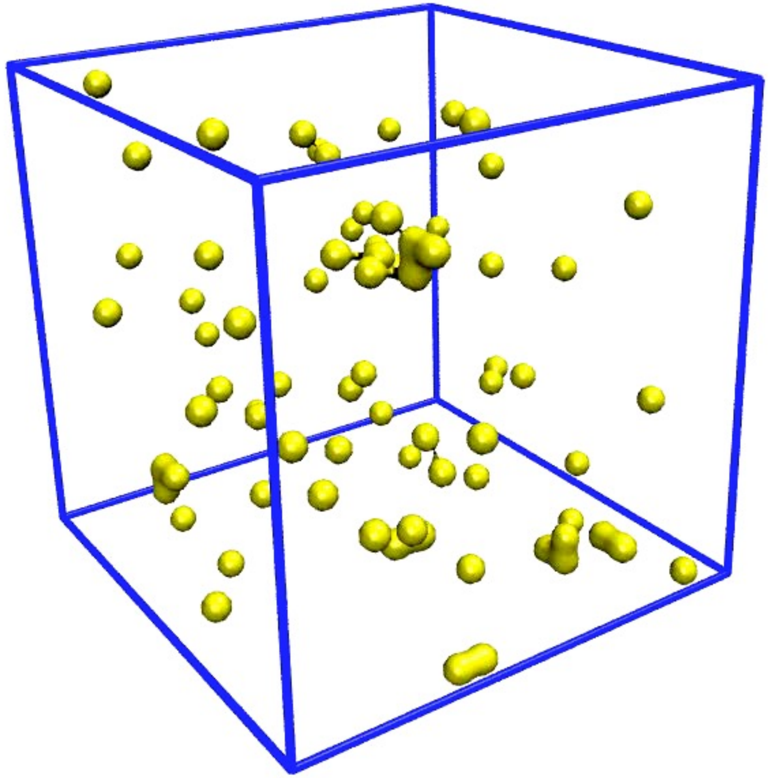
with the solution

$$f(t) = \mathrm{e}^{-kt}$$

(survival probability)

Bubble nucleation from MD simulations

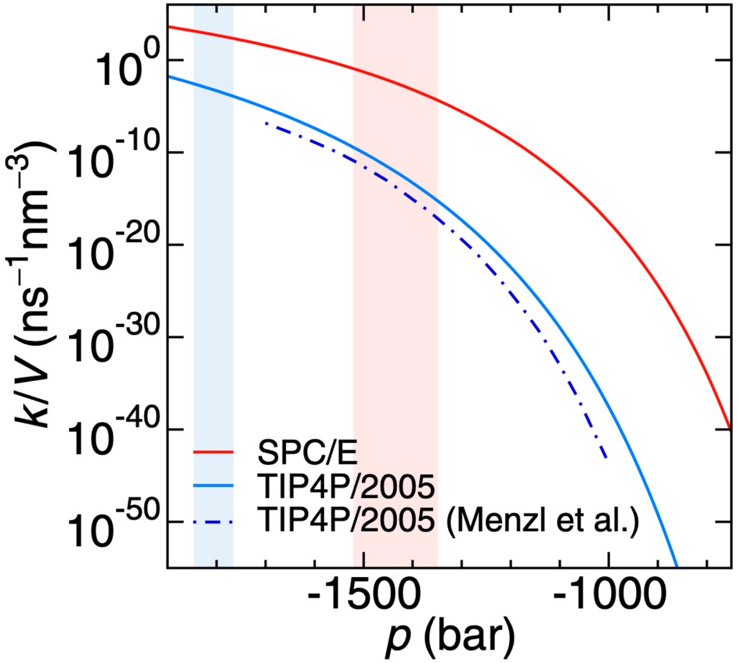
Nucleation event:
p = –1500 bar



parameters: κ_0, γ

Cavitation rate density

$$J = V^{-1}\left(-\frac{\mathrm{d}f}{\mathrm{d}t}\right)_{t=0}$$



practical example

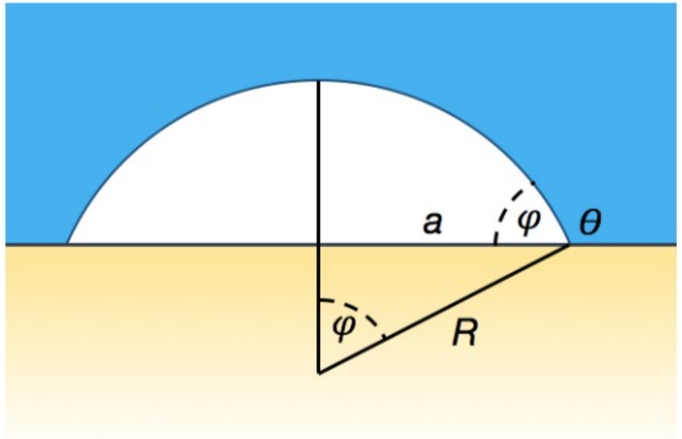
A liter (1 L) of pure water at p = –100 bar cavitates on average in

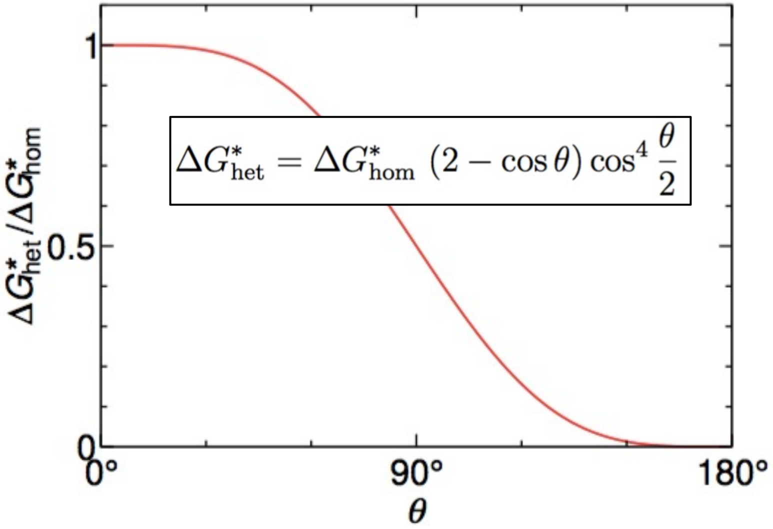
$$\tau_{\mathrm{cav}} = \frac{1}{\kappa_0 V}\,\mathrm{e}^{\beta \Delta G_{\mathrm{w}}^{*}} \sim 10^{2890 \pm 100}\ \mathrm{s}$$

*note: the age of the universe is only 4×10^{17} s

Cavitation triggers (catalysts)

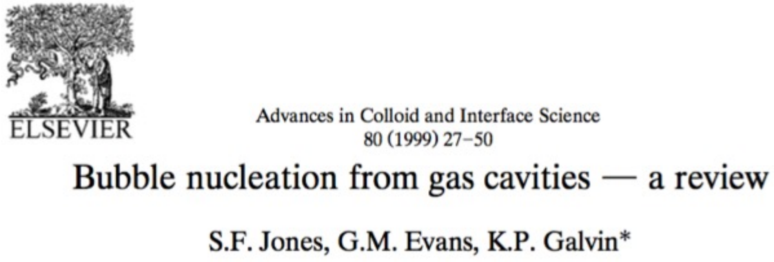
Heterogeneous cavitation





$$\Delta G^*_{\text{het}} = \Delta G^*_{\text{hom}}\,(2-\cos\theta)\cos^4\frac{\theta}{2}$$

Pre-existing nanobubbles

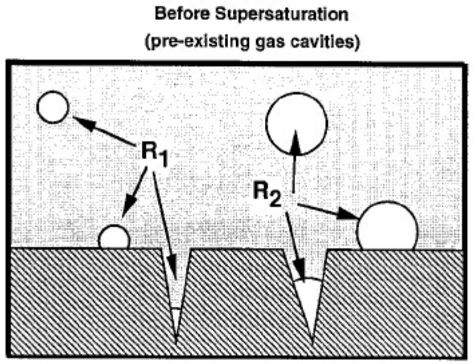


Advances in Colloid and Interface Science
80 (1999) 27–50

Bubble nucleation from gas cavities — a review

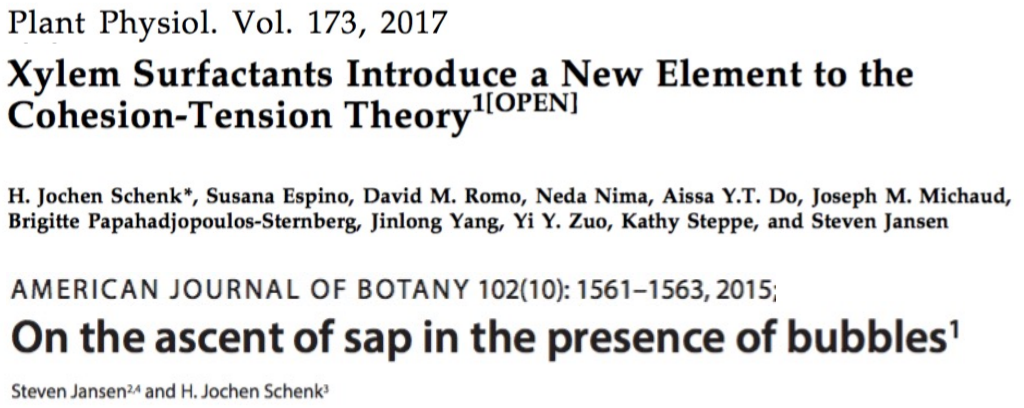
S.F. Jones, G.M. Evans, K.P. Galvin*

Type III
(pseudo-classical nucleation)



homogeneous & heterogeneous with pre-existing gas cavities: low levels of supersaturation

Sap contains much more...



Plant Physiol. Vol. 173, 2017

Xylem Surfactants Introduce a New Element to the Cohesion-Tension Theory[1][OPEN]

H. Jochen Schenk*, Susana Espino, David M. Romo, Neda Nima, Aissa Y.T. Do, Joseph M. Michaud, Brigitte Papahadjopoulos-Sternberg, Jinlong Yang, Yi Y. Zuo, Kathy Steppe, and Steven Jansen

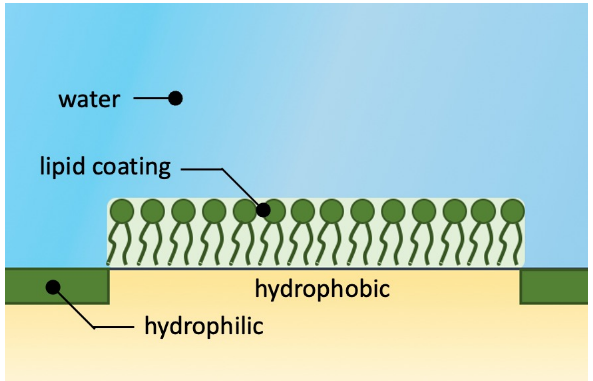
AMERICAN JOURNAL OF BOTANY 102(10): 1561–1563, 2015;

On the ascent of sap in the presence of bubbles[1]

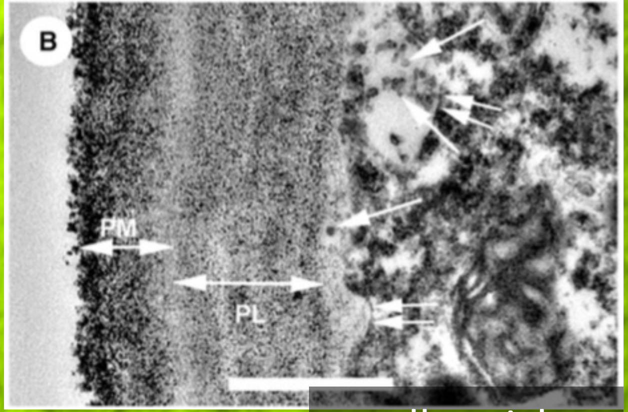
Steven Jansen[2,4] and H. Jochen Schenk[3]

Elements of vascular water (sap):

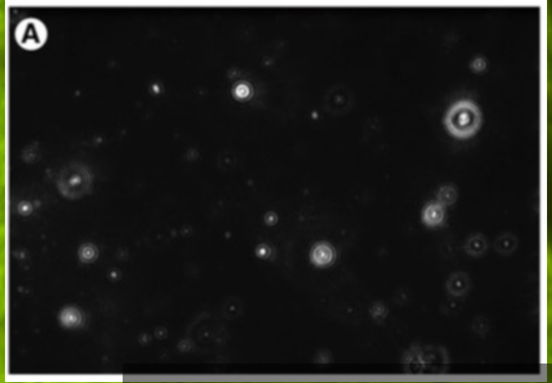
- supersaturated with some gases
- contains surface-active molecules
- xylem contains hydrophobic surfaces



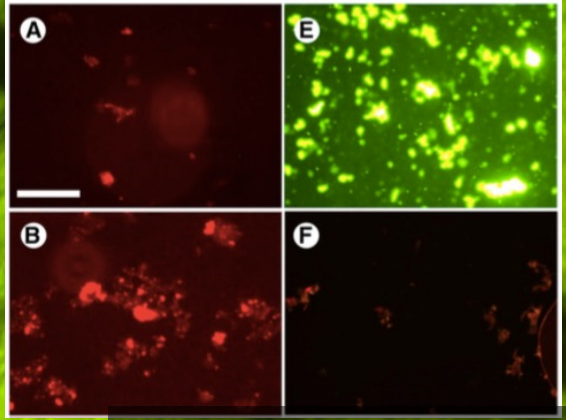
Solution?
Lipids cover up hydrophobic patches



small vesicles



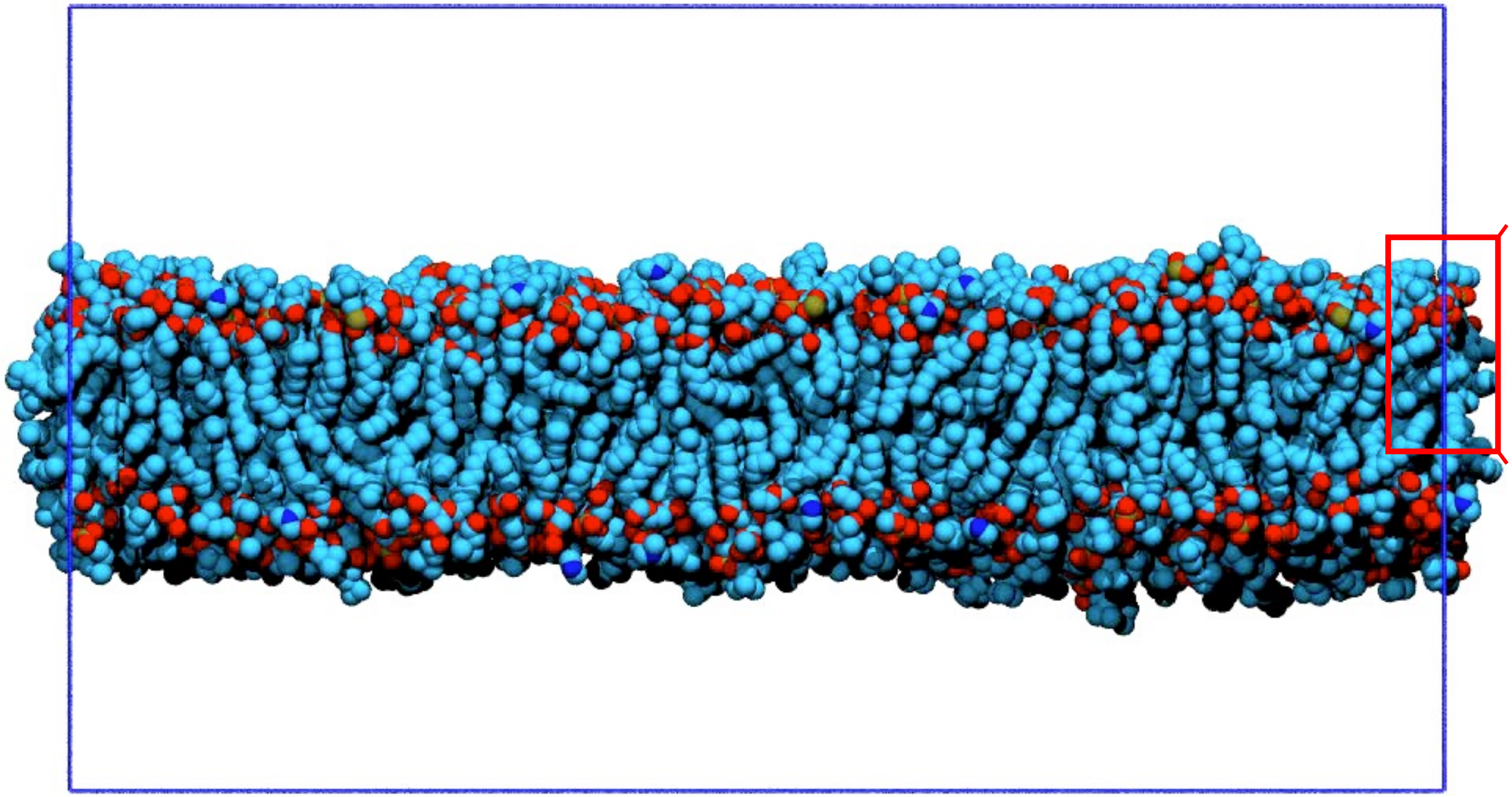
nanoparticles in sap



amphiphilic molecules

Electron micrograph of a surfactant monolayer-coated nanobubble

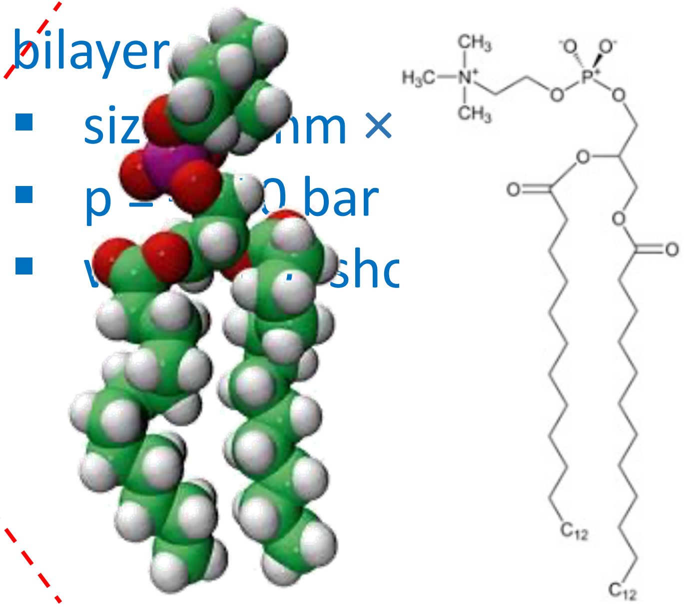
Cavitation of a lipid bilayer



12:0 PC (DLPC)

MD simulation of a connected bilayer

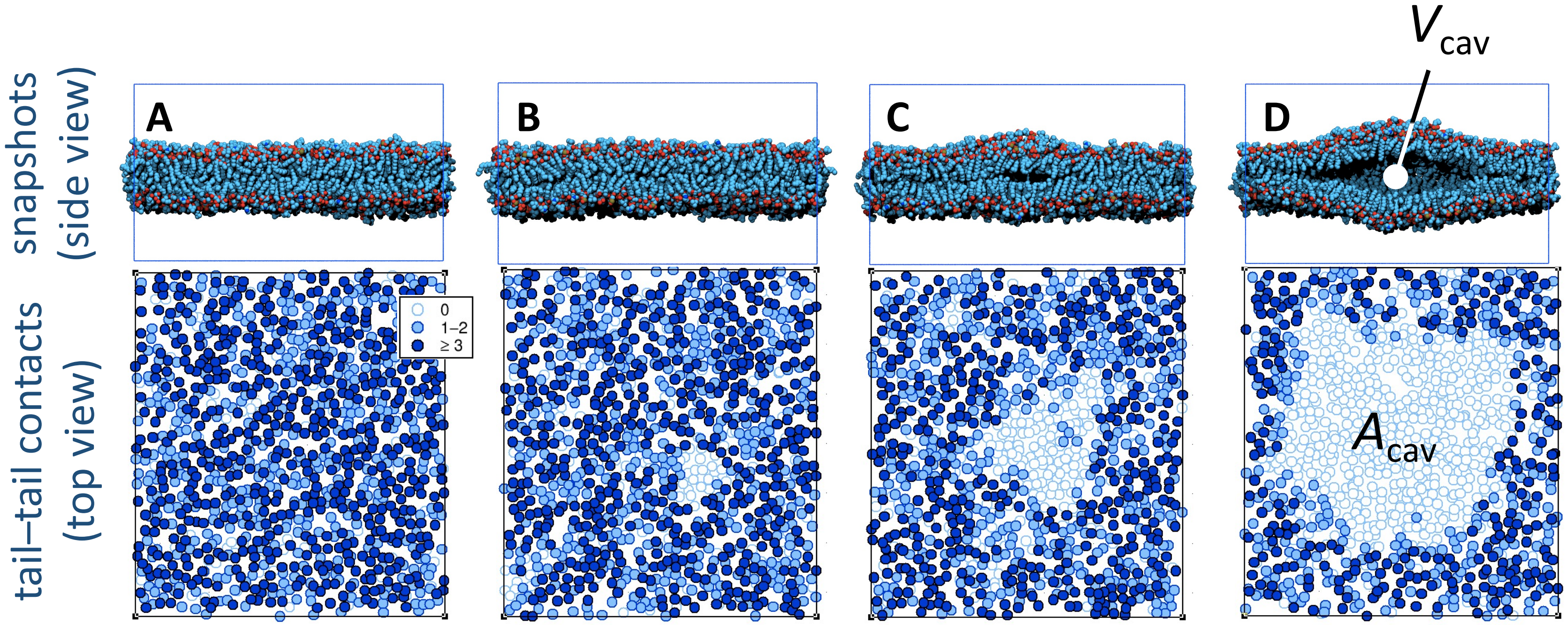
- siz nm ×
- p = 0 bar
- w sho

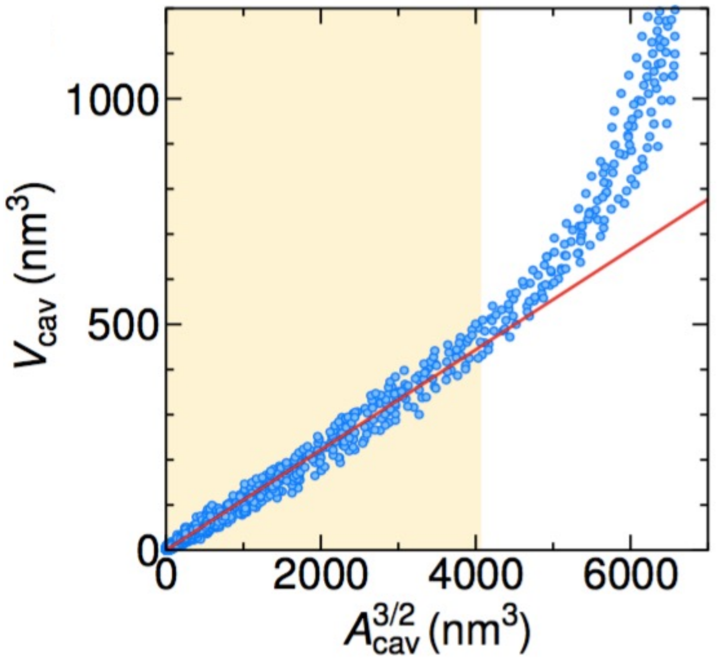


Kanduč et al., PNAS **117**, 10733 (2020)

Lipid bilayer cavitation

Top: consecutive bilayer cross-sections (water not shown) during a cavitation event at −215 bar. The lateral surface area of the simulation box: 18 nm × 20 nm.





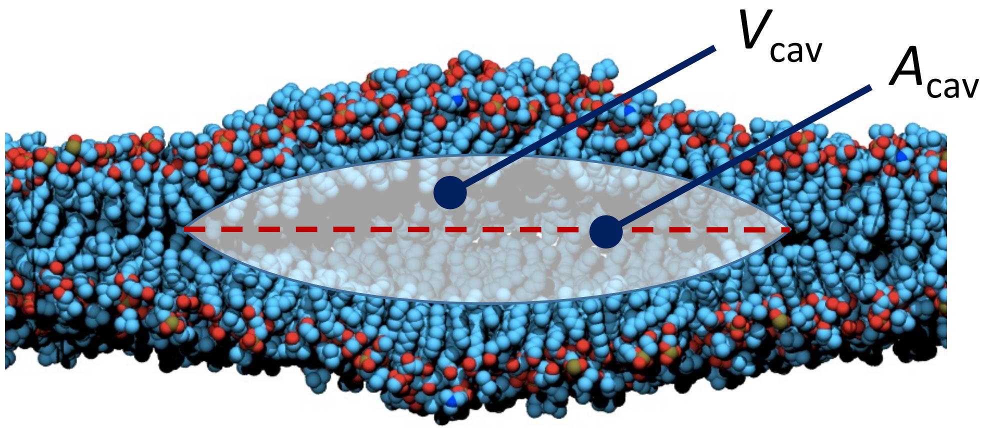
Correlation between the cavity volume and the cross section area of the cavity

$$V_{\mathrm{cav}} = \alpha_{\mathrm{lip}} A_{\mathrm{cav}}^{3/2}$$

$$\alpha_{\mathrm{lip}} = 0.11$$

Kanduč et al., PNAS **117**, 10733 (2020)

Bilayer cavitation



- Free energy of the bilayer cavity:

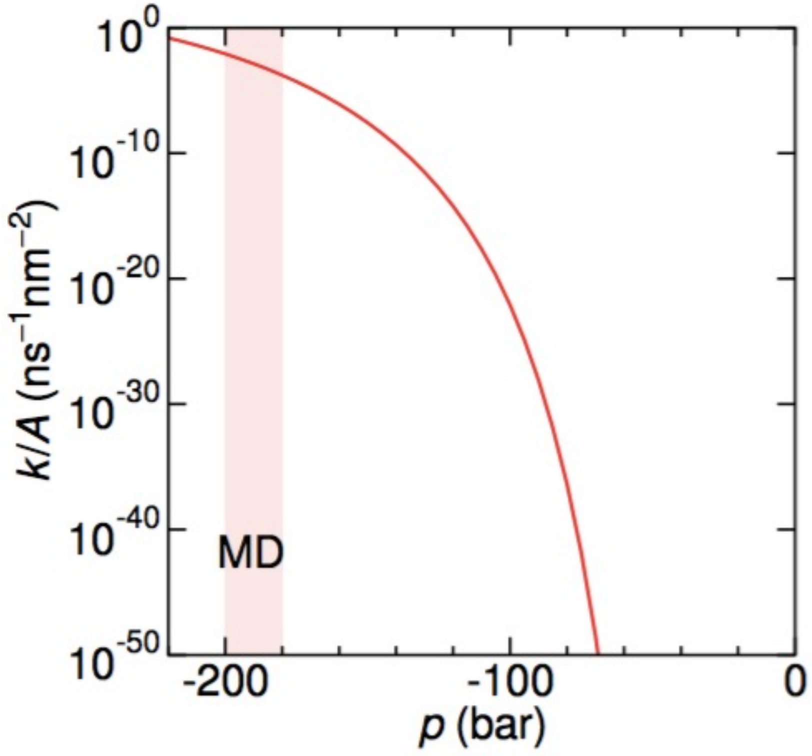
$$\Delta G_{\mathrm{lip}} = w_{\mathrm{lip}} A_{\mathrm{cav}} + p V_{\mathrm{cav}}(A_{\mathrm{cav}}).$$

- Free energy barrier:

$$\Delta G^*_{\mathrm{lip}} = \frac{4 w_{\mathrm{ll}}^3}{27 \alpha^2 p^2}$$

- Cavitation rate:

$$k/A = \kappa_0^{\mathrm{lip}} \exp(-\beta \Delta G^*_{\mathrm{lip}})$$



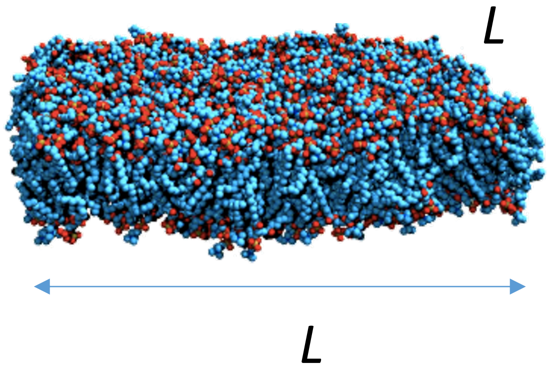
Kanduč et al., PNAS **117**, 10733 (2020)

Bilayer cavitation

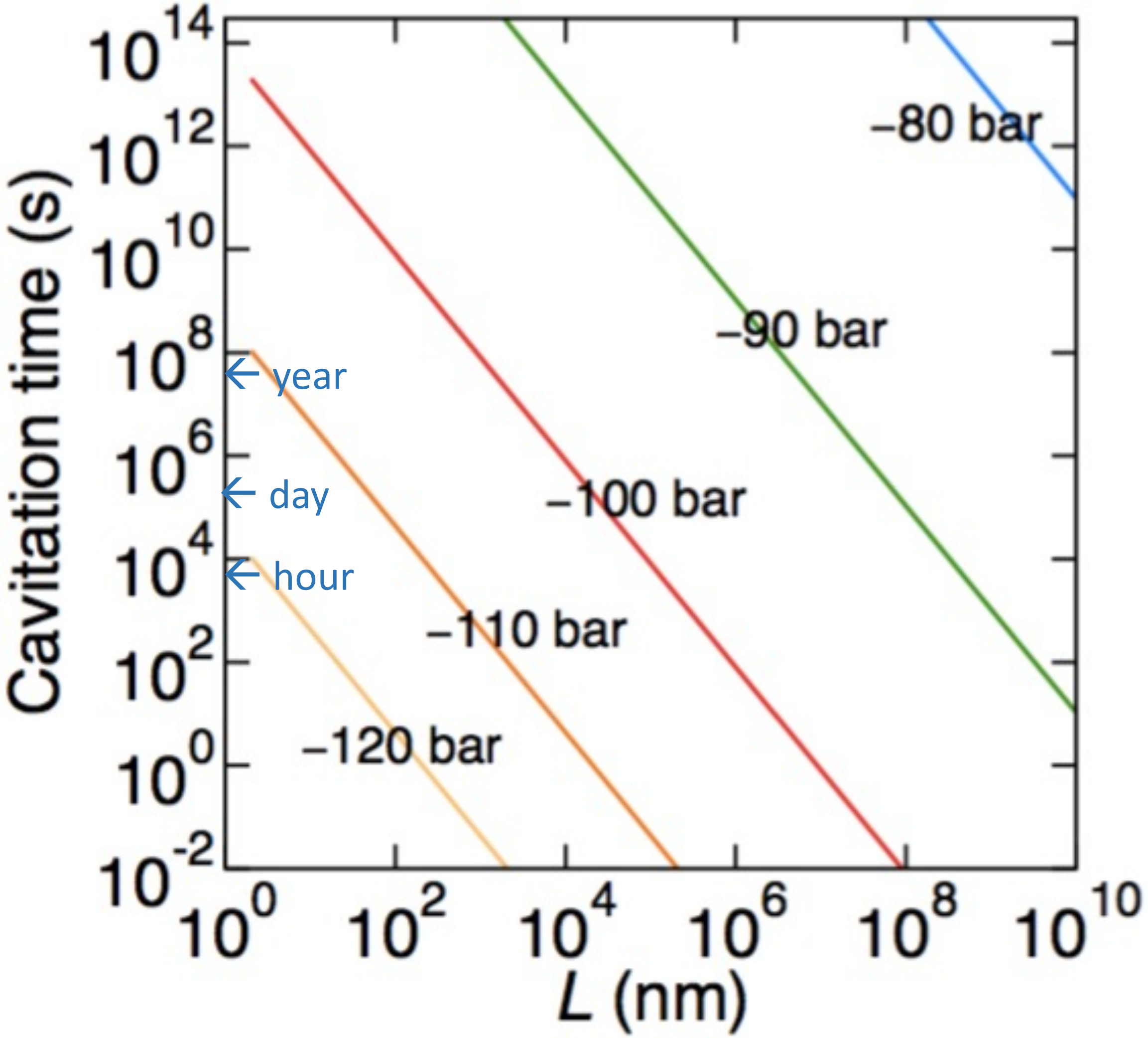
An example:

How long does it take
for a bilayer to cavitate?

- constant *p*
- Assuming square bilayer of *L* × *L*:



$$\tau_{\mathrm{cav}} = \frac{1}{\kappa_0^{\mathrm{lip}} A} \mathrm{e}^{\beta \Delta G^*_{\mathrm{lip}}}$$



Kanduč et al., PNAS **117**, 10733 (2020)

Maximal tensions

Cavitation pressure versus the mean cavitation time for different bilayer areas:

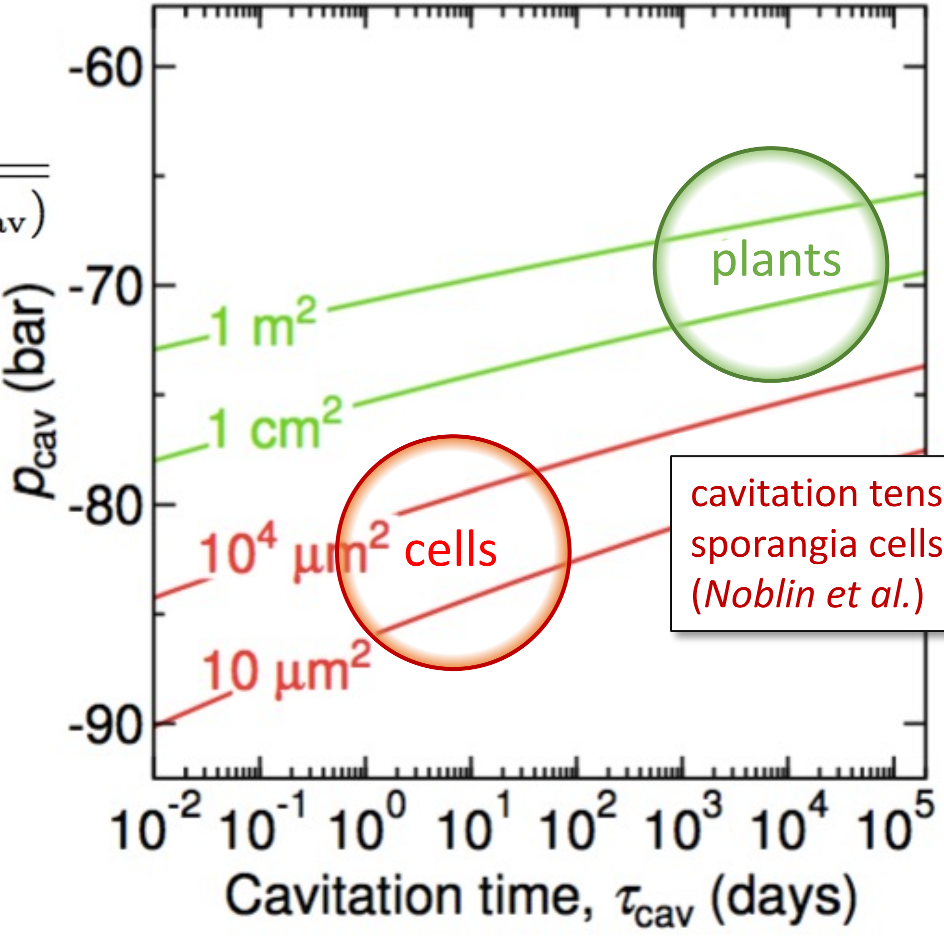
$$p_{\mathrm{cav}} = -\frac{2}{\alpha_{\mathrm{lip}}}\left(\frac{w_{\mathrm{lip}}}{3}\right)^{3/2}\frac{1}{\sqrt{k_{\mathrm{B}}T\ln(\kappa_0^{\mathrm{lip}}A\tau_{\mathrm{cav}})}}$$

parameters:

$$\alpha_{\mathrm{lip}} = 0.11$$

$$\kappa_0^{\mathrm{lip}} = 65 \pm 4\ \mathrm{ns}^{-1}\mathrm{nm}^{-2}$$

$$w_{\mathrm{lip}} = 7.6\ \mathrm{kJ/mol/nm}^2$$



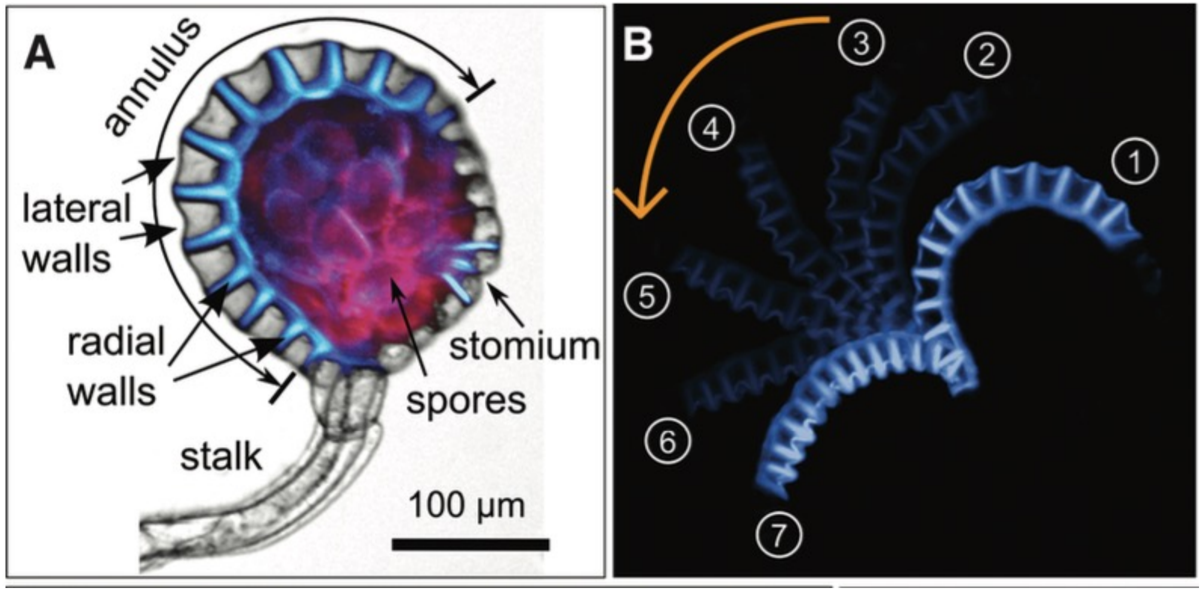
max. tension in dessert plants, –70 bar (*Stroock et al.*)

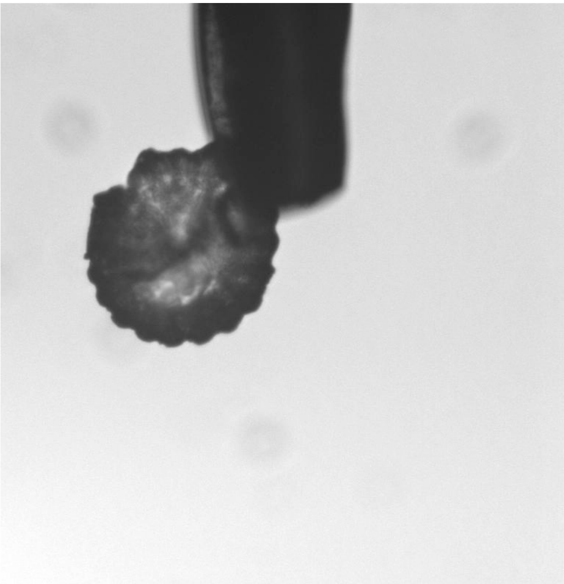
cavitation tension in sporangia cells, –90 bar (*Noblin et al.*)

Kanduč et al., PNAS **117**, 10733 (2020)

Water under negative pressures in cells

Catapulting mechanism of fern spores





- building tension through evaporation
- cavitation at $p_{\mathrm{cav}} = -90$ bar

Noblin et al., Science 2012

Conclusions

- **Combining simulation and kinetic modeling approaches:**
  All-atom simulations provide necessary molecular parameters
  Analytic continuum model enables the extrapolation to relevant time and length scales

- **bulk water** does not likely cavitate (in homogeneous way) under negative pressures (e.g., –100 bar)

- **bilayers** can cavitate (depends on the exposed negative pressure and detailed interactions)
  The presence of bilayers imposes strict upper limit of negative pressure (–70 to –90 bar) in a system

Acknowledgements

Physics

- Roland R. Netz, Free University Berlin
- Emanuel Schneck, Technical University Darmstadt
- Philip Loche, Free University Berlin

Botany

- Jochen Schenk, California State University, Fullerton
- Steven Jansen, Ulm University