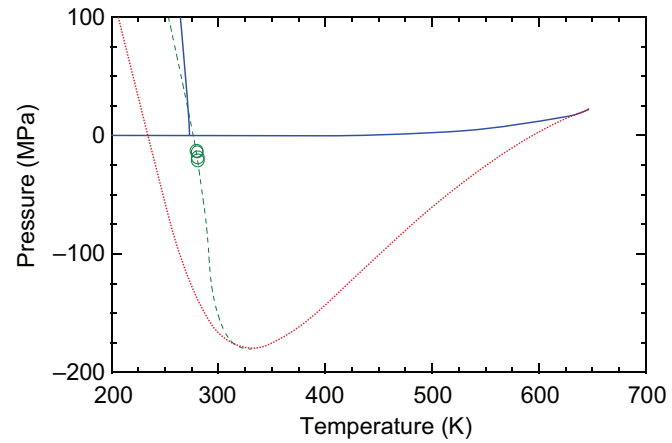
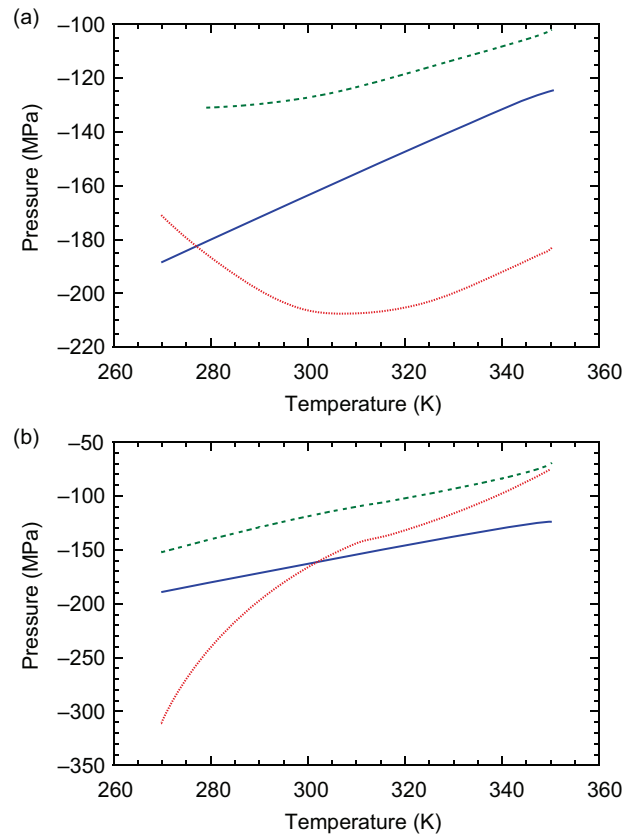


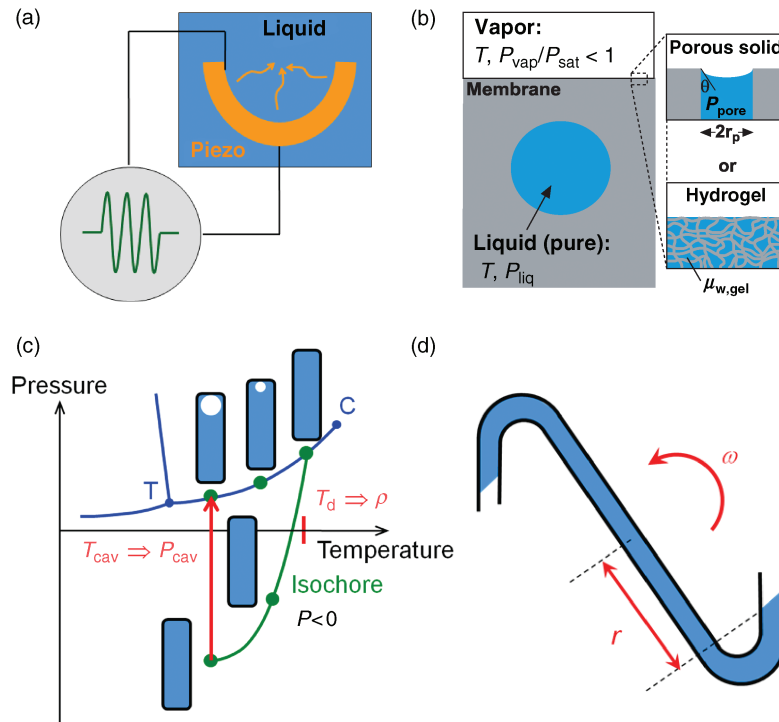
**Figure 3.1.** Schematic cuts of the phase diagram of a pure substance, showing the stable, metastable, and unstable regions: **(a)** a low-temperature isotherm with a metastable liquid branch reaching negative pressure, **(b)** temperature–density cut, and **(c)** pressure–temperature cut.



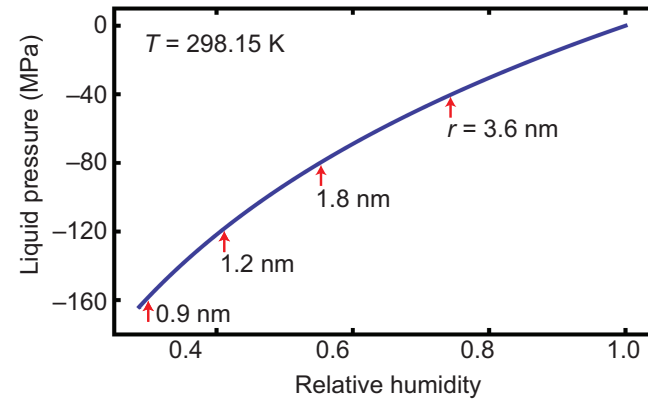
**Figure 3.2.** Phase diagram of water proposed by Speedy [18] plotted using the IAPWS EoS [25,26]. The blue curves are equilibrium lines, the red curve is the liquid–vapor spinodal, and the green curve the LDM. The green circles show the experimental determination of the LDM at negative pressure [27]. When the spinodal and the LDM meet, the spinodal pressure reaches a minimum, and (for this EoS) retraces to positive pressure at low temperature. However, note that this would imply an improbable crossing between the spinodal and the metastable liquid–vapor equilibrium (see text for details).



**Figure 3.4.** Cavitation pressure as a function of temperature for two scenarios for water: reentrant spinodal scenario **(a)** and liquid–liquid critical point scenario **(b)**. These scenarios predict a different temperature behavior for the liquid–vapor spinodal (dotted curve), either with a minimum (a, based on extrapolation of positive pressure data [40]), or monotonic (b, based on molecular dynamics simulations with the TIP5P potential [41]). The blue curve shows the prediction of CNT based on the bulk surface tension of water; it becomes unphysical when it goes beyond the liquid–vapor spinodal. The green curve is the DFT prediction [40] that correctly remains above the spinodal, and reflects its temperature dependence.

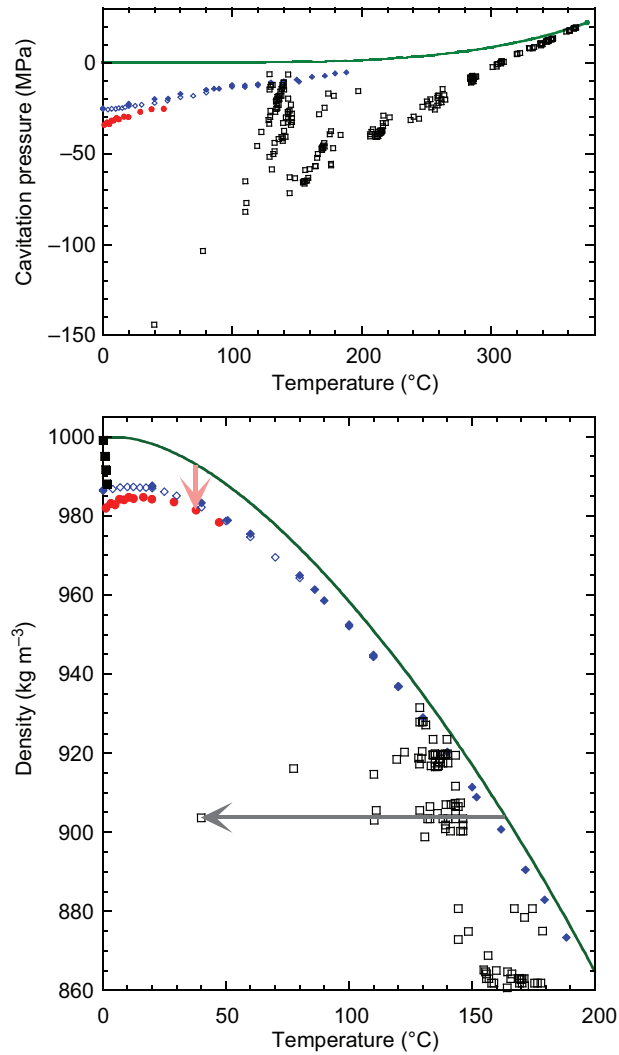


**Figure 3.5.** Sketches of several methods used to put a liquid under mechanical tension. **(a)** Acoustic method. A hemispherical piezoelectric transducer emits focused ultrasound bursts (yellow arrows) into a bulk liquid [43]. **(b)** Metastable vapor–liquid equilibrium. A nanoporous membrane or gel mediates the equilibrium of a bulk volume of liquid and its subsaturated vapor [15]. **(c)** Berthelot tube. A rigid container partially filled with a liquid in equilibrium with its vapor is heated until the liquid expands to fill the entire volume. Upon cooling, the liquid follows an isochore and its pressure decreases [44,45]. **(d)** Centrifugal method. A tube formed with two symmetrical bends at each end (a z-tube) is spun around its mid-point such that the pressure in the liquid drops due to the centripetal acceleration acting on the column of liquid [46].



**Figure 3.6.** Prediction of pressure in liquid water in metastable equilibrium with its vapor at subsaturated relative humidities (RH). Equation (2) was solved using the IAPWS EoS for  $v_{liq}(P, T)$  [25,26]. The labels of the red arrows present simple estimates of the radii of pores in a wettable material that would allow the pore liquid to reach the pressures indicated ( $-40$ ,  $-80$ ,  $-120$ , and  $-160$  MPa), based on Eq. (1).





**Figure 3.8.** Comparison of the cavitation pressure (top) and density (bottom) of water as a function of temperature obtained with acoustic method and water inclusions in quartz used as Berthelot tubes. The symbols represent: acoustic method with calibration by static pressure method (open diamonds [43] and solid blue diamonds [52]), acoustic method with fiber optic probe hydrophone (red bullets [51]), water inclusions in quartz (open squares [45]). In the lower panel, cavitation of an inclusion during melting is also included (black filled square [92]) and red and grey arrows indicate isothermal and isochoric paths, respectively. Green lines are the binodals. Lower panel reproduced with permission from Ref. [52].