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

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What limits the suction intensity of plants?

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**Botany**
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Hydraulic systems in plants

1. Roots take up water from the soil.
2. Water is drawn up the stem to the leaves.
3. Water evaporates from the leaves.

Stomata:
- Water vapor
- Water
Hydraulic systems in plants

Plants transport water from the roots under negative pressures

Problem: Water and the surrounding structures are metastable

$p \approx -80 \text{ bar!}$
Free energy of a bubble formation

Cavitation barrier

\[ \Delta G_w = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 p \]

Free energy of the bubble:

Free energy barrier:

\[ \Delta G_w^* = \frac{16\pi \gamma_0^3}{3 \frac{p^2}{r^2}} \]

Transition rate theory

- Arrhenius description of the transition rate over the barrier

\[ k = k_0 e^{-\beta \Delta G_w^*} \]

where

\[ k_0 = \kappa_0 V \]

- Cavitation rate:

\[ \frac{df}{dt} = -kf \]

with the solution

\[ f(t) = e^{-kt} \]

(survival probability)
Bubble nucleation from MD simulations

Nucleation event:
\( p = -1500 \text{ bar} \)

Cavitation rate density
\[ J = V^{-1} \left( -\frac{df}{dt} \right)_{t=0} \]

parameters: \( \kappa_0, \gamma \)

practical example
A liter (1 L) of pure water at \( p = -100 \text{ bar} \) cavitates on average in

\[ \tau_{\text{cav}} = \frac{1}{\kappa_0 V} e^{\beta \Delta G_w^*} \sim 10^{2890 \pm 100} \text{ s} \]

*note: the age of the universe is only \( 4 \times 10^{17} \text{ s} \)
Cavitation triggers (catalysts)

Heterogeneous cavitation

- **Type III** (pseudo-classical nucleation)

Pre-existing nanobubbles

- Bubble nucleation from gas cavities — a review
  - S.F. Jones, G.M. Evans, K.P. Galvin

- **Pre-existing nanobubbles** with low levels of supersaturation
Elements of vascular water (sap):
- supersaturated with some gases
- contains surface-active molecules
- xylem contains hydrophobic surfaces

Solution?
Lipids cover up hydrophobic patches
Cavitation of a lipid bilayer

MD simulation of a connected bilayer
- size: 15 nm × 15 nm
- p = −200 bar
- 12:0 PC (DLPC)

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: $18 \text{ nm} \times 20 \text{ nm}$.

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

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

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

Kanduč et al., PNAS 117, 10733 (2020)
Bilayer cavitation

- Free energy of the bilayer cavity:
  \[ \Delta G_{\text{lip}} = w_{\text{lip}} A_{\text{cav}} + pV_{\text{cav}}(A_{\text{cav}}) \]

- Free energy barrier:
  \[ \Delta G_{\text{lip}}^* = \frac{4w_{\text{ll}}^3}{27\alpha^2 p^2} \]

- Cavitation rate:
  \[ \frac{k}{A} = \kappa_0^\text{lip} \exp(-\beta \Delta G_{\text{lip}}^*) \]

Kanduč et al., PNAS 117, 10733 (2020)
An example:
How long does it take for a bilayer to cavitate?

- constant $p$
- Assuming square bilayer of $L \times L$:

$$\tau_{cav} = \frac{1}{\kappa_0^\text{lip} A} e^{\beta \Delta G_{\text{lip}}^*}$$

Kanduč et al., PNAS 117, 10733 (2020)
Maximal tensions

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

\[ p_{\text{cav}} = -\frac{2}{\alpha_{\text{lip}}} \left( \frac{w_{\text{lip}}}{3} \right)^{3/2} \frac{1}{\sqrt{k_{B}T \ln(\kappa_{0}^{\text{lip}} A \tau_{\text{cav}})}} \]

parameters:

\[ \alpha_{\text{lip}} = 0.11 \]
\[ \kappa_{0}^{\text{lip}} = 65 \pm 4 \text{ ns}^{-1} \text{nm}^{-2} \]
\[ w_{\text{lip}} = 7.6 \text{ kJ/mol/nm}^{2} \]

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 $p_{\text{cav}} = -90\ \text{bar}$

*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
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