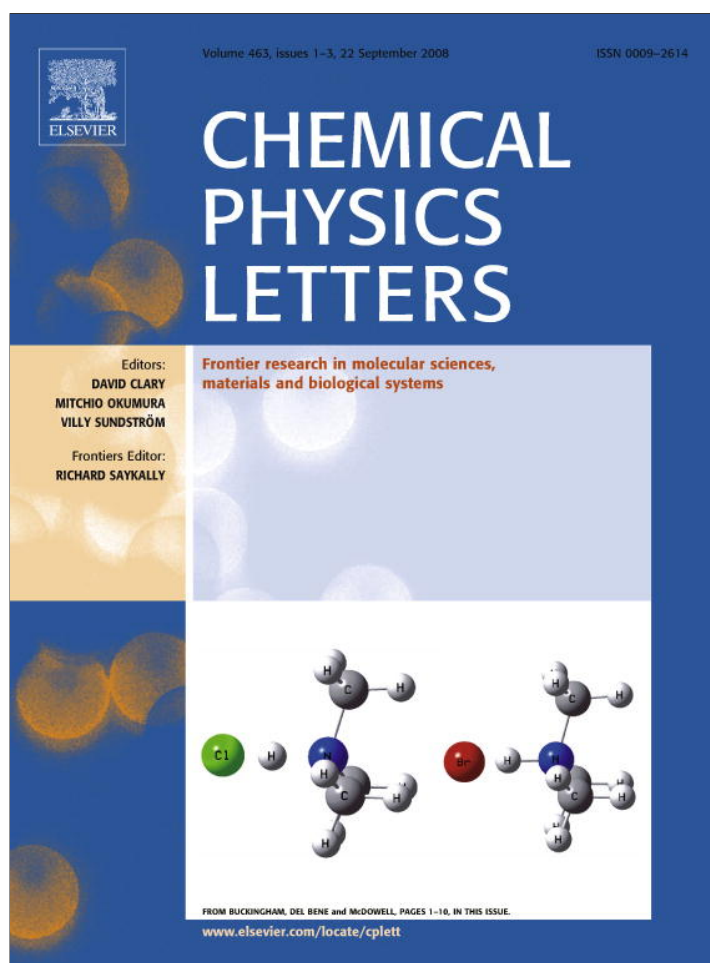


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## Comment

Comment on 'Nanoscale water capillary bridges under deeply negative pressure' [Chem. Phys. Lett. 451 (2008) 88] <sup>☆</sup>Frédéric Caupin <sup>a,\*</sup>, Eric Herbert <sup>a,1</sup>, Sébastien Balibar <sup>a</sup>, Milton W. Cole <sup>b</sup><sup>a</sup> Laboratoire de Physique Statistique de l'Ecole Normale Supérieure associé au CNRS et aux Universités Paris 6 et Paris 7, 24 rue Lhomond, 75005 Paris, France<sup>b</sup> Department of Physics, Penn State University, University Park, PA 16802, United States

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## ABSTRACT

Yang et al. reported pull-off force measurements between an atomic force microscope tip and a silicon wafer. They deduced the pressure of liquid water inside the capillary bridge formed in humid air. They claimed that their 'research shows that nanoscale water capillary bridges are metastable and have absolutely negative pressure approaching the limit of stability for water' (around  $-200$  MPa at room temperature). Indeed, pressures reaching  $-160$  MPa were reported, establishing a world record. However, we show that the bridges are not metastable, that the analysis used suffers from internal inconsistency, and that several assumptions made are questionable.

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In a recent Letter [1], Yang et al. presented a study of the pull-off force between an atomic force microscope (AFM) tip (radius  $R_t = 25$  nm) and a silicon wafer, in humid air and in ultrahigh vacuum (UHV). They use their results to deduce the pressure of liquid water inside the capillary bridge formed in humid air between the tip and the wafer surface. However, we put forward a number of arguments which question their claim that their 'research shows that nanoscale water capillary bridges are metastable and have absolutely negative pressure approaching the limit of stability for water'.

Any liquid can be brought to a pressure  $P$  below its saturated vapor pressure  $P_{\text{sat}}$ . Because of the cohesion forces between particles, the pressure can even be negative. A bulk liquid can exist in this metastable state of matter because the liquid–vapor transition is of first order: there is an energy barrier which hinders the formation of a bubble of the vapor phase (cavitation). The energy barrier decreases as the liquid is brought further away from the liquid–vapor equilibrium, and eventually vanishes at the spinodal pressure  $P_s$ , where the liquid becomes totally unstable. For water at room temperature,  $P_s$  is estimated around  $-200$  MPa [2]. Even in the absence of impurities or surfaces, homogeneous cavitation occurs when the thermal fluctuations exceed the barrier ( $E_b(P) < k_B T$ ), so that  $P_s$  is never reached in experiments. Cavitation in water has been extensively studied: see Ref. [3] for a review. The present world record for negative pressures in water was obtained in quartz inclusions with sizes in the range  $10$ – $100$   $\mu\text{m}$ : pressures

as negative as  $-140$  MPa were estimated, based on an equation of state extrapolated in the metastable range [4]. The next largest negative pressures were obtained with several experimental methods [3,5] and are around  $-25$  MPa at room temperature. In their Letter, Yang et al. report pressures as negative as  $-160$  MPa, which would thus establish a new world record. However, we show that the system they study is not metastable, that their derivation of the pressure is not consistent, and that several assumptions made are likely to be invalid.

First of all, we show that the water capillary bridges considered are perfectly stable. When the tip is in contact with the substrate in a humid atmosphere, the state where the capillary bridge is present is the state with lowest free energy. This can be understood in the capillary approximation, which treats the liquid–vapor interface as a sharp boundary with surface tension  $\gamma_{\text{LV}}$ . Consider as the thermodynamic system a fixed volume  $V$  in contact with a thermostat at temperature  $T$  and with a particle reservoir at fixed  $\mu$ . To find the most stable state, the thermodynamic potential to minimize is the grand potential  $\Omega = U - TS - \mu N$ . This imposes the liquid at pressure  $P_{\text{liq}}$  and the vapor at pressure  $P_{\text{vap}}$  to have the same chemical potential  $\mu$ . Defining the relative humidity  $\text{RH} = P_{\text{vap}}/P_{\text{sat}}$  and to first order in  $P_{\text{liq}} - P_{\text{sat}}$  (improved upon below):

$$\begin{aligned} \mu &= \mu_{\text{vap}}(T, P_{\text{vap}}) = \mu_{\text{vap}}(T, P_{\text{sat}}) + RT \ln \text{RH} = \mu_{\text{liq}}(T, P_{\text{liq}}) \\ &= \mu_{\text{vap}}(T, P_{\text{sat}}) + V_{\text{sat}}(P_{\text{liq}} - P_{\text{sat}}) \end{aligned} \quad (1)$$

where  $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$  is the perfect gas constant,  $T$  the temperature, and  $V_{\text{sat}}$  the molar volume of the liquid at  $P_{\text{sat}}$ . Therefore, to create a volume  $V_{\text{liq}}$  of liquid at the chemical potential  $\mu$ , it needs to be at a pressure

$$P_{\text{liq}} = P_{\text{sat}} + \frac{RT}{V_{\text{sat}}} \ln(\text{RH}) \quad (2)$$

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which is negative for small enough RH. This costs a work  $(P_{\text{vap}} - P_{\text{liq}})V_{\text{liq}}$ . But for a liquid that wets the tip and wafer surfaces (contact angle  $\theta < \pi/2$ ), it is always favorable to replace the vapor by the liquid in the vicinity of the tip–wafer contact. Indeed, for a given value of  $\phi$ , the azimuthal angle reached by the contact line of the meniscus on the spherical tip (see Fig. 1b of [1]), one can calculate the shape of the meniscus. For small  $\phi$ , the gain in surface energy  $2\pi R_t^2 \gamma_{\text{LV}} \cos \theta \phi^2$  exceeds the cost in volume energy  $(P_{\text{vap}} - P_{\text{liq}}) \pi R_t^3 \phi^4 / 4$ . This explains why the meniscus forms spontaneously. A complete calculation leads to the equilibrium geometry, which minimizes  $\Omega$ , and for which the meniscus is in thermodynamic ( $\mu_{\text{liq}} = \mu_{\text{vap}}$ ) and mechanical ( $P_{\text{liq}} - P_{\text{vap}} = \gamma_{\text{LV}}/R_K$ ) equilibrium. The equilibrium mean radius of curvature  $R_K$  is precisely given by the Kelvin equation (Eq. (8) of Ref. [1]):

$$\frac{1}{R_K} = \frac{RT}{\gamma_{\text{LV}} V_{\text{sat}}} \ln \text{RH} \quad (3)$$

where  $P_{\text{sat}} - P_{\text{vap}}$  has been neglected compared to  $P_{\text{liq}}$ . We thus reach the counterintuitive conclusion that, in the most stable state, the liquid is at negative pressure. However, cavitation cannot occur inside the liquid in the meniscus. Even accounting for heterogeneous nucleation on the walls, the critical bubble for nucleation would have a height  $\gamma_{\text{LV}}(1 + \cos \theta)/(P_{\text{vap}} - P_{\text{liq}})$ , whereas the meniscus height is less than  $2/R_K = 2\gamma_{\text{LV}}/(P_{\text{sat}} - P_{\text{liq}})$ . Therefore, only small bubbles can be created in the meniscus, for which the cost in surface energy exceeds the gain in volume energy, and such a bubble would vanish. Now, one should be careful when transposing to a confined system the considerations of stability valid for a bulk system. Here, for water confined between the tip and wafer, the pressure itself is not defined as a scalar quantity: it is rather a non-diagonal stress tensor which includes the effect of water–water and water substrate interaction. The direct comparison with the spinodal pressure of bulk water is therefore not possible.

Next, we show that the analysis proposed in the Letter is inconsistent. Let us recall the procedure used in [1]. What is measured is the pull-off force  $F_{\text{pull-off}}$ , the maximum force observed when retracting the tip away from the surface. It is written as the sum of different forces:

$$F_{\text{pull-off}} = F_L + F_T + F_{\text{others}} \quad (4)$$

where  $F_L$  is the Laplace force due to the negative pressure in the liquid,  $F_T$  is the capillary force on the contact line, and  $F_{\text{others}}$  stands for all the other forces (van der Waals, electrostatic, ...) [6]. Then, thermodynamic equilibrium is assumed, allowing the use of the Kelvin equation (Eq. (3)). With the further assumption that the tip is at the limit of contact with the wafer (tip–wafer distance  $a = 0$ ), the dimensions of the bridge are calculated:  $R_1$  is the radius of curvature of the liquid–vapor interface, and  $R_2$  is the horizontal radius of the meniscus (see Fig. 1b of [1]). Then  $\sin \phi = R_2/R_t$  and  $F_T = 2\pi R_t \gamma_{\text{LV}} \sin \phi \sin(\phi + \theta)$ .  $F_{\text{others}}$  is estimated from the value of  $F_{\text{pull-off}}$  in UHV, when no liquid bridge is present.  $F_L$  is deduced from Eq. (4), and the negative pressure finally obtained through<sup>2</sup>:

$$P_{\text{liq}} = -\frac{F_L}{\pi R_2^2} \quad (5)$$

But if the Kelvin equation is valid, it leads *directly* to the value of the pressure in the liquid (see Eq. 2)! At  $T = 293.15$  K,  $\gamma_{\text{LV}} = 72.7$  mN m<sup>-1</sup> and  $V = 1.8 \times 10^{-5}$  mol m<sup>-3</sup> [7] lead to:

$$P_{\text{liq}} = P_{\text{sat}} + \frac{\gamma_{\text{LV}}}{R_K} \simeq 135 \ln \text{RH} \text{ in MPa} \quad (6)$$

For the values of RH investigated in [1] (1%, 10%, 20%, 30%, and 40%), the corresponding pressures (−622, −311, −218, −163, and

−124 MPa, respectively) are markedly different from the pressures Yang et al. deduced from the pull-off force and Eq. (5) (around −130, −125, −120, −100, and −70 MPa, respectively). This internal inconsistency leads us to look for possible sources of error in the analysis carried by Yang et al.

The use of the Kelvin equation assumes that thermodynamic equilibrium holds during the pull-off force measurement. Some studies report that the pull-off force depends on the contact time when it is less than a few seconds [8–12]; this is interpreted as an effect of the finite time needed for liquid water to condense on and flow to the capillary bridge in order to reach thermodynamic equilibrium [11]. Unfortunately no details are given in [1] about the timescale of the experiment.

In the derivation of the Kelvin equation and the corresponding liquid pressure (Eq. 2), two assumptions are usually made: the vapor is a perfect gas, and the liquid is incompressible. Water vapor at 293.15 K is not exactly perfect; yet it follows the law  $PV_{\text{vap}} = R_{\text{eff}}T$  where  $V_{\text{vap}}$  is the molar volume of the vapor, and  $R_{\text{eff}} = 8.3060$  J K<sup>-1</sup> mol<sup>-1</sup> [7]. For low RH, the liquid pressure becomes highly negative, and it cannot be treated as incompressible: the expression of  $\mu_{\text{liq}}(T, P_{\text{liq}})$  in Eq. (1) has to be modified. Using Speedy's equation of state for liquid water, which gives the molar volume  $V$  down to the spinodal:

$$V(P) = \frac{V_s}{1 + \sqrt{\frac{1-P}{P_s}}} \quad (7)$$

where  $P_s = -208$  MPa,  $V_s = 2.23 \times 10^{-5}$  m<sup>3</sup>, and  $B = 17.8297$  at 293.15 K [2], the equilibrium liquid pressure as a function of RH is found by solving

$$\int_{P_{\text{sat}}}^{P_{\text{liq}}} V(P) dP = R_{\text{eff}}T \ln \text{RH} \quad (8)$$

For instance, for RH = 20%, the liquid pressure in the bridge becomes −204 MPa, instead of −223 MPa with the usual equation.<sup>3</sup> Following the reasoning of Ref. [1],  $R_K = \gamma_{\text{LV}}/(P_{\text{liq}} - P_{\text{sat}})$  and  $R_2$  (which is a function of  $R_K$ , see Eq. (7) of [1]) are also modified. For RH = 20%, with the new value of  $R_2$ , Eq. (5) gives  $P_{\text{liq}} = -112$  MPa instead of −120 MPa. The internal inconsistency mentioned above still remains.

Several geometrical approximations are used to derive the equations used in [1]: the tip–wafer separation  $a$  is taken to be zero, the tip is assumed to be a perfect sphere of radius  $R_t$  large compared to  $R_2$ , and the liquid–vapor interface is approximated by a portion of sphere. These approximations have been discussed in Refs. [13,14], where the exact shape of the meniscus was numerically calculated. The geometrical approximations just mentioned can introduce errors, especially for small tip size. In particular, the actual tip shape (deviation from a sphere) can have a strong effect [13–15].

In addition to the capillary force acting when a liquid bridge is present, van der Waals and electrostatic forces also act on the tip. Yang et al. write that these forces 'are assumed to have the same values in UHV as in air', so that they subtract the pull-off force measured in UHV from that in air to estimate the capillary force. Unfortunately, when the liquid bridge is present, it modifies the other forces because of its dielectric properties; in other words the Hamaker constant  $A$  between the tip and wafer depends on the dielectric medium. A calculation gives  $A_{\text{vac}} = 186.5 \times 10^{-21}$  J for the system silicon/vacuum/silicon, and  $A_{\text{water}} = 97.5 \times 10^{-21}$  J for the system silicon/water/silicon [16]. The Van der Waals force acting through a medium  $i$  between a sphere of radius  $R_t$  and a plane is [17]:

<sup>2</sup> Note that there is a misprint in [1]:  $R_1$  is used instead of  $R_2$  in the first occurrence of  $A$ , the horizontal area of the meniscus. The second occurrence is correct.

<sup>3</sup> Of course, the procedure fails for lower values of RH, because the equation of state used does not allow the liquid pressure to be less than  $P_s$ .

$$F_{\text{vdW}}^i = \frac{A_t R_t}{6a^2} \quad (9)$$

where  $a$  is the sphere-plane separation. In the presence of a meniscus characterized by the azimuthal angle  $\phi$ , a crude approximation of the modified force is [18]:

$$F_{\text{vdW}} = F_{\text{vdW}}^{\text{air}} \frac{1}{[1 + R_t(1 - \cos \phi)/a]^2} + F_{\text{vdW}}^{\text{water}} \left( 1 - \frac{1}{[1 + R_t(1 - \cos \phi)/a]^2} \right) \quad (10)$$

We use  $a = 0.23$  nm to fit the data in UHV from Yang et al.,  $F_{\text{UHV}} \approx 15$  nN. Then  $F_{\text{vdW}}$  decreases with increasing RH, reaching for RH = 40% the value 8 nN, which is of the same order as  $F_{\text{pull-off}} - F_{\text{UHV}}$ . This omission of screening from the van der Waals interaction can introduce large underestimates of the capillary force.

Finally we discuss the capillary approximation which consists in using the macroscopic surface tension  $\gamma_{\text{LV}}$  to describe the liquid–vapor interface. For a tip in contact with the wafer, the maximum thickness of the liquid layer  $h$  is reached near the contact line of the bridge:  $h = R_t(1 - \cos \phi)$ . Using the same formulas as in [1], the numerical value of  $h$  varies from 0.2 to 1 nm, for RH from 1% to 40%. This is to be compared with the size of a water molecule (around 0.3 nm), the thickness of a planar liquid–vapor interface (around 1 nm [19]), and the wafer average roughness (0.4 nm [1]). The use of the contact angle  $\theta$  of water on silicon taken from measurements on macroscopic drops, the description of the wafer as a flat surface, and the use of a simple capillary description (with a sharp water–vapor interface, the bulk surface tension  $\gamma_{\text{LV}}$  and the Kelvin equation) are therefore highly questionable. In addition, the structure of water in very thin films may be markedly different from that in the bulk liquid. Using attenuated total reflection infrared spectroscopy, Asay and Kim [20] studied water absorbed on a hydrophilic silicon oxide surface at room temperature. They observed that ‘a completely hydrogen-bonded icelike network of water grows up to three layers as the RH increases from 0% to 30%’. Major et al. [21] used interfacial force microscopy to study films of water on gold surfaces covered with different self-assembled monolayers. For films confined between hydrophilic surfaces in a gap less than 1 nm, they reported an effective viscosity 7 orders of magnitude greater than that of bulk water, and interpreted this with Monte Carlo simulations showing an enhancement of the

hydrogen bonds and their tetrahedral structure. Microscopic approaches, like Monte-Carlo simulations [22,23], are required to account for the behavior of molecularly thin films. In particular, the formation of wetting films with significant structural ordering reveals significant attractive interactions with the surface, which must be key ingredients in the energy balance.

In conclusion, we think that there are serious doubts about the interpretation of the data from Yang et al. [1] in terms of an extreme negative pressure reached in liquid water. The world record remains  $-140$  MPa, obtained in microscopic quartz inclusions and based on the extrapolation of the equation of state [4], or at least  $-25$  MPa in experiments with direct pressure calibration [3,5].

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