A careful physical analysis of gas bubble dynamics in xylem

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Abstract

Many studies have confirmed that cavitation in xylem is caused by air bubbles. Recently Shen et al. (Tree Physiol. 22 (2002) R655), analysed the expansion of a pre-existent bubble in xylem and one formed by air seeding. The present paper makes a further analysis of bubble expansion by the equilibrium criterion of the Helmholtz function. It has been proved that when xylem pressure $P_0$ decreases to a special value $P_0/l$ from a value higher than, or equal to, or lower than $P_0$ (where $P_0$ is atmospheric pressure), an air bubble in xylem can grow up steadily, corresponding to minimums of the Helmholtz function $F(r)$: As soon as $P_0/l$ is lower than $P_0/l$, since $F(r)$ will be a decreasing function when $P_0/l > P_0/l$, resulting in non-equilibrium of the bubble, it will break inducing a cavitation event.

The analysis is consistent with the results of mechanism. Given $P_0/X > P_0/l$, if an air bubble could enter a conduit, it would be in a stable equilibrium. When $P_0/l < P_0/l$, an air bubble entering a conduit will be in an unstable equilibrium. As the water further vaporizes, it will break at once. This is the case to which the former published formula $P_0/l = 2\sigma/r_0$ is applicable.

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1. Introduction

Since the discovery that plants produce acoustic emissions a body of literature has developed interpreting this intriguing feature of plant response to the environment (Jackson and Grace, 1996). A cavitation event causes a rapid relaxation of a water tension that produces an acoustic emission of energy (Tyree and Sperry, 1989).

Scientists have found substantial evidence, which shows that the vulnerability of xylem to cavitation is an important factor in the adaptation of plants to the environment. The cavitation events of xylem (drought-induced embolism) has been detected in stems, leaves and roots and has appeared to limit effectively the possible distribution areas of plant species (Tyree et al., 1999). Many studies have confirmed that cavitation in xylem conduits system is induced by air seeding. Air can enter conduits through pores of pit membranes and finally form bubbles (Tyree, 1997). After Tyree reviewed four mechanisms for the nucleation of cavitation in plants and introduced the vulnerability curve from his experiment, he proposed that “This is the strongest evidence presented to date that the air-seeding mechanism explains how cavitation occur, though there is other circumstantial evidence” (1997). Zimmermann (1983) studied the process of air seed entering into the water of xylem. He indicated that once a single small bubble formed by air seeding enters into vessel, it immediately expands until the tension forces on the wall is released. Using experimental methods, Salleo et al. (1992) and Tyree (1997) demonstrated the verification of air seeding hypothesis. Otherwise, cavitation events are caused by tiny air bubbles adhering to the crack of vessel wall as well (Pickard, 1981; Milburn, 1993).

With regard to temporary stability of air bubbles in xylem conduits under negative absolute xylem pressure $P_0$, recently Shen et al. (2002) suggested that there are two equilibrium states for a very small air bubble in xylem: one is temporarily stable with a bubble radius $r_1$; the other is unstable with a bubble radius $r_2$ (where $r_1 < r_2$). In each equilibrium state, the bubble collapse pressure $2\sigma/r_0$, where $\sigma$ is the surface tension of water, is balanced by the pressure difference between the gas...
pressure \( P \) and the absolute xylem pressure \( P_l \) across its surface. In the case of a bubble with radius \( r_1 \) from a crack in a conduit wall, the expansion of the bubble will occur steadily as xylem pressure decreases. The bubble will burst only if the xylem pressure \( P_l (= P_l - P_o) \) drops below a threshold value \( P_l^* \). On the condition that the bubble is produced from previous air seeding through a pore of a pit membrane with radius \( r_p \) a formula \( P_l^* = (-8\sigma/9)\sqrt{3\sigma / 2P_o r_p^3} - P_o \) was proposed, giving the xylem threshold pressure \( P_l^* \) for bubble breaking. Otherwise, when an air seed enters xylem conduit, because of its radius \( r = r_p = r_2 \) its equilibrium will be unstable. As water vaporizes the bubble will burst, inducing a cavitation event. This is in accordance with the air-seeding hypothesis. This paper makes a further analysis of the expansion of a bubble by using the equilibrium criterion of the Helmholtz function with regard to the second law of thermodynamics. Based on the analysis, some new conclusions are reached.

2. Analysis of the equilibrium criterion of the Helmholtz function

Suppose an air bubble just sucking out of a crack of conduit wall is in a temporary equilibrium state. The equation \( P = nRT / V_g \) holds for the air, where \( V_g \) is bubble volume, \( R \) is gas constant, \( T \) is absolute temperature and \( n \) is the molar number of the bubble gas. Generally speaking, an analysis of the second law of thermodynamics is important in the study of equilibrium of a system. For an isothermal and isovolumetric one in equilibrium its Helmholtz function has to take an extremum: a minimum corresponding to a stable equilibrium and a maximum corresponding to an unstable one. We have dealt with the expansion of a bubble as an isothermal process (Shen et al., 2002). In the process of its steady expanding, the radii of the bubble are in the order of magnitude \( 10^{-7} \) m. It is much less than the dimension of the surrounding lump of water in the conduit, leading the migration of water from the conduit to the surrounding cells in the process to be neglected and the process can also be regarded as isovolumetric. Thus, the increment of the gas volume \( dV_g \) is equal to the decrement of the water volume \( dV_l \), or \( dV_g = -dV_l \). The system consists of three parts: an air bubble, the surrounding water and the interface between the gas and the water. Suppose a fluctuation takes place in the system at constant total volume and temperature. The changes of the Helmholtz function for the three parts are: \( dF_g = -P dV_g \) for the air, \( dF_l = -P_l dV_l = P_l dV_g \) for the water, and \( dF_s = \sigma dA \) for the increase of the gas/water interface \( dA \). Thus, the total change of the Helmholtz function \( dF \) of the three parts is obtained by

\[
\begin{align*}
\frac{dF}{dV_g} &= -P dV_g + P_l dV_g + \sigma \frac{dA}{dV_g} \\
\end{align*}
\]

Differentiating volume \( V_g = (4\pi r^3)/3 \) and surface area \( A = 4\pi r^2 \) of a spherical bubble results in \( dV_g = 4\pi r^2 \, dr \) and \( dA = 8\pi r \, dr \). Substituting the former and \( P = nRT / V_g \) into Expression (1) gives

\[
\begin{align*}
\frac{dF}{dV_g} &= -(3nRT/r) \, dr + P_l 4\pi r^2 \, dr + 8\pi r \, dr \\
\end{align*}
\]

the derivative of which, with respect to radius \( r \), is

\[
F'(r) = \frac{dF}{dr} = 4\pi P_l r^2 + 8\pi r - 3nRT / r. \tag{2}
\]

And the second derivative of the function is obtained by

\[
F''(r) = 8\pi P_l r + 8\pi r + 3nRT / r^2. \tag{3}
\]

Integrating Expression (2) gives

\[
F(r) = (4\pi P_l r^3)/3 + 4\pi r^2 - 3nRT ln r + C. \tag{4}
\]

If we ignore the change in \( n \), according to Zimmermann’s (1983) study of the process of an air seeding, we have \( nRT = P_l V = P_o (4/3)\pi r_p^3 \). Substituting it with \( r_p = 0.146 \mu m \) into Expression (4) we drew the graphs of \( F(r) - r \) in Fig. 1.

Once \( F(r) \) reaches an extreme value, or \( F'(r) = 0 \), a bubble of radius \( r \) will attain its equilibrium. Thus, from Expression (2) we have

\[
4\pi P_l r^3 + 8\pi r^2 - 3nRT = 0 \tag{5}
\]

It is obvious that the real values satisfying this equation are the radii of the bubble in equilibrium.

Letting the left side of Eq. (5) be a function of \( r \) gives

\[
f(r) = 4\pi P_l r^3 + 8\pi r^2 - 3nRT. \tag{6a}
\]

Its derivative is

\[
f'(r) = 12\pi P_l r^2 + 16\pi r. \tag{6b}
\]

Fig. 1. Graphs of Helmholtz function \( F(r) \). All lines are drawn with \( r_p = 0.146 \mu m \).
and the second derivative is
\[ f''(r) = 24\pi P_3 r + 16\pi \sigma. \] (6c)

If \( f(r) = 0 \), Expression (6a) returns to Eq. (5). Therefore, the real roots of Eq. (5) are the intersections of the curve \( f(r) \) with \( r \)-axis.

Now we shall discuss the graphs of \( f(r) \).

First, if \( P_l \geq 0, (P_l^* \geq -P_o) \), then \( f'(r) > 0 \) for all \( r > 0 \) from Eq. (6b). Hence, \( f(r) \) is an increasing function over \((0, \infty)\) for \( P_l \geq 0 \). Since \( f(0) = -3nRT < 0 \), \( f(r) \) intersects \( r \)-axis only at \( r_o \) or \( r_m \), corresponding to \( P_l > 0 \) and \( P_l = 0 \), respectively (Fig. 2a). This means that \( f(r) \) has only one extremum, which is a minimum since \( f''(r) > 0 \) for all \( r > 0 \). A bubble of radius \( r_o \) or \( r_m \) is certainly in a stable equilibrium as has been mentioned in the mechanical analysis (Shen et al., 2002).

Second, if \( P_l < 0 \), from Expression (6b) the only \( r \) satisfying \( f'(r) = 0 \) for \( r > 0 \) is
\[ r_m = -4\sigma/3P_l. \] (7)

Substituting \( r_m = -4\sigma/3P_l \) into Expression (6c),
\[ f''(r_m) = -16\sigma\sigma < 0, \] indicating that curve \( f(r) \) is concave downward and reaches its maximum at \( r_m \), which is
\[ f(r_m) = (128\pi^3 - 81P_l^2nRT)/27P_l^2. \] (8)

Because \( f(0) < 0 \) and \( f(r) \) is concave down, the number of intersections of curve \( f(r) \) with \( r \)-axis depends only on the sign of \( f(r_m) \).

When \( f(r_m) > 0 \), i.e. \( 128\pi^3 - 81P_l^2nRT > 0 \) or \((-8\sigma/9)\sqrt{2\pi\sigma/nRT} < P_l < 0 \) from Expression (8), \( f(r) \) intersects \( r \)-axis at \( r_1 \) or \( r_2 \) \( (r_2 < r_1) \), at which \( F(r) \) takes extremum \( F(r_1) \) or \( F(r_2) \). Thus, a bubble of radius \( r_1 \) or \( r_2 \) is in equilibrium. Below is the reason why a bubble of radius \( r_1 \) is stable and that of radius \( r_2 \) unstable.

Expression (3) can be rewritten as
\[ f''(r) = [(4\pi P_3 r^3 + 8\pi \sigma^2 - 3nRT) \rightleftharpoons 4\pi P_3 r^3 + 6nRT]/r^2. \] (9)

Since \( F(r_2) \) is extremum, the first term of the numerator \( (4\pi P_3 r_2^3 + 8\pi \sigma^2 - 3nRT) \) is \( 0 \) from Eq. (5) so that \( f''(r_2) = (4\pi P_3 r_2^3 + 6nRT)/r_2^2. \) Moreover, since \( 4\pi P_1 < 0, 6nRT > 0 \) and \( r_2 > r_m = -4\sigma/3P_l > 0 \), the numerator \( 4\pi P_3 r_2^3 + 6nRT \) of \( f''(r_2) \) is
\[ 4\pi P_3 r_2^3 + 6nRT < 4\pi P_1(-4\sigma/3P_l)^3 + 6nRT \]
\[ = 2(81P_l^2nRT - 128\pi^3)/27P_l^2. \] (10)

As \( f(r_m) > 0 \), i.e. \( 81P_l^2nRT - 128\pi^3 < 0 \) (Expression (8)), \( 4\pi P_3 r_2^3 + 6nRT \) in the above expression should be less than zero so that \( f''(r_2) < 0 \), meaning that \( F(r_2) \) is a maximum and a bubble of radius \( r_2 \) is in an unstable equilibrium.

\( F(r) \) is a continuous function with only two extreme values \( F(r_1) \) and \( F(r_2) \). Since \( F(r_2) \) is a maximum, it is obvious that the only choice of \( F(r_1) \) is a minimum value, indicating that a bubble of radius \( r_1 \) is steady temporarily.

For \( f(r_m) = 0 \), meaning \( P_l = P_l^* = (-8\sigma/9)\sqrt{2\pi\sigma/nRT} \) (and \( P_l^* = P_l^* = (-8\sigma/9)\sqrt{3\sigma/2P_l^2\sigma^2 - P_o} \) for a bubble resulting from previous air seeding), the tangent line of \( f(r) \) is \( r \)-axis and \( f(r) < 0 \), indicating that \( F(r) \) is a decreasing function and a bubble of radius \( r \) cannot be in equilibrium, for all \( r > 0 \) except when \( r = r_m \). Thus, \( F(r) \) reaches its inflection point at \( r_m \). The expression of \( P_l^* \) is none other than the equation of xylem threshold pressures for bubble bursting we have got by the mechanical analysis, indicating that when \( f(r_m) = 0 \) the \( r_m \) is \( r_\sigma \) which has been mentioned in Shen’s paper (Shen et al., 2002).

If \( f(r_m) < 0 \), i.e. \( P_l < P_l^* \), then \( f(r) < 0 \) for all \( r > 0 \), also indicating that \( F(r) \) is decreasing, so that a bubble of radius \( r \) will be in non-equilibrium.

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Fig. 2. (a) Graphs of \( f(r) \). All lines are drawn with \( r_p = 0.146 \mu m \). Comparison of graphs of \( f(r) \) in the range of \( P_l^* = < -P_o \). Note: from the graph of \( f(r) \) with \( r_p = 0.350 \mu m < 0.487 \mu m \), corresponding to \( P_l^* = -0.417 MPa \) for an air seed entering, we can see \( r_2 = r_p = 0.350 \mu m \). Should it undergo a daily cycle, its threshold pressure of breaking would be at \( P_l^* = -0.428 MPa \). If \( r_p = 0.600 \mu m > 0.487 \mu m \), corresponding to \( P_l^* = -0.243 MPa, r_1 = r_p = 0.600 \mu m \). The separating radius for an air seed taking \( r_1 \) or \( r_2 \) as its radius is \( r_p = r_\sigma = 0.487 \mu m \) with \( P_l^* = -0.300 \mu m \).
3. Development of a pre-existent air bubble in xylem

The development of a pre-existent air bubble in xylem can be deduced from the above analyses. When \( P_f^* - P_o \) is the Helmholtz function of the system, \( F(r) \) takes a minimum \( F(r_0') \) or \( F(r_o) \), corresponding to a stable equilibrium of the bubble of radius \( r'_o \) or \( r_o \). As \( P_f^* \) decreases to be in the range of \( P_f^* < P_f^* < -P_o \), \( F(r) \) has two extrema at \( r = r_1 \) and \( r_2 \) with a minimum \( F(r_1) \), corresponding to a stable equilibrium of the bubble of radius \( r_1 \), and a maximum \( F(r_2) \), corresponding to an unstable equilibrium of the bubble of radius \( r_2 \). During this process, \( r_1 \) and \( r_2 \), or \( F(r_1) \) and \( F(r_2) \), are getting closer and closer to each other gradually. At last the two extrema \( F(r_1) \) and \( F(r_2) \) merge to a point at \( r = r_s \), where \( P_f^* = P_f^* \) (the development of \( r_1 \) and \( r_2 \) is not shown in Fig. 1). This means that an air bubble pre-existing in xylem can grow up steadily from the radius of \( r'_o \), \( r_0 \), or \( r_1 \) to reach the value \( r_o \). Thereafter, as \( P_f^* \) decreases further, \( F(r) \) will be a decreasing function for all \( r > 0 \), resulting in non-equilibrium of the bubble. For this reason \( P_f^* \) represents the threshold xylem pressure for bubble breaking. All the analyses of the equilibrium criterion of the Helmholtz function are consistent with the results of mechanism (Shen et al., 2002).

4. Values that a bubble by air seeding would take as its radius

It is known that air seeding is one of the causes of cavitation and the radius of an air seed is of \( r = r_p = -2\sigma/P_o \) when it enters a conduit. We have pointed out that the air bubble may be in an unstable equilibrium, for it takes \( r = r_p = r_0 \) as its radius (Shen et al., 2002). Then, there is no denying that it is possible for an air seed to take \( r'_o \), \( r_o \), or \( r_0 \) as its radius in a stable equilibrium temporarily. First, if \( P_f^* > P_o \) or \( P_f^* > 0 \), \( r_p \) is negative from \( r_p = -2\sigma/P_o \) so that the sap would leak out from xylem.

Second, if \( 0 \leq P_f \leq P_o \) or \( -P_o \leq P_f^* \leq 0 \), an air seed could be let to enter a conduit through a pore of pit membrane in the range of radius 1.46 mm \( \leq r_p < \infty \) with \( P_o = 0.10 \text{ MPa} \) and \( \sigma = 0.073 \text{ J/m}^2 \), also from \( r_p = -2\sigma/P_o \). The radius of the bubble would be of \( r_o \) or \( r'\), meaning the bubble would be in a stable equilibrium temporarily when \( 0 \leq P_f \leq P_o \) \( F(r) \) has only one minimum. Based on \( P_f^* = -8\sigma/3\sqrt{3\sigma/2P_o}d^3 \), \( P_o \) its bursting pressure would be \(-0.14 \) to \(-0.10 \text{ MPa} \). Therefore, the uppermost theoretical value of threshold xylem pressure for cavitation event by air seeding would be at \( P_f^* = -P_o = -0.10 \text{ MPa} \).

Third, when \( P_f \leq 0 \) or \( P_f^* \leq -P_o \), the ratio between \( \frac{r_m}{r_p} = -4\sigma/3P_o \) and \( \frac{r_p}{P_f} = -2\sigma/P_f^* \) is

\[
\frac{r_m}{r_p} = 4\frac{P_f}{3(P_o + P_f^*)}.
\]

There are two situations from Eq. (11). One is \( r_m/r_p > 1 \), or \( 2P_f^*/3(P_o + P_f^*) > 1 \), i.e. \(-3P_o < P_f^* \leq 0 \). This means that the radius of an air seed \( r_p \) would be less than the abscissa \( r_m \) of maximum of \( f(r) \) so that \( r_p \) would be \( r_1 \) certainly. Combining \( r_p = -2\sigma/P_f^* \) with \(-3P_o < P_f^* \leq 0 \) gives \( 0.487 \mu \text{ m} \leq r_p \leq 1.46 \mu \text{ m} \), corresponding to bursting pressures in the range of \(-0.30 \) to \(-0.14 \text{ MPa} \), according to the expression of \( P_f^* \) as well.

On the other hand, when \( r_m/r_p < 1 \), or \( 2P_f^*/3(P_o + P_f^*) < 1 \), i.e. \( P_f^* < -3P_o \) the abscissa \( r_m \) of the maximum of \( f(r) \) is less than the radius of the air seed \( r_p \). For this reason, the bubble must take \( r_2 = r_p < 2\sigma/3P_o = 0.487 \mu \text{ m} \) as its radius, making its equilibrium unstable. As water further vaporizes, the air seed will break at once. Since the radius of a pore of pit membrane is generally less than 0.487 m, this is a very common situation for air seeding. The results are shown in Fig. 2b.

5. Conclusion

When an air bubble expands in xylem, the system, consisting of the bubble, can be regarded as an isothermal and isovolumetric. For such a system, its Helmholtz function \( F(r) \) vs. the bubble’s radii is \( F(r) = (4\pi P_r r^3)/3 + 4\pi\sigma r^2 - 3nRT \ln r + C \), with its derivative being \( F'(r) = 4\pi P_r r^2 + 8\pi\sigma r - 3nRT/r \). By the aid of expression \( f(r) = 4\pi P_r r^2 + 8\pi\sigma r - 3nRT \), the extrema of \( F(r) \) can be found as \( P_f^* \) decreases.

When \( P_f^* > P_o \), \( F(r) \) has only one minimum, \( F(r'_0) \) or \( F(r_o) \). In the range of \( P_f^* < P_f^* < -P_o \), \( F(r) \) has a minimum \( F(r_1) \) and a maximum \( F(r_2) \) \( (r_1 < r_2) \), corresponding to the bubble’s stable and unstable equilibrium, respectively. \( F(r) \) becomes a decreasing function except at its inflection point \( r = r_s \), when \( P_f^* = P_f^* \). Thereafter, \( F(r) \) will be decreasing for all \( r > 0 \) with \( P_f^* < P_f^* \).

The development of a bubble pre-existing in xylem can be deduced from the changes of \( F(r) \).

When xylem pressure \( P_f^* \) decreases to \( P_f^* \) from a value higher than, or equal to, or lower than \(-P_o \), an air bubble in xylem can grow up steadily, corresponding to minimums of \( F(r) \) with \( r \) getting larger and larger. As soon as \( P_f^* \) is lower than \( P_f^* \), since \( F(r) \) will be a decreasing function when \( P_f^* < P_f^* \), resulting in non-equilibrium of the bubble, it will break inducing a cavitation event.

For air seeding, if \( P_f^* \geq 0 \), the sap in xylem would leak out from xylem. When \(-P_o \leq P_f^* \leq 0 \), since \( F(r) \) has only one minimum, an air seed would be in a stable equilibrium. In this situation, based on the expression of \( P_f^* \) the uppermost theoretical threshold of xylem pressure for cavitation would be at \( P_f^* = -0.10 \text{ MPa} \) rather than the former result of \( P_f^* = 0 \). From \( P_f^* = -2\sigma/P_o \) when \( r_p \rightarrow \infty \). If \( -3P_o \leq P_f^* \leq 0 \), the radius of an air seed would be \( r_1 \), also corresponding to a stable
equilibrium. To sum up, no air bubbles could enter a conduit when $P_i^* \geq -3P_o$ without any other mechanical stresses like wind, for it needs $r_p$ to be larger than 0.487 μm. If $P_i^* < -3P_o$ an air seed must take $r_2$ as its radius, making its equilibrium unstable and inducing breaking event. This is a very common situation for air seeding. The former published formula $P_i^* = -2\sigma/r_p$ is applicable to this case.

In a word, the analyses have not only further confirmed the outcomes of mechanism, but also given the results of various situations about air seeding, which provides us with an insight into cavitation events.

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References