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Liquid–solid interaction at nanoscale and its application in vegetal biology

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ABSTRACT

The water ascent in tall trees is subject to controversy: the vegetal biologists debate on the validity of the *cohesion–tension theory* which considers strong negative pressures in microtubes of xylem carrying the crude sap. This article aims to point out that liquids are submitted at the walls to intermolecular forces inferring density gradients making heterogeneous liquid layers and therefore disqualifying the Navier–Stokes equations for nanofilms. The crude sap motion takes the disjoining pressure gradient into account and the sap flow dramatically increases such that the watering of nanolayers may be analogous to a microscopic flow. Application to microtubes of xylem avoids the problem of cavitation and enables us to understand why the ascent of sap is possible for very high trees.

1. Introduction

The model we develop makes it possible to investigate the behavior of the fluids in the nanofilms, and its applications extend to life sciences. A particularly interesting example concerns vegetable biology: the rise and the motion of sap in the highest trees focus many polemics and debates between biologists. Many of them regard the approach known as the *cohesion–tension theory* (*CTT*) proposed at the end of the nineteenth century by Dixon and Joly as the only valid one [1].

As an obvious fact, Flindt reports huge trees as eucalyptus and giant sequoias of more than 130 m [2], but the biophysical determination of maximum size to which trees can grow is not well understood and calculated. The main problem with the understanding of water transport is why the sap is able to irrigate up very high levels in tall trees.

The crude sap contains diluted salts but its physical properties are roughly comparable with the water ones. Hydrodynamics, capillarity and osmotic pressure create a ascent of sap of only few tens of meters [3]. To explain the sap ascent phenomenon, Dixon and Joly proposed a cohesion–tension model, followed by a quantitative attempt [4]: liquids are assumed to be subjected to tensions generating negative pressures compensating gravity effects.

As pointed out in [5], a turning-point in the confidence of the opponents to the cohesion–tension theory for the sap ascent was the experiment which demonstrated that tall trees survive by overlapping double saw-cuts made through the cross-sectional area of the trunk to sever all xylem elements [6]. This result confirmed by several authors does not seem in agreement with the possibility of strong negative pressures in microtubes [7,8]. Using a xylem pressure probe, the apparatus does not measure any water tension in many circumstances: xylem tension exceeding 0.6 MPa seems not to be observed and in normal state most vessels may be embolized at a level corresponding about 60 m height. Moreover, gas–vapor transportation in xylem tubes seems to appear at the top of high trees ([5] and its references herein).

As comments and questions, M.H. Zimmerman wrote in 1983 [3]:

"We don't yet fully understand all aspects of xylem-water supply to leaves and have here a wide-open filed of potential very interesting future research. The heartwood is referred to as a wet wood. It may contain liquid under positive pressure while in the sapwood the transpiration stream moves along a gradient of negative pressures. Why is the water of the central wet core not drawn into the sapwood? Free water, i.e. water in tracheids, decreases in successively older layers of wood as the number of embolized tracheids increases. The heartwood is relatively dry, i.e. most tracheids are embolized. It is rather ironic that a wound in the wet wood area, which bleeds liquid for a long period of time, thus appears to have the transpiration stream as a source of water, in spite of the fact that the pressure of the transpiration stream is negative most of the time! It should be quite clear by now that a drop in xylem pressure below a critical level causes cavitations and normally puts the xylem out of function permanently. The cause of such a pressure

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drop can be either a failing of water to the xylem by the roots, or excessive demand by transpiration."

Many proponents of the *CTT* wrote a letter [9] to protest against the recent review [5]. They said that "the *CTT* is widely supported by biological scientists as the only theory consistent with the preponderance of data on water transport of plant".

Nonetheless, the problem of possible cavitation in trees remains. Such liquids are strongly metastable and can generate cavitations causing embolisms in xylem tubes made of dead cells [10]. For example, it is interesting to note that in xylem tube – where diameters range between 50 and 400 μm – the crude sap has a surface tension γ_{lv} lower than the surface tension of pure water which is 72 cgs at 20 °C. If we consider a microscopic gas–vapor bubble inside the crude sap with diameter $2R$, the difference between the gas–vapor pressure P_{vapor} and the liquid sap pressure P_{liquid} can be expressed by the Laplace formula: $P_{vapor} - P_{liquid} = 2\gamma_{lv}/R$. But P_{vapor} being positive, unstable bubbles must appear when $R \geq -2\gamma_{lv}/P_{liquid}$. For a negative pressure $P_{liquid} \leq -0.6$ MPa corresponding to more than 60 m height, we get $R \geq 0.24$ μm. In such a case, dynamical bubbles spontaneously appear from germs naturally existing in a crude liquid and cavitation makes the tubes embolized. Consequently, without any biological known process it is difficult to be convinced that xylem tubes are not embolized when they are filled enough with sap up to altitude significantly more important than 100 m corresponding to the highest trees.

Our understanding of the ascent and the motion of sap in very high trees differs from the *CTT*: at a higher level than a few tens of meters – corresponding to the pulling of water by capillary and osmotic pressure – we assume that xylem microtubes are embolized. In addition, we also assume that a thin liquid film – with a thickness of a few nanometers [11,12] – wets xylem walls up to the top of the tree. At this scale, long range molecular forces stratify liquids and the ratio between tube diameter and sap film thickness allows us to consider tube walls as plane surfaces.

In Section 2, using the calculations presented in [13,14], we reconsider the analytic expression in density-functional theory for a thin heterogeneous liquid film which takes account of the power-law tail behavior dominant in a thin liquid film in contact with a solid [15]. The effects of the vapor bulk bordering the liquid film are simply expressed with an other density-functional located on a mathematical surface. With such a functional, we obtained the equations of equilibrium, motion and boundary conditions [16] for a thin vertical liquid film wetting a vertical solid wall and we computed the liquid layer thickness as a function of the film level; these previous results can be extended to mixtures of fluid and perfect gas [13]. Then, the so-called *disjoining pressure* of thin liquid layers yields a natural tool for very thin films [11]. The minimal thickness for which a stable wetting film wets a solid wall is associated with the *pancake layer* when the film is bordering the dry solid wall and corresponds to the maximal altitude [11,17,18]. The normal stress vector acting on the wall remains constant through the liquid layer and corresponds to the gas–vapor bulk pressure which is currently the atmospheric pressure and consequently, no negative pressure appears in the liquid layer. At the top of very high trees, the thickness of the sap layer is of a few number of nanometers. The negative pressure is only present for the liquid bulk in micropores. Numerical calculations associated with physical values for water yield the maximal film altitude for a wood material corresponding to a good order of the height of the tallest trees.

In Section 3, we consider the flow of sap at high levels. For shallow water, the flows of liquids on solids are mainly represented by using the Navier–Stokes equations associated with adherence conditions at the walls. Recent experiments in nanofluidics seem to prove, also for liquids, that at nanoscales corresponding to sap layers at very high tree levels, the conditions of adherence are disqualified [19,20]. With the aim of explaining experimental results, we reconsider the fluids as media whose motions generate slips along the walls; so, we can draw consequences differing from results of classically adopted models as reconsidered in [21]. The new model we are presenting reveals an essential difference between the flows of microfluidics and those of nanofluidics. In the latter, simple laws of scales cannot be only taken anymore into account.

The transpiration in the leaves induces a variation of the sap layer thickness in microtubes. Consequently, the gradient of thickness along microtubes creates a gradient of disjoining pressure which induces driving forces along the layer. For thin layers, the sap flow depending on the variations of the layer thickness can be adapted to each level of leaves following the tree requirement. This is an important understanding why the flow of sap can be non negligible at a level corresponding to the top of the tallest trees. Moreover, we notice that the stability criterium of the flow issued from the equation of motion fits with the results of Derjaguin's school [11].

2. A study of inhomogeneous fluids near a solid wall

In this section, we recall the main results presented in [13,14]. Thanks to these results, in Section 3, we shall consider sap layers of the highest trees with a thickness of some nanometers only.

The density-functional of an inhomogeneous fluid in a very thin isothermal layer domain (O) of wall boundary (S) and liquid–vapor interface (Σ) was chosen in the form:

$$F = \iiint_{(O)} \varepsilon \, dv + \iint_{(S)} \phi \, ds + \iint_{(\Sigma)} \psi \, ds. \tag{1}$$

- The first integral is associated with a square-gradient approximation when we introduce a specific free energy of the fluid at a given temperature T as a function of density ρ and $\beta = (\operatorname{grad} \rho)^2$ such as [22,23]:

$$\rho\varepsilon = \rho\alpha(\rho) + \frac{\lambda}{2}(\operatorname{grad} \rho)^2,$$

where term $(\lambda/2)(\operatorname{grad} \rho)^2$ is added to the volume free energy $\rho\alpha(\rho)$ of a compressible fluid and scalar λ is assumed to be constant at a given temperature [24]. Specific free energy α enables liquid and vapor bulks to be continuously connected and the pressure $P(\rho) = \rho^2\alpha'_\rho(\rho)$ is similar to van der Waals one.

- For a plane solid wall (S), the solid–liquid surface free energy is in the form [15,25]:

$$\phi(\rho) = -\gamma_1\rho + \frac{1}{2}\gamma_2\rho^2. \tag{2}$$

Here ρ denotes the fluid density value at surface (S); constants γ_1, γ_2 and λ are generally positive and given by the mean field approximation:

$$\gamma_1 = \frac{\pi c_{ls}}{12\delta^2 m_l m_s}\rho_{sol}, \quad \gamma_2 = \frac{\pi c_{ll}}{12\delta^2 m_l^2}, \quad \lambda = \frac{2\pi c_{ll}}{3\sigma_l m_l^2}, \tag{3}$$

where c_{ll} and c_{ls} are two positive constants associated with Hamaker constants; σ_l and σ_s denoting fluid and solid molecular diameters, $\delta = (1/2)(\sigma_l + \sigma_s)$; m_l, m_s denote masses of fluid and solid molecules; ρ_{sol} is the solid density.

- For the plane liquid–vapor interface (Σ) the surface free energy ψ is reduced to [13,14]: