

# **The influence of the wall contact angle on gas bubble behaviour in xylem conduits under tension and possible consequences for embolism**

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## **Abstract**

Gas-filling of conduits decreases hydraulic conductance of the xylem vessels. Therefore, embolism formation and reversal is one of the crucial topics in plant water transport. The negative pressure (=tension) in xylem water during plant transpiration may cause embolism in two ways: (i) Homogeneous nucleation, the spontaneous formation of a water vapour bubble within the water column due to statistical fluctuations. (ii) Heterogeneous nucleation, the development of bubbles by air seeding, the drawing of gas present in already embolized conduits through pit membrane pores into functioning conduits. This contribution deals with the behaviour of gas bubbles caused by heterogeneous nucleation. These bubbles usually contain both water vapour and air and float either freely in the xylem water (which is under tension) or attach themselves to the vessel wall (which is characterised by its shape and contact angle). Based on the reversible free energy of this system, we derive conditions for two kinds of equilibria: (a) Mechanical equilibrium (and its stability or instability) between the forces which try to contract and expand bubbles containing air and water-vapour. (b) Equilibrium with respect to the exchange of air particles between the bubble and the surrounding xylem water by dissolution mechanisms.

The results — given as relations between xylem water pressure, bubble radius, bubble particle content and xylem wall morphology and contact angle — allow to predict whether appearing bubbles lead to embolism or not.

## **Introduction**

Based on arguments from statistical physics and thermodynamics it has been shown ([4], [5]) that for the negative pressures to be expected in plant conduits spontaneous cavitation (= homogeneous nucleation) plays only a minor role in causing embolism because the tension values occurring in the xylem are not high enough to permit a significant formation rate of expanding bubbles.

Embolism is usually caused by air seeding (= heterogeneous nucleation), i.e. a group of “air” molecules finds its way into a tree water conduit through cracks and openings in the wood. If such a passage remains open, at least one segment of the embolised conduit is permanently lost for water transport. If it closes, however, after a limited number of “air molecules” has entered the conduit these form one or several embryonic air bubbles which may — but need not necessarily — cause the rupture of the water column (see Fig. 1).

As will be shown below, embryonic bubbles which do no harm as long as they are completely immersed into the xylem fluid may, however, cause embolism if they come into contact with the vessel wall.

The hazardousness of a given bubble is related to its ability to comply with the following equilibrium conditions:

- (i) Mechanical equilibrium: (a) the randomly moving gas particles in the bubble act as an outward directed force which tries to expand the bubble; (b) the surface tension of the gas/liquid interface tries to contract the bubble; (c) the pressure  $p_s$  of the xylem water contributes for  $p_s < 0$  to the expanding force, for  $p_s > 0$  to the contracting force. Equilibrium exists if these forces sum up to zero ([6], [7]).
- (ii) Diffusional equilibrium: the number of air molecules remains constant only if a balance with respect to the exchange of air molecules with the bubble's surroundings prevails between the air partial pressure within the bubble and the concentration of air molecules dissolved in the xylem water. Otherwise, air molecules from within the bubble either dissolve at the bubble's gas/liquid interface in the xylem water and diffuse towards regions of lower air molecule concentration, or else a diffusional current through the xylem water delivers air molecules to the bubble.

The exchange process between water vapour and water is faster than the exchange of air by a factor of about  $10^6$ . Hence, mechanical equilibrium is a necessary prerequisite for diffusional equilibrium.

The development of a bubble is essentially controlled by the mechanical forces. We assess them (and the equilibria they possibly adopt) by analysing the reversible free energy associated with the formation of an embryonic bubble of radius  $R$  (see [1], [4], [5], [6], [7]). In doing so we assume (i)  $p_w \approx p_{sat}$  ( $p_{sat}$ : saturation pressure of water vapour): Because the exchange of water molecules between bubble and surrounding liquid is a very intensive one, the water vapour partial pressure in the bubble readjusts to the water vapour saturation pressure almost immediately. (ii)  $n_a \approx \text{const.}$ : This simplifying assumption is only valid on the very short time scale of bubble formation considered here. The assumption is based on the low solubility of air in water, implying that only a small fraction of the air molecules in the bubble's interior are lost to the surrounding liquid within the considered time scale.

## Results and discussion

### Floating bubble

The formation energy of a bubble filled with water vapour and  $n_a$  air molecules reads (see [1], [7])

$$W = 4\pi\gamma R^2 - \frac{4\pi}{3} (p_w - p_s) R^3 + 3\mathcal{R}T n_a \log\left(\frac{R_{max}}{R}\right) \quad (1)$$

where  $R_{max} := -2\gamma/p_s$ ,  $\mathcal{R}$  is the gas constant and  $T$  the temperature. The bubble radii where equilibrium of forces prevails are found from the zeros of

$$\frac{\partial W}{\partial R} = [8\pi\gamma R] - \left\{ 4\pi (p_w - p_s) R^2 + \frac{3\mathcal{R}T n_a}{R} \right\} \quad (2)$$

and their stability is assessed by evaluating  $\partial^2 W / \partial R^2$  at the equilibrium point(s). Notice that the term in brackets on the right hand side of equation (2) represents the surface tension and thus the contracting force acting on the bubble while the terms in braces represents expanding forces due to gas pressure and negative xylem water pressure. Bubble equilibrium radii (i.e. the solutions of  $\partial W / \partial R = 0$ ) are located at

$$\begin{aligned} R_{stab} &= \frac{R_{vap}}{3} \left( 1 - 2 \cos \left[ \frac{1}{3} \arccos \left( 1 - \frac{2n_a}{n_{crit}} \right) + \frac{\pi}{3} \right] \right) \\ R_{inst} &= \frac{R_{vap}}{3} \left( 1 + 2 \cos \left[ \frac{1}{3} \arccos \left( 1 - \frac{2n_a}{n_{crit}} \right) \right] \right) \end{aligned} \quad (3)$$

where  $n_{crit} := 128\pi\gamma^3 / [81\mathcal{R}T (p_w - p_s)^2]$  and  $R_{vap} = 2\gamma / (p_w - p_s)$ . For a pure water vapour bubble ( $n_a = 0$ ) the equilibrium radii simplify to  $R_{stab} = 0$  and  $R_{inst} = R_{vap}$ . Evaluating  $\partial^2 W / \partial R^2$ , we find that a bubble at radius  $R_{stab}$  is in stable, at radius  $R_{inst}$ , however, in unstable equilibrium. For  $n_a > n_{crit}$  both  $R_{stab}$  and  $R_{inst}$  become undefined, meaning that the bubble expands without limits (see Figures 2(b) and 3).

The bubble behaviour is illustrated by Figure 2(b). A bubble which contains  $n_{a,3} > n_{crit}$  air molecules fulfills for all  $R > 0$  the condition  $\partial W / \partial R < 0$ . Equation (2) implies then that the bubble can

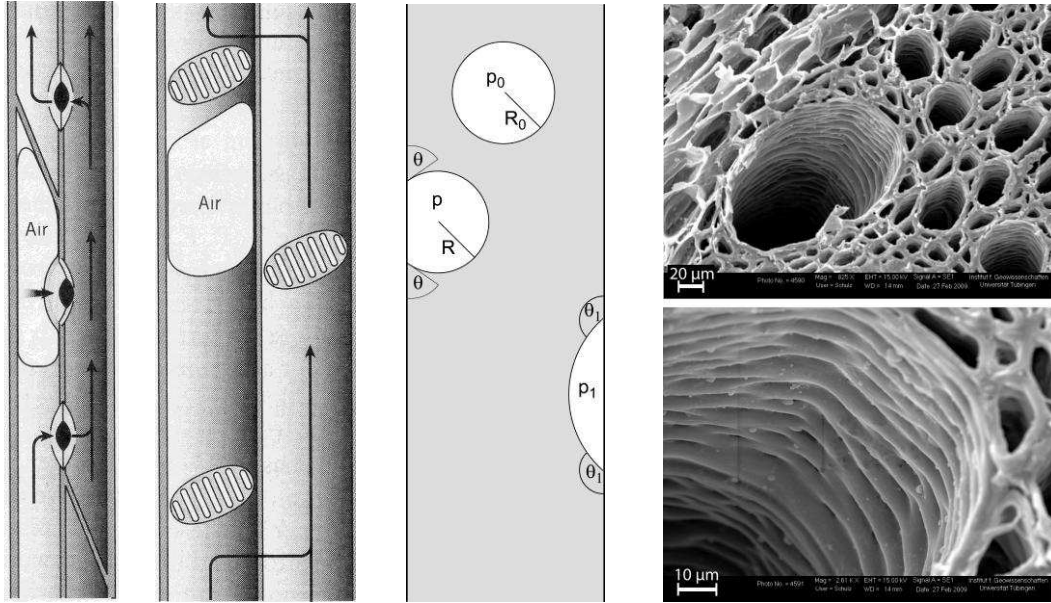


Fig. 1 Left/centre left: Conduit elements connected by torus-margopits (left) and membrane pits (centre left). In each case one embolised element has been hydraulically isolated and the water flow is redirected through its neighbours (Drawing taken from [8]). Centre right: Conduit with stable gas bubbles. Two of them are attached to the conduit walls forming the contact angles  $\theta$  and  $\theta_1$ . Right: Cross section through the xylem of *Aristolochia macrophylla* showing an assemblage of conduits (upper right) and the ornamented inner wall of one conduit (lower right)(Photos:Tatiana Miranda , Institute for Geosciences, University of Tübingen).

only expand. If the bubble contains  $n_{a,1} < n_{crit}$  air molecules its future depends also on its initial radius  $R$ : in the case  $R > R_{inst}$  it expands, in the case  $0 < R < R_{inst}$  the bubble expands or contracts towards  $R_{stab}$ .

Figure 3 illustrates the interdependence of initial radius and air content in a stability diagram in the  $(n_a, R)$ -plane:

- (i) The ability of an air-water vapour bubble to seed embolism increases with its air content (with the water pressure  $p_s$  being constant): A bubble of initial radius  $R_2$  containing  $n_1$  air molecules contracts towards the stable radius  $R_{stab}$ , a bubble of the same initial radius containing  $n_4$  air molecules (with  $n_4 > n_1$ ), however, bursts.
- (ii) If  $p_s$  decreases (i.e. becomes more negative) the stability region which represents all bubbles (of radius  $R$  and containing  $n_a$  air molecules) drifting to stable equilibrium shrinks. Hence, bubbles which were within the stability region at a given water pressure may become unstable because the borderline between stability and instability has wandered across their (fixed) location in the  $(n_a, R)$ -plane, due to the drop in  $p_s$ .
- (iii) Immediate collapse of an air-water vapour bubble is impossible. This is because — different to the water vapour molecules in the bubble — the air molecules cannot condensate to the liquid state (at least not under temperatures and pressures compatible with living plants). Hence, a stable air-water vapour bubble can only disappear by dissolution via diffusion of the air content into the surrounding water. Whether or not this will happen depends on the concentration  $C_{air}$  of air molecules already dissolved in the surrounding water.

#### Bubble attached to a flat portion of the vessel wall

In order to describe an air/water vapour bubble attached to the vessel wall we have to extend expression (1) to

$$W = \left[ 4\pi\gamma R^2 - \frac{4\pi}{3} (p_w - p_s) R^3 \right] \xi(\theta) + 3RT n_a \log\left(\frac{R_{max}}{R}\right) \quad (4)$$

where  $\theta$  denotes the contact angle at the line where solid, liquid and gaseous phase meet, and  $\xi(\theta) := (2 + 3 \cos \theta - \cos^3 \theta) / 4$ . Due to  $\xi(0) = 1$ , expression (4) reduces in the limit  $\theta = 0$  to expression (1).

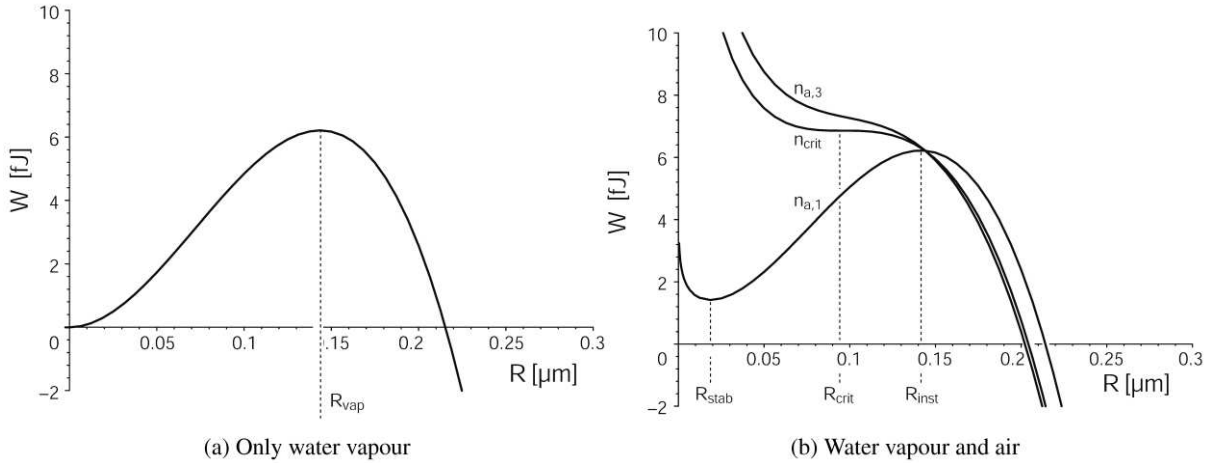


Fig. 2 Energy of bubble formation  $W$  plotted against bubble radius  $R$ . Water pressure in the conduit amounts to  $p_s = -1 \text{ MPa}$ . Equilibrium between expanding and contracting forces is realised only at bubble radii  $R$  representing extrema of  $W(R)$ . Maxima indicate unstable, minima stable equilibrium. (a) Bubble filled only with water vapour. (b) Bubble filled with water vapour and air. Curves are plotted for the following numbers of air molecules:  $n_{a,1} = 7.5 \times 10^{-20} \text{ mol}$ ,  $n_{\text{crit}} = 7.5 \times 10^{-19} \text{ mol}$  and  $n_{a,3} = 9 \times 10^{-19} \text{ mol}$ .

Thus, in the case of complete wettability a freely floating bubble and one attached to the vessel wall behave in the same way.

Exploiting  $\partial W / \partial R = 0$ , we find that the (mechanical) equilibrium radii of an attached bubble have exactly the same form as those (see (3)) of its freely floating counterpart, provided we include into the critical (maximum) number  $n_{\text{crit}}$  the factor  $\zeta(\theta)$  (i.e.  $n_{\text{crit}} \rightarrow n_{\text{crit}} \zeta(\theta)$ ). The other features of the equilibrium radii (stability, the limits for  $n_a \rightarrow 0$  and  $n_a \rightarrow n_{\text{crit}}$  and the behaviour for  $n_a > n_{\text{crit}}$ ) are as for a freely floating bubble.

Figure 3(c) illustrates that because of  $0 \leq \zeta(\theta) \leq 1$  an attached bubble can not accommodate as many particles as a freely floating bubble (apart from the case  $\theta = 0^\circ$  when  $\zeta = 1$ ). This feature turns out to be potentially hazardous: Mechanically stable floating bubbles may realise during attachment that the number of air particles they house and the vessel wall's contact angle are incompatible. Thus, they can not settle to a new stable mechanical equilibrium and burst. The upper bubble on the curve related to  $\theta = 0^\circ$  in part (c) of Figure 3 will suffer this fate if it tries to attach to a wall with contact angle  $\theta = 90^\circ$ . The lower bubble on the same curve is more lucky: it houses less particles than  $n_{\text{crit}}(\theta = 90^\circ)$  allows and finds a new stable mechanical equilibrium. From the family of curves depicted in Figure 3(c) it is obvious that the radius of the attached bubble segment is always greater than the radius of the freely floating bubble, i.e.  $R_{\text{stab}}(n_a, \theta) > R_{\text{stab}}(n_a, 0)$  for  $\theta > 0$ . (Recall that we assume that the floating bubble attaches to an at least approximately flat vessel wall. Hence, attached bubbles are shaped like segments of a sphere with radius  $R$ .)

### Conditions for spontaneous attachment

In order to explore whether (and if so, under which conditions) a mechanically stable floating bubble attaches spontaneously to an (approximately flat) vessel wall we have to compare the energies associated with the formation of a floating and of an attached bubble. If the free energy of the final state is smaller than the free energy of the initial state, the process proceeds spontaneously. The energies related to the two bubble states have already been calculated in (1) and (4).

Since the formation energy of a floating and of an attached bubble coincide in the case  $\theta = 0$  we may first calculate what happens to  $W_{\text{stab}}(\theta)$  if  $\theta$  is infinitesimally increased and integrate afterwards up to

$$dW_{\text{stab}} = \left[ \frac{\partial W_{\text{stab}}}{\partial \theta} + \frac{\partial W_{\text{stab}}}{\partial R} \frac{dR}{d\theta} + \frac{\partial W_{\text{stab}}}{\partial \xi} \frac{d\xi}{d\theta} \right] d\theta \quad (5)$$

the desired value of  $\theta$ . Because we compare mechanically stable bubbles (with  $n_a$  and  $p_s$  fixed) the rules of partial differentiation yield

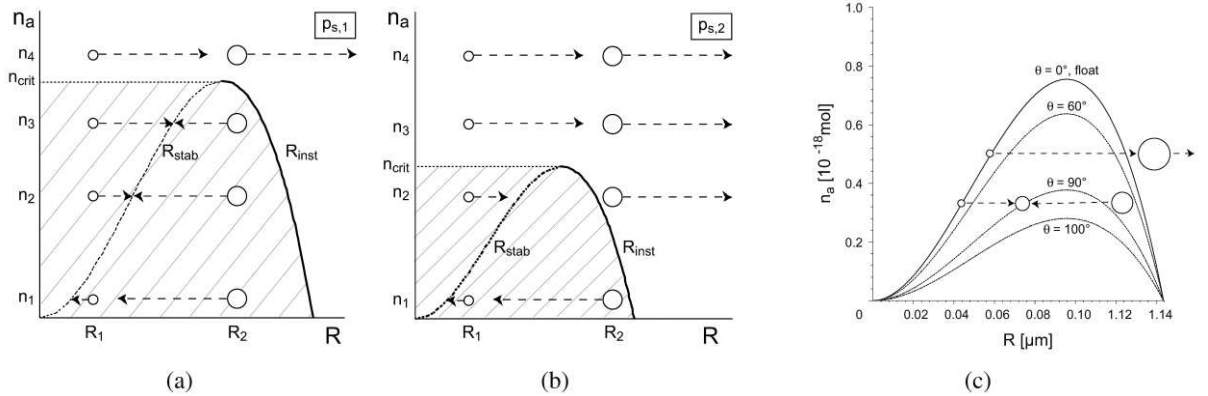


Fig. 3 Regions of stability and instability of bubbles of radius  $R$ , filled with water vapour and  $n_a$  air molecules. (a): Stability diagram for a given water pressure  $p_{s,1}$ . (b): Stability diagram for a water pressure  $p_{s,2}$  with  $p_{s,2} < p_{s,1}$  (i.e.  $p_{s,2}$  is more negative than  $p_{s,1}$ ). Only bubbles lying on the curves  $R_{stab}$  (broken line) and  $R_{inst}$  (solid line) are in stable resp. unstable equilibrium. Bubbles represented by other  $(n_a, R)$ -values either contract or expand (indicated by broken arrows). Bubbles belonging to the hatched region (left and below the solid curve  $R_{inst}$ ) contract or expand towards the stable radius  $R_{stab}$  lying on the dotted curve. Bubbles characterised by  $(n_a, R)$ -values outside the stability region expand. If  $p_s$  decreases, the region of stability shrinks. Hence, bubbles which are in equilibrium under water pressure  $p_{s,1}$  (like those inhabited by  $n_3$  air molecules in part (a) of the figure) fall outside of the equilibrium region if  $p_s$  drops to  $p_{s,2} < p_{s,1}$  (see part (b) of the figure). (c): Bubbles attached to a flat vessel wall with contact angles  $\theta = 0^\circ, 60^\circ, 90^\circ, 100^\circ$ .  $R_{stab}$  of a completely wetting vessel wall ( $\theta = 0^\circ$ ) is identical to  $R_{stab}$  of a floating bubble.

The first two terms of the right hand side of this expression vanish because  $W$  depends not explicitly on  $\theta$  (hence,  $\partial W / \partial \theta = 0$ ), and mechanical equilibrium requires  $\partial W / \partial R = 0$ . Thus,

$$dW_{stab} = \left[ \frac{\partial W_{stab}}{\partial \xi} \frac{d\xi}{d\theta} \right] d\theta = \left[ 4\pi\gamma R_{stab}^2(\theta) - \frac{4\pi}{3} (p_w - p_s) R_{stab}^3(\theta) \right] \left( -\frac{3}{4} \sin^3 \theta \right) d\theta < 0 \quad (6)$$

Manipulations based on the Young-Laplace-Equation imply that the expression in brackets is positive and  $\sin^3 \theta$  is positive within the interval  $0 < \theta < 180^\circ$ . Therefore, an increase of  $\theta$  by the amount  $d\theta > 0$ , is related to a decrease of the formation energy  $W_{stab}(\theta)$  by  $dW_{stab}(\theta) < 0$ . Thus, the formation energy of a floating bubble (characterised by  $\theta = 0$ ) which attaches to a vessel wall (characterised by  $\theta > 0$ ) changes by the necessarily negative amount

$$\Delta W_{stab} = \int_0^\theta dW_{stab} < 0 \quad (7)$$

The last relation allows the following conclusions:

- (i) The attachment process of a floating bubble proceeds spontaneously and without energy input.
- (ii) Detachment needs energy input, spontaneous bubble detachment is therefore improbable.
- (iii) The conclusion  $\Delta W_{stab}(\theta) < 0$  applies for any  $\theta > 0$ .
- (iv) If the contact angle  $\theta$  varies across the vessel wall, the bubble will show a tendency to move (and enlarge) its contact circle towards regions of higher  $\theta$ . (The contact circle is the line where the air/water-interface touches the flat, solid vessel wall.)

#### Diffusional equilibrium and dissolution of bubbles

The following reasoning applies both to freely floating bubbles and to bubbles which are attached to the conduit wall. The “long term” behaviour of an mechanically equilibrated bubble rests upon two physical effects ([2]):

- (i) At the bubble’s air/water-interface, air particles dissolve into or escape from the water. Thus, the (partial) pressure  $p_a$  of the air inside the bubble and the concentration  $C_R$  of the dissolved air particles in the liquid in the near vicinity of the bubble are proportional to

each other as stated by Henry's Law  $C_R = k_H p_a$  where the constant  $k_H$  depends on the gas and liquid species involved.

- (ii) If the concentration  $C_R$  of dissolved gas particles close to the bubble deviates from the value  $C_{air}$  farther away in the liquid, diffusional currents, directed from areas of higher to areas of lower concentration arise

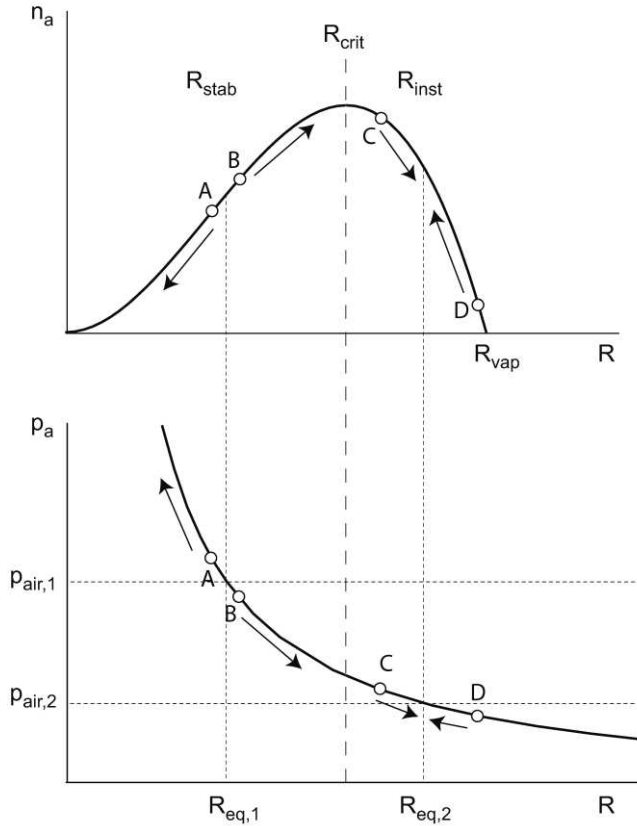


Fig. 4 Diagram explaining the behaviour of gas bubbles which are in equilibrium with respect to mechanical forces but not with respect to exchange of air particles between bubble and surrounding water (for explanation see text).

As the combined result of both processes we expect that air particles are transported either out of and away from the gas bubble or into the opposite direction until an diffusional equilibrium situation between the concentrations  $C_R$  and  $C_{air}$  is attained. To facilitate further notation we define in analogy to Henry's Law a (fictitious) pressure  $p_{air} := C_{air}/k_H$  which allows to state diffusional equilibrium as  $p_{air} = p_a$ . The Young-Laplace-Equation

$$p = p_s + \frac{2\gamma}{R} \quad (8)$$

connects the gas pressure  $p$  within an mechanically(!) equilibrated bubble with the surface tension  $\gamma$  at the liquid/gas-interface, the bubble radius  $R$  and the pressure  $p_s$  of the liquid surrounding the bubble. Splitting the gas pressure into the partial pressures of water vapour and air according to  $p = p_w + p_a$  we find from (8) for bubbles in mechanical equilibrium  $p_a = p - p_w = p_s - p_w + 2\gamma/R$ . Observing that this relation establishes a one-to-one correspondence between  $p_a$  and  $R$  we use  $p_{air} = p_a$  to define an equilibrium radius

$$R_{eq} := \frac{2\gamma}{p_{air} + p_w - p_s} \quad (9)$$

Notice, that  $R_{eq}$  defines an equilibrium with respect to the exchange of air particles between the bubble and the surrounding water whereas the radii  $R_{stab}$  and  $R_{inst}$  (which were defined in (3)) represent equilibria with respect to the mechanical forces which try to expand or contract the bubble.

We can now understand the behaviour of gas bubbles which are in equilibrium with respect to mechanical forces but not with respect to exchange of air particles between bubble and surrounding

water (consult Figure 4): Exchange equilibrium exists if  $p_a = p_{air}$  is realised. (In the lower part of Figure 4, this case is indicated by the intersections between the broken, horizontal lines and the  $p_a(R)$ -curve at  $(R_{eq,1}, p_{air,1})$  and  $(R_{eq,2}, p_{air,2})$ .) Depending on whether  $R_{eq}$  lies in the interval  $0 < R_{stab} < R_{crit}$  or  $R_{crit} < R_{inst} < R_{vap}$ , the bubble goes through qualitatively different developments:

- (i) The bubble starts at position **A** or **B**, close to  $(R_{eq,1}, p_{air,1})$  in the interval  $0 < R_{stab} < R_{crit}$ :
  - a) At position **A** the inequality  $p_a > p_{air}$  is valid, causing air particles to leave the bubble. This loss entails a contraction of the bubble, as can be seen from the  $n_a(R)$  diagram in the upper part of the figure. This contraction raises the bubble's partial air pressure  $p_a$  which accelerates the particle loss and so on, until the bubble has dissolved.
  - b) At position **B** we have  $p_a < p_{air}$ . Now air particles from the surrounding water enter the bubble which reacts by an expansion, according to the  $n_a(R)$ -diagram. The bubble's partial air pressure  $p_a$  decreases whereupon still more air particles enter the bubble and so on. This process continues either until  $n_a$  exceeds  $n_{crit}$ , or until all air particles within the xylem water have assembled in the bubble.
- (ii) The bubble starts at positions **C** or **D**, close to  $(R_{eq,2}, p_{air,2})$  in the interval  $R_{crit} < R_{inst} < R_{vap}$ . Applying the same reasoning as in case (i), the bubble is found to move towards the equilibrium position  $(R_{eq,2}, p_{air,2})$ .

Obviously, equilibria with respect to the exchange of air particles related to a bubble radius  $R_{eq}$  lying within the interval  $0 < R_{eq} < R_{crit}$  are unstable, similar equilibria within  $R_{crit} < R_{eq} < R_{vap}$  are, however, stable.

Hence, stable mechanical and exchange equilibria preclude each other: For  $0 < R < R_{crit}$  the mechanical equilibrium is stable and the exchange equilibrium is unstable, for  $R_{crit} < R < R_{vap}$  it is the other way round. The different time scales on which the processes connected with the two equilibria operate impose a clear hierarchy on their relevance: Since the exchange of air particles is a very slow process, compared to the action of the expanding and contracting forces, a mechanically unstable bubble with  $R_{inst}(n_a)$  has negligible chances to settle down to a stable exchange equilibrium. It is much more probable that it either bursts or shrinks to the corresponding stable radius  $R_{stab}(n_a)$  where an unstable exchange equilibrium awaits it. Depending on the relation between  $p_a$  and  $p_{air}$  this state will finally develop into a bubble burst due to congestion (i.e.  $n_a > n_{crit}$ ) or to complete bubble dissolution.

A condition which guarantees that dissolution occurs can be read off from Figure 4: If the inequality  $R_{eq} > R_{crit}$  holds all bubbles in stable mechanical equilibrium dissolve. This condition can be reformulated as a relation between the concentration  $C_{air}$  of gas particles dissolved in the surrounding liquid, the (negative) pressure  $p_s$  of this liquid, and the water vapour saturation pressure  $p_w$ , namely  $C_{air} = k_H p_{air} < k_H (p_w - p_s)/2$ . Solving this relation for  $p_s$  we find  $p_s < -2 p_{air} + p_w$ . Since groundwater in the soil is in contact with air of atmospheric pressure it is reasonable to assume  $p_{air} \approx p_{atmosphere} \approx 10^5$  Pa. Neglecting the term  $p_w$  on the right hand side (at 25 °C we find  $p_w \approx 3167$  Pa  $\ll$  100 000 Pa  $\approx p_{air}$ ) this equation reduces to

$$p_s \lesssim -2 \times 10^5 \text{ Pa} \quad (10)$$

Hence, if condition (10) is fulfilled embryonic bubbles appearing in the stability regions depicted in Figure 3 dissolve after a while in the surrounding water.

As stated above, the results related to bubble dissolution apply to floating and to attached bubbles. Fig. 3 shows that the bubble radius  $R$  increases if attachment occurs and results in mechanical stability. This increase in bubble radius entails a second potential hazard (cf. Figure 4): A floating bubble in situation **A** (with  $p_{air} = p_{air,1}$ ) is on the route to dissolution because its radius is slightly smaller than the equilibrium radius  $R_{eq,1}$ . If its particle content and the wall's contact angle allow a new stable mechanical equilibrium after attachment it may well happen, that the bubble finds itself, due to the inevitable radius increase, after attachment at position **B** from where its radius and particle content increases until it bursts.

## Conclusion

**Spontaneous cavitation (“homogenous nucleation”):** The spontaneous emergence of a water vapour filled bubble is extremely unlikely for the water tensions found in plants of  $p_s \geq -1$  MPa. Should

homogenous nucleation occur nonetheless, the fate of the emerging bubble depends on its initial radius  $R$ : For  $R < R_{\text{vap}} = 2\gamma/(p_w - p_s)$  the bubble disappears immediately, for  $R > R_{\text{vap}}$  it bursts, causing cavitation of the befallen vessel segment.

**Air seeding (“heterogenous nucleation”):** Decisive for the fate of a bubble containing air and water vapour are two different processes each of which may or may not lead to an equilibrium. They occur on different time scales:

- (i) **Mechanical stability/instability (quick adjustment):** If initial bubble radius  $R$  and initial number of air particles  $n_a$  satisfy the inequalities  $n_a < n_{\text{crit}}$  and  $R < R_{\text{inst}}(n_a)$  simultaneously the bubble approaches mechanical stability at the radius  $R = R_{\text{stab}}(n_a)$ . Otherwise, the bubble bursts.
- (ii) **Diffusional stability/instability (slow adjustment):** A bubble which has established mechanical stability (i.e.  $R = R_{\text{stab}}(n_a)$ ) either loses air molecules to the surrounding xylem water (and dissolves eventually completely) or it accumulates air from the xylem water. This accumulation lasts until the bubble bursts (when  $n_a = n_{\text{crit}}$  is achieved) or until no more air molecules are available in the xylem water. If the xylem water is in contact with the atmosphere, mechanically stable bubbles dissolve completely, provided the xylem water pressure  $p_s$  satisfies  $p_s \leq -2 \times 10^5$  Pa.

**Bubble attachment to vessel wall:** Basically, an attached bubble behaves like a freely floating bubble. The major difference is that its maximum particle capacity may fall short of or exceed  $n_{\text{crit}}$  of a freely floating bubble. Whether this happens or not depends on the contact angle and one (or more parameters) describing the vessel wall morphology.

This gives rise to two effects which make themselves felt when a floating bubble attaches to a flat wall with contact angle  $\theta$ :

- (i) A bubble that is mechanically stable while it is floating, bursts during wall attachment if  $n_a > n_{\text{crit}}(\theta)$ .
- (ii) Depending on the value of the diffusional equilibrium bubble radius  $R_{\text{eq}}$ , a floating bubble which is mechanically stable, loses particles, and fulfills point (i), may remain stable upon attachment but will start to accumulate particles (instead of losing them). This accumulation lasts until the bubble bursts (when  $n_a = n_{\text{crit}}(\theta)$  is achieved) or until no more air molecules are available in the xylem water.

Comparison of the reversible free energies associated with the formation of a floating and an attached bubble reveals:

- (i) Bubble attachment to a flat vessel wall happens spontaneously and without energy input for any  $\theta > 0$ .
- (ii) If the contact angle  $\theta$  varies across a flat vessel wall, the bubble will show a tendency to move (and enlarge) its contact circle towards regions of higher  $\theta$ .

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