# On the mechanical stability of the air volume trapped within the diving bell of the water spider *Argyroneta aquatica* (Araneae; Cybaeidae); a thermodynamic analysis based on a model

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In this contribution it is shown that the effective surface property of silk threads used by the spider *Argyroneta aquatica* to produce a diving bell in which air is trapped in a mechanically stable state has to be hydrophilic. The arguments leading to this conclusion are based on a model. This approach is similar to the one followed by Crisp and Thrope who analysed the water-protecting property of insect hairs (1).

The water spider *Argyroneta aquatica* has several adaptations to its aquatic life. Its systematic status is still uncertain (2). In Germany, *A. aquatica* is an endangered species. The results reported here can contribute to conservation efforts for this species because the stability of the air trapped in the diving bell can be influenced by the absorption of surfactant molecules on the surface of the silk threads forming the diving bell. Such surfactants are most likely present in polluted water of the aquatic habitat of this spider.

In a recent publication DE BAKKER et al. reported on the structure of silk threads produced by the water spider *A. aquatica* (2). It uses silk threads to build its diving bell, which functions as an air reservoire. DE BAKKER et al. noticed "that a kind of film was drapped over and woven between the strands. It is not certain whether this film is produced by the spider (serving probably as a water repellent layer) or deposited by other aquatic organisms." It is the primary aim of this study here to charaterize the effective surface property of the silk using a theoretical approach on which future experiments can be based. Futhermore, the results of this study contribute to the knowledge of surface functions in biology, a subject that is currently attracting considerable interest in botany, zoology, and biophysics (see the recent review (3)).

The analysis of the mechanical stability of an air volume trapped within the diving bell of *A. aquatica* is based on the law of Laplace in the form of equation(1),(4). It is assumed that the meshes of the diving bell are circular with the same radius.

$$P_e^w(x) = \rho_w \cdot g \cdot x = \left[ P^w(x) - P^a(x) \right]_e = -\frac{2 \cdot \gamma_{a/w} \cdot \cos(\theta_e)}{r_m} \quad (1)$$

Whereby $P$ is the hydrostatic pressure, $\rho_w$ the density of water, $g$ the gravitational constant, $x$ a space coordinate (see Fig. 1), $r_m$ the radius of a circular mesh and $\theta_e$ the effective contact angle at the line of contact between air, water and silk. By definition the contact angle $\theta_e$ is measured across the liquid. The subscript $e$ refers to mechanical equilibrium state. The term "effective contact angle" takes into account the possibility that the silk threads carry an adsorbed layer that can give a surface a property different from that of pure silk. The parameter $\gamma_{a/w}$ is the air/water surface tension.

The surface tension can have positive values only (e.g. $\gamma_{a/w} > 0$). This is due the fact that a differentially small amount of mechanical work $\delta W$ ($> 0$) has to be done on a constant mass of water to increase its air/water surface A by a differentially small amount $\delta A$ ($> 0$): at constant temperature: $\delta W = \gamma_{a/w} \delta A$. Mechanical work has to be done to bring a water molecule from the interior of the liquid to its surface to increase the surface area between air and water. This requires a certain amount of energy (mechanical work). Therefore a molecule located in the surface of a liquid in contact a gas is in a state of higher energy compared to a molecules in the bulk. (Mechanical work is the amount of energy transferred by a force through a distance.)

In the present context, the term "mechanical equilibrium" means that the air trapped in the diving bell remains trapped even when the (hydrostatic) pressure $P^w(x)$ and the pressure difference $[P^w - P^a]$ change slightly, caused by external disturbances (fluctuations). In mechanical equilibrium, the value of the term $[P^w(x) - P^a(x)]_e$ on the left hand side of equation (1) is equal to the value of the term

$$\left[ -\frac{2 \cdot \gamma_{a/w} \cdot \cos(\theta_e)}{r_m} \right]$$

on the right hand side.

Figure 1 shows a schematic drawing of a vertical cut across a few cubic centimetres of air enclosed in a net-like structure submerged in a container filled with water. The net enclosing the air is shown as a curved, dashed line in this figure. The distances between the dashes indicate the positions of the curved air/water surfaces bordered by the silk threads that form the diving bell. The net carries at its bottom a large opening where the spider can enter or leave the interior of the diving bell. The diameter of this opening is so large that the air/water surface there can be considered as flat. The position of the entire net is fixed by additional threads. It is not taken into account here that the threads forming the diving bell could consist of more than one type of thread as suggested by DE BAKKER et al. (2).

It can be concluded from equation (1), that the sign of the pressure difference $[P^w(x) - P^a(x)]_e$ across the bulged air/water surface bordered by silk threads is determined by the sign of the term $[\cos \theta_e]$. If the value

of the contact angle $\theta_e$ along the line of contact of air, water and silk is found to be smaller than 90° i.e. (cos $(\theta_e) > 0$), the effective surface property of the silk is, by definition, called hydrophilic. Consequently (see equation (1)), the pressure of the trapped air in the diving bell has to be larger than the pressure in the water surrounding the diving bell at the same space coordinate x (i.e. $P^a_e(x) > P^w_e(x)$). If the value of the contact angle $\theta_e$ along the line of contact between air, water and silk is larger than 90° (i.e. $\cos(\theta_e < 0)$), the effective surface property of the silk is, by definition, called hydrophobic. Consequently (see equation (1)), the pressure in the water surrounding the diving bell has to be higher than the pressure of the air trapped in the diving bell at the same space coordinate x (i.e. $P^w_e(x) > P^a_e(x)$).

It will turn out (see below) that along the path $x_1 \rightarrow x_2$ (see Fig. 1) the pressure of the air trapped in the diving bell is higher than that in the water surrounding the diving bell (i.e. $P^a_e(x) > P^w_e(x)$). If this fact is taken into account in equation (1), it must be concluded that the effective surface property of the silk threads forming the diving bell of *A. aquatica* must be hydrophilic to keep the air trapped within the diving bell mechanically stable.
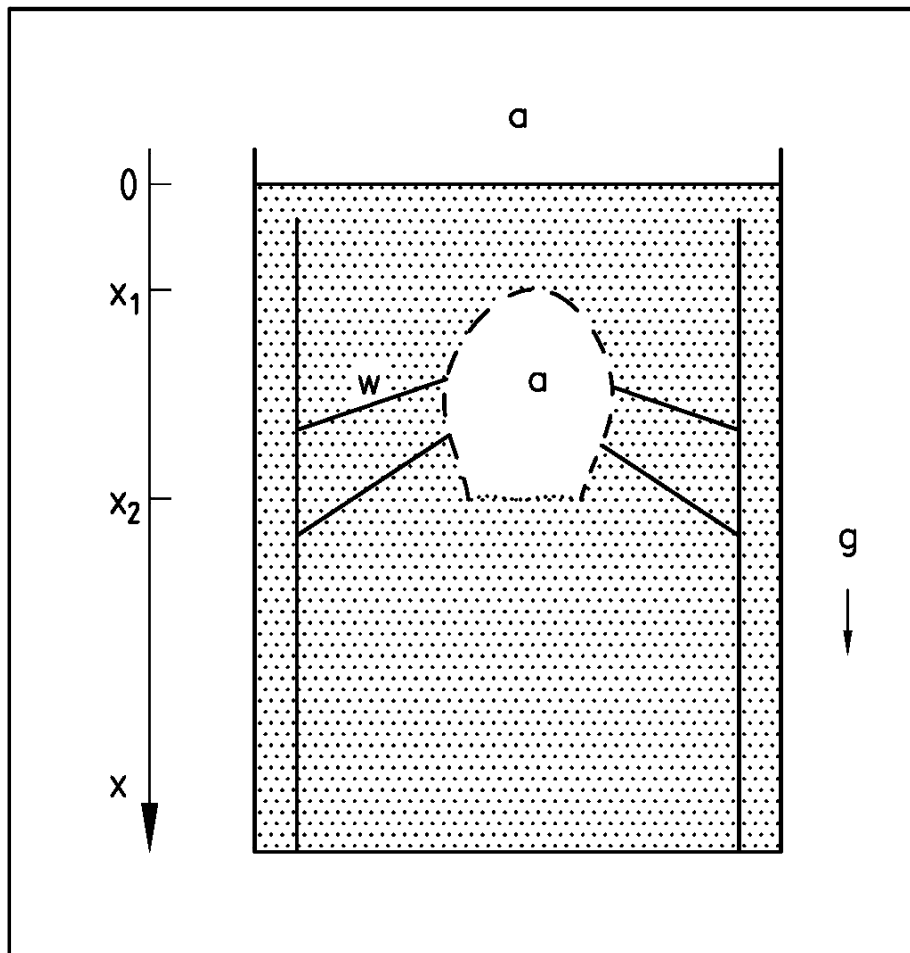


Fig. 1. – Schematic drawing of a vertical cut across a diving bell of the water spider *Argyroneta aquatica* (not drawn to scale). The contour of the bell is marked by a curved and dashed line. The unmarked distances between the dashes refer to the locations of the air/water surfaces bordered by silk threads. The bell is filled with a small, macroscopic volume of air. The diving bell is submerged in water. The position of the bell is stabilized against the force of buoyancy by threads. Abbreviations: *a*, air; *w*, water; *g*, standard gravity; *x*, space coordinate. The coordinate $x_1$ is the location of the highest point of the diving bell. $x_2$ is the location of a flat, macroscopic opening of the diving bell. It is the location at which the spider can enter or leave the interior of the diving bell. Figure 1 refers to equation (1).

What are the arguments leading to the statement that the pressure difference $[P^w(x) - P^a(x)]$ along the path $x_1 \rightarrow x_2$ has negative values? The values of the pressure $P^w$ in the water surrounding the diving bell as a function of the space coordinate x increase linearly along this path: $P^w(x) = \rho_w gx$ (see Fig. 1). The value of the pressure $P^a$ in the volume of air enclosed by the diving bell remains constant along this path: $P^a = P^w(x_2)$. This leads to the equation: $(P^w(x) - P^a(x_2)) = -\rho_w g (x_2 - x)$ (see Fig. 1). The location $x = x_2$ marks the point at which the spider can enter or leave the interior of the diving bell through a comparatively large opening in which the air/water surface is flat. The statement $P^a(x_2) = P^w(x_2)$ expresses the condition of mechanical equilibrium of water and air across a flat surface at constant temperature.

What conclusions can be drawn from this analysis on the mechanical stability of the air trapped within the diving bell of the water spider *A. aquatica* using the proposed model?

(1) A stable trapping of air volume in a diving bell formed by silk threads requires an effectively hydrophilic surface of the threads. The speculation of DE BAKKER et al. that a kind of film on silk forming the diving bell serves as a water repellent (hydrophobic) layer is not confirmed (2).

(2) At first sight, this finding may be unexpected. *A. aquatica* carries outside its diving bell a volume of air trapped on its abdomen under a layer of comparatively long hairs oriented parallel to each other. This air volume is completely covered by a layer of hairs without a (comparably) large opening. This (mobile) air volume acts as physical gill of the spider in a similar manner to the air volume enclosed in the diving bell. It is known that the surface of the hairs covering the trapped air on the abdomen is effectively hydrophobic (1),(5). It is also known that – outside the diving bell – the pressure of the trapped air on the abdomen has a value that is lower than that in the water surrounding the spider (1).

This suggests that the adaptation of *A. aquatica* to a life under water has led to the ability to produce materials in its body with different wetting properties depending on the function of the surfaces of the materials. The function of a diving bell requires an opening at its bottom. Its diameter has to be large enough to give the spider access to the interior of the bell. From a physical point of view, this has the consequence that the effective surface of the silk threads has to be effectively hydrophilic to trap air within the diving bell in a stable way. The pressure of the trapped air on the abdomen of the spider outside its diving bell is smaller than the pressure of the water surrounding the spider. From a physical point of view, this means that the surface of the hairs trapping the air on the abdomen of the spider has to be effectively hydrophobic. Thus, the chemical composition of the silk threads forming the diving bell can be expected to be different from the composition of the hairs on the abdomen (silk consisting of polypeptides while hairs consist of chitin/protein complexes).

(3) Equation (1) can be used to estimate the upper limit of the water pressure $P_e^w$ at which the air volume, trapped within the diving bell of *A. aquatica* immersed in water, can be expected to be mechanically stable. The values of the parameters $\theta_e$ and $r_m$ are necessary for this estimation. The choice of values of the contact angle can only be based on an "educated guess" because no experimental data for $\theta_e$ could be found: $\theta_e < 90°$, $\theta_e = 60°$ $\theta_e = 80°$. For the mesh radius $r_m$ of the diving bell values between $1\mu m \leq r_m \leq 5\mu m$ are used. They are taken from published scanning electron microscope pictures (2). For the air/water surface tension $\gamma_{a/w}$ a value $\gamma_{a/w} = 72.5 \ 10^{-7}$ Jcm$^2$ (room temperature) is used, taken from the literature (6). The results of this estimation are compiled in Table 1. The range of the estimated values of $P_e^w$ is in relative agreement with results of field studies (5).

(4) Scanning electron microscope pictures of sections of the diving bell show that the area of the air/water surfaces bordered by silk threads varies strongly, especially for the parameter $r_m$ (2). On the basis of equation (1) it can be expected that the mesh with the largest diameter is the weakest point in the overall stability of the entire air volume trapped in the diving bell. The pressure difference $[P^a(x) - P^w(x)]$ has its largest value at the top of the diving bell ($x = x_1$). It vanishes at its bottom ($x = x_2$; $P^a(x_2) = P^w(x_2)$).

TABLE 1

Estimate of the upper limits of hydrostatic pressure $P_e^w$ up to which a volume of air is trapped in a stable state within the diving bell of *A. aquatica*. The estimation is based on equation (1). It is assumed that the threads of the diving bell are made of material with hydrophilic surface properties. The parameters used for the calculation are: diameter of the mesh, $2 r_m$; contact angle, $\theta_e$ $10^{-7}$ J=$10^{-2}$bar, corresponding to the height of a water column of 10cm.

| $2 r_m$ [μm] | $P_e^w$ [$10^{-3}$ Jcm$^{-3}$] | $P_e^w$ [$10^{-3}$ Jcm$^{-3}$] |
|---|---|---|
| | $\theta_e = 80°$ | $\theta_e = 60°$ |
| 2 | 12.6 | 72.5 |
| 4 | 6.3 | 36.3 |
| 6 | 4.2 | 24.2 |
| 8 | 3.1 | 18.1 |
| 10 | 2.5 | 14.5 |

# ACKNOWLEDGEMENTS

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