Stability Limit of Liquid Water in Metastable Equilibrium with Subsaturated Vapors

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A pure liquid can reach metastable equilibrium with its subsaturated vapor across an appropriate membrane. This situation is analogous to osmotic equilibrium: the reduced chemical potential of the dilute phase (the subsaturated vapor) is compensated by a difference in pressure between the phases. To equilibrate with subsaturated vapor, the liquid phase assumes a pressure that is lower than its standard vapor pressure, such that the liquid phase is metastable with respect to the vapor phase. For sufficiently subsaturated vapors, the liquid phase can even assume negative pressures.

The appropriate membrane for this metastable equilibrium must provide the necessary mechanical support to sustain the difference in pressure between the two phases, limit nonhomogeneous mechanisms of cavitation, and resist the entry of the dilutant (gases) into the pure phase (liquid). In this article, we present a study of the limit of stability of liquid water—the degree of subsaturation at which the liquid cavitates—in this metastable state within microscale voids embedded in hydrogel membranes. We refer to these structures as vapor-coupled voids (VCVs). In these VCVs, we observed that liquid water cavitated when placed in equilibrium with vapors of activity $a_{\text{vap}} = 0.85$ (relative humidity $\leq 85\%$). When expressed as a pressure in the liquid based on thermodynamic calculations, the liquid cavitated at pressures $P \leq -22 \text{ MPa}$ ($-220 \text{ bar}$). This limiting pressure is smaller in magnitude than the limit predicted by homogeneous nucleation theory or molecular simulations ($P_{\text{ cav}} = -140$ to $-180 \text{ MPa}$). To determine the cause of the disparity between the observed and predicted stability limit, we examine experimentally the likelihood of several nonhomogeneous mechanisms of nucleation: (i) heterogeneous nucleation caused by hydrophobic patches on void walls, (ii) nucleation caused by the presence of dissolved solute, (iii) nucleation caused by the presence of pre-existing vapor nuclei, and (iv) invasion of air through the hydrogel membrane into the voids. We conclude that, of these possibilities, (i) and (ii) cannot be discounted, whereas (iii) and (iv) are unlikely to play a role in determining the stability limit.

Introduction

Water is among the most important and most studied substances on earth, yet the thermodynamic and dynamic properties of the metastable state of liquid water at negative pressures (dark gray regions in Figure 1A) have been only sparsely studied experimentally and rarely used technologically. A more complete understanding of this state could shed light on its role in natural processes such as transpiration in vascular plants, on means of exploiting this state for technological applications, and, more generally, on important questions about the unusual properties of the liquid state of water. The lack of a simple and versatile means of placing addressable volumes of liquids under well-defined, constant negative pressure, or tension has limited both fundamental studies and practical uses of this state.

We recently introduced a system in which bulk volumes of nearly pure, liquid water encapsulated in an organic hydrogel can reach metastable equilibrium with subsaturated water vapor in air (vapor activity, $a_{\text{vap}} = [(\text{relative humidity})/100] < 1$), we refer to these structures as vapor-coupled voids (VCVs; Figure 1B,C).

This metastable equilibrium is depicted on an isotherm in the schematic illustration of the $P-T$ phase diagram of water in Figure 1A: reduced pressure in liquid water at point A allows for equilibrium (equality of chemical potentials) with the subsaturated water vapor at point B. On the basis of the condition of equilibrium, the pressure in the liquid contained by the VCV can be estimated to be $P_{\text{ cav}} = P_{\text{ atm}} - \Pi$, where $\Pi = -(RT/V_{\text{ liq}}) \ln (a_{\text{ vap}}) \text{[Pa]}$, at temperature $T\text{[C]}$ and for vapor of activity $a_{\text{ vap}}$ ($P_{\text{ atm}} = 1.8 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ is the molar volume of liquid water and $\Pi$ [J mol$^{-1}$] is the ideal gas constant; see Theory section). For even a minute degree of subsaturation in the vapor ($a_{\text{ vap}} < 0.99927$), $P_{\text{ cav}} < P_{\text{ atm}}$, the saturated partial pressure of water vapor in air, and the liquid phase becomes metastable with respect to the vapor phase; under this condition, liquid water is superheated and transition to the vapor phase by cavitation (boiling) is favored thermodynamically. Yet, for $P_{\text{ cav}} > P_{\text{ hom}}$, the liquid phase is kinetically stable due to an activation barrier for the formation of the vapor phase.

We have observed that liquid water in VCVs can remain stable in equilibrium with vapors of activity down to $a_{\text{ vap}} = 0.85$, corresponding to estimated pressures down to $P_{\text{ cav}} = -22 \text{ MPa}$. This limit of stability is commensurate with that observed in the vast majority of other studies of liquid water under tension. Nonetheless, this limiting pressure is significantly above.

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(less negative) than the limit predicted for homogeneous nucleation of the vapor phase, $P_{\text{hom}} = -140$ to $-180$ MPa (at room temperature). This discrepancy suggests that cavitation in our system may occur by a different mechanism, such as heterogeneous nucleation, cavitlation due to the presence of solutes or pre-existing vapor nuclei, or by invasion of air into the VCV via pores in the hydrogel membrane (see Figure 2). Clarification of these possible mechanisms may help to explain why all experimental studies of the stability limit of water, except one obtained in quartz inclusions, find a threshold pressure $P_{cav} \geq -28$ MPa.

In this work, we investigate each of the possible mechanisms of cavitation listed above in order to clarify which mechanism determines the observed stability limit in VCVs. Our approach is to determine, experimentally, the statistics of cavitation as

Figure 1. Schematic phase diagrams of water and illustration of the generation of negative pressures in liquid water in vapor-coupled voids. (A) Schematic illustrations of the $P-T$ (left) and $P-V$ (right) phase diagrams of water with superheated water regime (shaded area), melting curve (m), binodal (b), spinodal (s), isotherm (t), solid phase (S), liquid phase (L), and vapor phase (V) indicated. The darker shaded region represents liquid water at negative pressures. The kinetic stability limit (k) predicted by homogeneous nucleation theory is represented as the dashed-dot curve positioned between the binodal and spinodal. The intersection of an isotherm (t) with the kinetic stability limit curve defines the kinetic stability limit ($P_{\text{hom}}$ [MPa]) for that temperature. In the $P-V$ phase diagram of water, hydrostatic pressure $P$ is used for liquid branches and partial pressure $p_w$ is used for vapor branches. Under standard conditions, liquid water at atmospheric pressure, $P_{\text{atm}}$, is in equilibrium with water vapor in air at saturation vapor pressure $p_{w,\text{sat}}$ [MPa] (blue circles). Liquid water at negative pressure, $P_{\text{void}}$, is in metastable equilibrium with subsaturated water vapor in the air at vapor pressure, $p_w$ (red squares). (B) A hydrogel membrane saturated with water separates pure liquid water in the spherical void from water vapor in the air. The membrane may be viewed either as a cross-linked polymer network saturated with water; such a system behaves thermodynamically as a molecular-scale mixture of water and polymer (left inset), or as discrete water and polymer phases as in a porous material (right inset). As a component of the polymer–water mixture of the first case, water has chemical potential $\mu_{w,\text{gel}}$ [J mol$^{-1}$]. When situated in a pore of radius, $r_p$ [m], with a contact angle between the liquid and the surface, $\theta$ [deg], the pressure of the water under the concave meniscus is $P_{\text{pore}} = P_{\text{atm}} - 2\sigma \cos \theta/r_p$, where $\sigma$ [N m$^{-1}$] is the surface tension of water. Water in the liquid phase entrapped within the void at temperature $T$ and pressure $P$ has chemical potential $\mu_{w,\text{void}}(T,P)$ and water in the vapor phase in the air has chemical potential $\mu_{w,\text{vap}}(T,P)$. At time $t = 0$, water vapor in the air is saturated, with activity $a_{w,\text{vap}} = 1$, the chemical potentials are equal, and water in the two phases is at equilibrium. At time $t = 0^+$, the concentration of water vapor in the air is reduced and $a_{w,\text{vap}} < 1$. (C) Once equilibrium is re-established, as time $t \rightarrow \infty$, pure, liquid water in the void with activity $a_{w,\text{vap}} = 1$ at pressure $P_{\text{void}} = P_{\text{atm}} - \Pi$ (eq 6) is in metastable equilibrium with subsaturated water vapor in the air having activity $a_{w,\text{vap}} < 1$ at atmospheric pressure $P_{\text{atm}}$. For sufficient degrees of subsaturation of water vapor in the air, the pressure in the liquid is predicted to be less than $p_{w,\text{sat}}$ and even negative (eq 6). A mechanical balance exists between the tension in the liquid within the void (solid red arrows) and a restoring force exerted by the hydrogel membrane (dashed red arrows); this balance prevents the collapse of the void.

Figure 2. Mechanisms of cavitation. (A) Illustration of features in a void that potentially lead to cavitation thresholds above the kinetic stability limit imposed by homogeneous nucleation. These features include (i) hydrophobic moieties on the surface of the void, (ii) dissolved gas or solute present in the liquid within the void, (iii) a bubble trapped in a micrometer-scale crevice on the walls or on particulate impurities (an ideal, conical crevice is illustrated with radius $r_0$ and half-angle $\beta$, in the surface of the void), and (iv) pores in the wall of the void with a meniscus at the surface of the hydrogel membrane that is connected to the void. (B) Once water in the void is placed at sufficiently reduced pressures relative to the pressure of the air, cavitation may occur due to features i–iii or the meniscus in the pore may recede through the wall of the void. (C) After cavitation or dry out, a mixture of gas (water vapor and air) and liquid water at atmospheric pressure is present in the void.

A function of the activity in the vapor phase for populations of voids formed (1) by two methods of fabrication, (2) with three chemical formulations having distinct molecular structure and interaction with water, and (3) with distinct preparations prior to equilibration with subsaturated vapors (the degree of purification of liquid water in the voids and degree of prepressurization). We interpret the results of experiments in the light of established theories of cavitation and of cross-linked polymer networks. We also use this opportunity to expand on our previous description of our methods, our interpretation of the coupling between subsaturated water vapor and volumes of liquid water, and the historical background of this means of generating negative pressures in liquid water.

Background of Studies of Stability of Liquid Water at Negative Pressures. Since the 1850s, most experimental studies have exploited one of the following three methods to generate negative pressures in water: (1) static methods based on approximately isochoric cooling of liquid water in sealed glass capillaries either with or without direct measurement of pressure or in liquid-filled inclusions in mineral crystals. The experiments without direct pressure sensing depended on an extrapolation of the equation of state of water into the negative pressure regime and the assumption of constant volume. (2) Static methods based on isothermal extension of liquid water in a z-shaped capillary tube exposed to centrifugation. With this method, the entire volume of water in the capillary is not at the same pressure; there is a gradient in the pressure along the capillary. An attempt was made to use this method to obtain data for three thermodynamic state variables ($PVT$) and therewith describe the behavior of water in the negative pressure regime. However, the deformation of the capillary tube caused by varying temperatures and tensions hindered the acquisition of accurate data. (3) Dynamic methods based on approximately isothermal extension of liquid water using acoustic waves. These methods benefit from the possibility of working in the bulk of the fluid, far from solid boundaries. Yet, they require careful calibration of the pressures generated by the waves and render difficult the interrogation of the liquid volume under tension. Cavitation and bubble collapse caused by the oscillating pressure waves of acoustic methods have been used technologically in fields such as sonochemistry, ultrasonic cleaning, and lithotripsy. Audio methods have also provided a useful basis for understanding the dynamics of cavitation both in the bulk and at surfaces. However, the transient nature of the pressures generated by acoustic methods makes the study of the thermodynamic and dynamic properties of liquids at negative pressure challenging. Limiting pressures attained in these three systems fall primarily between $-15$ and $-28$ MPa. The largest reported negative pressures in liquid water have been attained in inclusions in quartz, including one measurement of $-140$ MPa, close to the theoretical stability limit of water near room temperature.

A number of investigators have exploited the strategy similar to that used by VCVs to reach small tensions ($P_{\text{void}} > -1.5$ MPa in water). In the majority of these studies, the material separating the liquid and the vapor was a porous solid. To our knowledge, the earliest such experiments were aimed at verifying the cohesion–tension theory of transpiration in plants: water was allowed to evaporate from a porcelain cup attached to a water-filled glass tube. Pressure was measured directly via the rise of mercury against gravity up the other end of the tube; the lowest pressure reported was $-0.1$ MPa. A more recent study, a soil tensiometer was formed with a nanoporous, ceramic membrane. Pressure was measured in the liquid-filled voids via a pressure transducer; the lowest pressure reported was $-1.25$ MPa. A third system, designed to study liquids at negative pressures, used a tube formed of nanoporous Vycor glass. The sealed, porous tube was filled with liquid butane and was exposed to atmospheres containing subsaturated butane vapor. Pressure was estimated as described above and in the Theory section below (eq 6), based on the activity of the vapor. This system reached $-4$ MPa, a pressure that was comparable to the predicted maximum Laplace pressure ($P_{\text{cap}} = -5.9$ MPa) set by the size of the pores and the surface tension of butane. The author reported several difficulties associated with using capillarity in nanoscale pores to generate negative pressures: refilling an

emptied network of nanoscale pores required several days, and the nanoporous glass would often fracture during refilling or during use. The tendency to fracture increased when the pores were filled with liquids having higher surface tension, such as water.

The failure of these experiments to generate large tensions in water with porous, solid membranes points to an inherent weakness of this approach: to generate negative pressures in liquid water via capillarity, the membrane must have pores with radius \( r_p < \sim 1.5 \mu m \) if perfectly wetted by water (from the Young–Laplace equation, \( \Delta \mu = \sigma (1/2r_p - P/\rho) \) when \( r_p < \sim 1.5 \mu m \), \( \Delta \mu = 0.1 \text{MPa}, \sigma = 0.072 \text{ (N m}\^{-1}) \) is the surface tension of water). The material must also have a sharp upper cutoff in the distribution of pore sizes and be free of defects: if there is a single pore that is greater than \( \sim 1.5 \mu m \) in radius, or if there are fractures in the material that result in pores of this dimension, the meniscus will recede through this path before negative pressures are achieved. These challenges motivated our use of a chemically cross-linked, polymeric hydrogel as an alternative to a porous solid to act as the membrane in VCVs. The primary advantage of hydrogels for this application is that the molecular-scale mixing of the water with the host polymer provides significant thermodynamic stabilization of the water, such that the material can maintain hydration and mobility of water when equilibrated with vapors of arbitrarily low activity. Hydrogels, thus, do not suffer from the precipitous drop in permeability to water and the invasion of air that are seen in porous materials. That set a precedent for this approach with his work on capillary rise in glass tubes coupled to ceramic cups; he demonstrated that coating the ceramic cup with a physically cross-linked hydrogel increased the maximum height to which water rose relative to the uncoated ceramic and improved the reproducibility of results. He reported a minimum pressure of \( \sim 0.20 \text{MPa} \), twice the minimum pressure obtained for uncoated ceramics.

**Summary of Article.** The primary goals of this work are to (1) determine the limit of stability of liquid water in VCVs defined in hydrogels and (2) ascertain the most likely mechanisms of cavitation of water in VCVs. After a summary of experimental methods, we describe the mechanism by which equilibration of a liquid with a subatmospheric vapor generates negative pressures, and we develop a thermodynamic theory for predicting these pressures. We then discuss the two limiting cases of the nature of a hydrogel membrane that can mediate this coupling: a molecular-scale mixture of water and polymer and a porous material in which pure liquid water resides in nanoscale pores. Following this discussion, we summarize the kinetic theory of homogeneous nucleation used to interpret cavitation experiments and other possible mechanisms of cavitation. We then describe experiments performed to ascertain the possible influence of several nonhomogeneous mechanisms of cavitation (summarized in Figure 2) on the observed limit of stability of water in VCVs and interpret the results of these experiments. We conclude with a discussion of the implications of generation of negative pressures by this strategy for the study of liquid water.

**Experimental Methods**

**Materials and Instruments.** Ethylene glycol dimethacrylate (EGDMA), methacrylic acid (MAA), acrylic acid (AA), 2,2-dimethoxy-2-phenylacetophenone (DMAP), magnesium sulfate, heptadecahydrate (MgSO₄·7H₂O), and potassium sodium tartrate (KNa Tartrate) were purchased from Acros Organics (Geel, Belgium). 2-Hydroxyethyl methacrylate (HEMA) and 1- vinyl-2-pyrrolidone (nVP) were purchased from Sigma-Aldrich (St. Louis, MO). Potassium sulfate (K₂SO₄), sodium phosphate, dibasic, heptadecahydrate (Na₂HPO₄·7H₂O), sodium citrate (Na citrate), potassium carbonate (K₂CO₃), magnesium chloride (MgCl₂), and ammonium sulfide (NH₄Cl) were obtained from Fisher Scientific (Fair Lawn, NJ). Potassium chloride (KCl) and sodium chloride (NaCl) were obtained from Mallinkrodt (Hazelwood, MO). (Tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane was obtained from Gelest, Inc., Morrisville, PA). Sylgard 184, a thermally curable poly(dimethylsiloxane) (PDMS), was obtained from Dow Corning (Midland, MI). SU-8 2100 was obtained from MicroChem Corp. (Newton, MA). Silicon wafers were obtained from Wafer Works Corp. (http://www.waferworks.com/index_en.php). A Fisherbrand Mini vortexer used in VCV fabrication, Fisherbrand microscope slides (75 × 50 mm), Parafilm M, glass vials (15 mL), disposable Fisherbrand Petri dishes (95 × 15 mm), Bitran SX 6 in. × 6 in. × 6 in. storage bags, Precision Econotherm oven, and Mettler Toledo AL204 analytical balance were obtained from Fisher Scientific (Fair Lawn, NJ). A Harrick Model PDC-001 plasma cleaner was obtained from Harrick Plasma (Ithaca, NY). Sylgard 184, a Leica MZFLIII stereo microscope (Leica Microsystems GmbH, Wetzlar, Germany) and a QImaging Retiga 1300 camera (Qimaging, Surrey, Canada) were used. Equilibrium contact angles were measured with a VCA Optima XE goniometer (Advanced Surface Technology Products, Inc., Billerica, MA), and dynamic contact angles were measured with a Cahn DCA-315 (Thermo Fisher Scientific, Inc., Waltham, MA). Elastic moduli were measured using a Perkin-Elmer DMA 7e (Perkin-Elmer, Inc., Waltham, MA), Spectra Max Plus 384 (Molecular Devices, Inc., Sunnyvale, CA) was used to measure the UV–vis spectra of water. A Spectroline XX-15A UV lamp with a wavelength of 365 nm was obtained from Fisher Scientific and used to initiate photopolymerization of hydrogel samples.

**Hydrogel Composition.** The compositions of hydrogels used in experiments are summarized in Table 1. Prior to hydrogel casting and polymerization, a solution of radical initiator (DMAP in nVP, 600 mg/mL) was added to the monomer solution at 1% [v/v], with respect to the total volume of the monomer solution (100 μL of initiator solution were added to 10 mL of monomer solution). A Spectroline XX-15A UV lamp with a wavelength of 365 nm was obtained from Fisher Scientific and used to initiate photopolymerization of hydrogel samples.

**Fabrication of Spherical VCVs.** The fabrication of spherical VCVs is described in detail in the Supporting Information of ref 6. Briefly, hydrogel solution that contained bubbles of air was injected between two glass slides held apart by spacers and wrapped in Parafilm. The solution was then polymerized by irradiation with UV light while under nitrogen. The spherical voids obtained with this fabrication method had diameters between 50 and 300 μm. The voids were filled by soaking in boiling deionized water (which also extracted unreacted monomer) or by pressurization, as described in the Pressurization of VCVs section.

**Fabrication of Microchannel VCVs.** This form of void was only fabricated and tested for formulation A (Table 1). The fabrication process used to create microchannel VCVs is described in detail in the Supporting Information of ref 6. Briefly, the microchannels were defined in the hydrogel material using a soft lithographic technique. The pattern (81 parallel rectangles, 50 μm × 5 cm, center-to-center distance of 250 μm) was first defined using standard photolithography techniques in an SU-8 layer (100-μm-thick) spun onto a silicon wafer, then transferred to a PDMS stamp through casting of the elastomer over the SU-8 master, and finally transferred to the hydrogel through cavi-
Prepressurization of VCVs. The pressurization of samples was conducted in an OC-3 high-pressure vessel (High Pressure Equipment Co., Erie, PA) with samples submerged in deionized water. Two means of applying pressure were used: a cylinder of nitrogen gas (Airgas, Radnor, PA) for pressurization up to 18 MPa and a piston screw pump, model 37-6-30 (High Pressure Equipment Co., Erie, PA) with samples submerged in deionized water. The salt solution was then exchanged for the solution corresponding to an activity of water vapor of 0.75 in a Petri dish, as described in the Prepressurization of VCVs section. Following depressurization, samples were soaked in deionized water for at least 2 h to allow the concentration of dissolved gases in the liquid within VCVs to equilibrate with ambient conditions.

Equilibration with Subsaturated Water Vapor. A detailed description of the means by which water within VCVs was equilibrated with subsaturated water vapor can be found in the Supporting Information of ref 6. Briefly, saturated salt solutions were used to control the activity of the water vapor, \( a_{\text{vw,subsat}} \), in an enclosed volume of air (a Petri dish wrapped with Parafilm and placed in a plastic storage bag). Samples of hydrogel containing VCVs were then placed in this enclosed volume. Equilibration experiments were conducted at room temperature: 21.6 ± 0.7 °C.

Drying and Equilibration Time. In order for the estimate of the pressure present in a VCV used in this work (eq 6) to be valid, the time required for the hydrogel samples to completely equilibrate with the subsaturated vapors had to be allowed to pass. The generation of negative pressures is linked to the transfer of water from the hydrogel sample ceases. It is therefore possible to determine when negative pressures are fully developed by measuring the time it takes for the mass of the sample to stabilize. To determine this time, samples of hydrogel material A were exposed to an atmosphere of water vapor of 0.75 in a Petri dish, as described in the Equilibration with Subsaturated Water Vapor section. The samples had the same dimensions as those used to determine the probability of cavitation (~1.5 cm × ~3 cm × 1 mm). Three samples were allowed to equilibrate with the vapor for a period of 7 days. The mass of each sample was monitored over time to determine the time it takes for the mass of the sample to stabilize. To determine this time, samples of hydrogel material A were exposed to an atmosphere of water vapor of 0.75 in a Petri dish, as described in the Supporting Information of ref 6. The salt solutions used to control the activity of water vapor at 0.75 were potassium carbonate and magnesium chloride, respectively. The measurement of equilibrium water content proceeded as follows: beginning with the highest water vapor activity, four samples (disks with diameters of ~22 mm and thicknesses of ~250 μm) of each material were placed in Petri dishes containing pads soaked with salt solution and weighed using an analytical balance until the mass measurements were within 0.003 g of preceding measurements. The salt solution was then exchanged for the solution corresponding to the next lowest water vapor activity, and the mass of each sample was monitored until subsequent measurements were within 0.003 g of preceding measurements. To obtain the dry weight of the hydrogel samples, \( m_p \) [g], samples were baked in an oven at 65 °C until the weights of the samples were within 0.003 g of preceding measurements. Reported values of equilibrium water content are averages and standard deviations of volume fractions, \( \phi_w \), calculated for the four samples of each material using the equation:

\[
\phi_w = \frac{(m_T - m_p)/\rho_w}{(m_T - m_p)/\rho_w + m_p/\rho_p}
\]  

where \( m_T \) is the mass of the sample in the tank, \( m_p \) is the mass of the sample in the Petri dish, and \( \rho_w \) and \( \rho_p \) are the densities of water and polyurethane, respectively.

Measurement of Contact Angles. The equilibrium, advancing, and receding contact angles for deionized water on samples of each hydrogel material used in experiments using the theory developed by Flory. In this application, the Flory interaction parameter, \( \chi \), of the hydrogel materials used in experiments was determined using the equation given in ref 6, for the four samples of each material using the equation:

\[
\phi_w = \frac{(m_T - m_p)/\rho_w}{(m_T - m_p)/\rho_w + m_p/\rho_p}
\]  

The values of the shear moduli reported in Table 2 are averages and standard deviations of three measurements of three samples, for a total of nine measurements.
Equilibrium volume fractions of polymer in the hydrogels, $\phi$, were determined for several water vapor activities, $a_{w,vap}$, and the shear modulus, $G$, was calculated from elastic modulus measurements (assuming a Poisson ratio $\nu = 0.5$). In eq 2, $V_{w,liq}$ was taken to be $1.8 \times 10^{-2}$ m$^3$ mol$^{-1}$. The results of this calculation are presented in Figure 5. Values of $\chi$ at saturation (i.e., when the hydrogel is in equilibrium with $a_{w,vap} = 1$), reported in Table 2, were used to determine the mesh size of the polymer network of each hydrogel material.

**UV–vis Detection of Solutes Released by Cross-Linked Hydrogels.** The purity of water entrapped in voids fabricated in sheets of hydrogel material A was tested indirectly by measuring the purity of the deionized water in which samples were soaked during filling. Inherent to this method, was the assumption that the composition of the water in the voids was the same as the composition of the water in which the samples were soaked. The validity of this assumption was determined by examining the UV–vis spectrum of the soaking water over time. These spectra are shown in Figure 6A. The spectra used to assess the purity of the water within VCVs are shown in Figure 6B. To ensure the detection of dissolved impurities, a volume of 100 mL of soaking water was used for these experiments, in contrast to the 1 L used during the fabrication process, so that the final concentration of dissolved species would be higher in these tests than in the preparation for experimental samples. Soaking water lost due to evaporation was replenished prior to each measurement, and 2 mL was removed for analysis. UV–vis spectra were obtained using a Spectra Max Plus 384 spectrometer.

**Conversion of Monomer.** To estimate the concentration of solute present in the water within VCVs immediately after fabrication, the conversion of monomers by the polymerization reaction by which the hydrogels were formed was measured. This measurement was made by weighing dry samples of each hydrogel formulation immediately after synthesis and again after 4 days of soaking in boiling, deionized water. Samples were dried by baking at 65 °C in a Precision Econotherm oven until the measured weight was constant (consecutive measurements were within 0.003 g). Three samples, one of each formulation, were soaked in 1 L of boiling water. The soaking water was exchanged with fresh water twice each day. During this soaking period of 4 days, we assumed that unreacted monomer was completely extracted from the hydrogel samples. The mass of each sample after soaking

Figure 3. Observation of voids in hydrogel sheets. (A) Optical micrographs showing several spherical voids within a hydrogel membrane. The top image shows voids that are full of water in equilibrium with $a_{w,vap} = 1.00$. The bottom image shows the same voids after 7 days of equilibration with $a_{w,vap} = 0.85$. A distinct change in appearance is seen between voids in which water has cavitated; full voids have a bright center and empty voids have a dark center. Scale bars represent 500 μm. (B) Optical micrographs of microchannel-shaped VCVs before and after equilibration with $a_{w,vap} = 0.85$, as in (A). A distinct difference in appearance is seen between full and empty voids. Scale bars represent 500 μm.

Figure 4. Drying curve for hydrogel material A. Normalized mass (with respect to initial mass) of three samples measured over time while the samples equilibrated with an atmosphere of water activity $a_{w,vap} = 0.75$. Error bars represent the standard deviation of mass measurements of three samples.

where $m_T$ [g] is the total mass measured at each activity, $m_P$ [g] is the mass of polymer component, $\rho_w$ [g cm$^{-3}$] is the density of water, and $\rho_p$ [g cm$^{-3}$] is the density of the polymer and equal to 1.274 g cm$^{-3}$. The polymer volume fraction, $\phi_p$, is given by $\phi_p = 1 - \phi_w$.

Values of the Flory interaction parameter, $\chi$, were calculated using the equation

$$\ln(a_{w,vap}) = \ln(1 - \phi_p) + \phi_p + \chi \phi_p^2 + \frac{V_{w,liq} G}{R T} \left( \phi_p^{2/3} - \frac{\phi_p}{2} \right)$$

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Figure 3. Observation of voids in hydrogel sheets. (A) Optical micrographs showing several spherical voids within a hydrogel membrane. The top image shows voids that are full of water in equilibrium with $a_{w,vap} = 1.00$. The bottom image shows the same voids after 7 days of equilibration with $a_{w,vap} = 0.85$. A distinct change in appearance is seen between voids in which water has cavitated; full voids have a bright center and empty voids have a dark center. Scale bars represent 500 μm. (B) Optical micrographs of microchannel-shaped VCVs before and after equilibration with $a_{w,vap} = 0.85$, as in (A). A distinct difference in appearance is seen between full and empty voids. Scale bars represent 500 μm.

Figure 4. Drying curve for hydrogel material A. Normalized mass (with respect to initial mass) of three samples measured over time while the samples equilibrated with an atmosphere of water activity $a_{w,vap} = 0.75$. Error bars represent the standard deviation of mass measurements of three samples.

where $m_T$ [g] is the total mass measured at each activity, $m_P$ [g] is the mass of polymer component, $\rho_w$ [g cm$^{-3}$] is the density of water, and $\rho_p$ [g cm$^{-3}$] is the density of the polymer and equal to 1.274 g cm$^{-3}$. The polymer volume fraction, $\phi_p$, is given by $\phi_p = 1 - \phi_w$.

Values of the Flory interaction parameter, $\chi$, were calculated using the equation

$$\ln(a_{w,vap}) = \ln(1 - \phi_p) + \phi_p + \chi \phi_p^2 + \frac{V_{w,liq} G}{R T} \left( \phi_p^{2/3} - \frac{\phi_p}{2} \right)$$

Equilibrium volume fractions of polymer in the hydrogels, $\phi_p$, were determined for several water vapor activities, $a_{w,vap}$, and the shear modulus, $G$, was calculated from elastic modulus measurements (assuming a Poisson ratio $\nu = 0.5$). In eq 2, $V_{w,liq}$ was taken to be $1.8 \times 10^{-2}$ m$^3$ mol$^{-1}$. The results of this calculation are presented in Figure 5. Values of $\chi$ at saturation (i.e., when the hydrogel is in equilibrium with $a_{w,vap} = 1$), reported in Table 2, were used to determine the mesh size of the polymer network of each hydrogel material.

**UV–vis Detection of Solutes Released by Cross-Linked Hydrogels.** The purity of water entrapped in voids fabricated in sheets of hydrogel material A was tested indirectly by measuring the purity of the deionized water in which samples were soaked during filling. Inherent to this method, was the assumption that the composition of the water in the voids was the same as the composition of the water in which the samples were soaked. The validity of this assumption was determined by examining the UV–vis spectrum of the soaking water over time. These spectra are shown in Figure 6A. The spectra used to assess the purity of the water within VCVs are shown in Figure 6B. To ensure the detection of dissolved impurities, a volume of 100 mL of soaking water was used for these experiments, in contrast to the 1 L used during the fabrication process, so that the final concentration of dissolved species would be higher in these tests than in the preparation for experimental samples. Soaking water lost due to evaporation was replenished prior to each measurement, and 2 mL was removed for analysis. UV–vis spectra were obtained using a Spectra Max Plus 384 spectrometer.

**Conversion of Monomer.** To estimate the concentration of solute present in the water within VCVs immediately after fabrication, the conversion of monomers by the polymerization reaction by which the hydrogels were formed was measured. This measurement was made by weighing dry samples of each hydrogel formulation immediately after synthesis and again after 4 days of soaking in boiling, deionized water. Samples were dried by baking at 65 °C in a Precision Econotherm oven until the measured weight was constant (consecutive measurements were within 0.003 g). Three samples, one of each formulation, were soaked in 1 L of boiling water. The soaking water was exchanged with fresh water twice each day. During this soaking period of 4 days, we assumed that unreacted monomer was completely extracted from the hydrogel samples. The mass of each sample after soaking
was divided by the mass of each sample before soaking to obtain the mass conversion of the monomer for each formulation.

Determination of Probability of Cavitation. After 7 days of equilibration with the activities established by the saturated salt solutions, micrographs of the VCVs were taken using a stereoscope and a CCD camera. Examples of images used to determine the probability of cavitation for a given water vapor activity are shown in Figure 3A for spherical voids and in Figure 3B for microchannel voids. Bright VCVs (still containing water) and dark VCVs (no longer containing water) were counted in these micrographs to determine the probability of cavitation (probability = number of dark voids/total number of voids). Roughly 100 voids were observed in each hydrogel sample. The experiments for the probability of cavitation of water in spherical voids in hydrogels made using formulation A were performed with five samples (n \(\geq\) 500 voids) and repeated three times for samples that had been soaked for 2 days (Figures 7–10) and repeated two times for samples that had been soaked for 5 months (Figure 9). For formulations B and C (Figure 8), 100 or more voids in three or more samples (for a total of n \(\geq\) 300 voids) were observed at each activity to generate data for the probability of cavitation. For microchannel voids in samples made using formulation A, 81 or more voids in three samples (for a total of n \(\geq\) 243 voids) were observed at each activity to generate data for the probability of cavitation (Figure 10).

Theory

Coupling of Liquid Water to Its Vapor via a Semipermeable Membrane. We begin with the analysis of the membrane-mediated, thermodynamic equilibrium between a liquid solution of water and water vapor in air. In Figure 1B,C, a membrane separates liquid water contained in a spherical void and water vapor contained in the air. We assume that the membrane is semipermeable: it allows passage of liquid water, but not of water vapor or the other gases in air. In the next subsection, we will consider the characteristics of the membrane that are required to achieve this selectivity in more detail.

Table 2. Hydrogel Characteristics

<table>
<thead>
<tr>
<th>formulation</th>
<th>(\theta_{a,w}(\text{deg})) (n = 10)</th>
<th>(\theta_{a,v}(\text{deg})) (n = 9)</th>
<th>(\Delta G_{\text{a,v}}(\text{deg})) (n = 9)</th>
<th>(G(\text{MPa})) (n = 3)</th>
<th>(z_S)</th>
<th>(d(\text{nm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>40.3 ± 3.6</td>
<td>24.7 ± 0.6</td>
<td>65.2 ± 3.2</td>
<td>1.28 ± 0.15</td>
<td>0.94</td>
<td>2.3</td>
</tr>
<tr>
<td>B</td>
<td>44.6 ± 4.5</td>
<td>18.1 ± 1.2</td>
<td>53.9 ± 1.2</td>
<td>50.3 ± 7.2</td>
<td>0.23</td>
<td>0.4</td>
</tr>
<tr>
<td>C</td>
<td>13.4 ± 1.8</td>
<td>0.4 ± 0.9</td>
<td>57.2 ± 3.0</td>
<td>1.10 ± 0.08</td>
<td>0.95</td>
<td>2.5</td>
</tr>
</tbody>
</table>

*Uncertain values due to the potential invalidity of Flory thermodynamics.

The chemical potential of liquid water in the void shown in Figure 1B is

\[
\mu_{w,\text{liq}}^{\text{void}}(T, P_{\text{void}}) = \mu_0(T) + \int_{P_{\text{atm}}}^{P_{\text{void}}} \hat{\mu}_{w,\text{liq}}(P, T) \, dP + RT \ln(\alpha_{w,\text{liq}}^{\text{void}}) \tag{3}
\]

where \(\mu_0(T)\) is the chemical potential of water at atmospheric pressure and temperature, \(T\), \(P_{\text{void}}\) is the pressure of the liquid water in the void, \(R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}\) is the ideal gas constant, and \(\alpha_{w,\text{liq}}^{\text{void}}\) is the activity (equal to the mole fraction in dilute solutions) of the liquid water in the void. The chemical potential of the water vapor in the air at atmospheric pressure \(P_{\text{air}} = P_{\text{atm}}\) is

\[
\mu_{w,vap}^{\text{air}}(T, \alpha_{w,vap}^{\text{air}}) = \mu_0(T) + RT \ln(\alpha_{w,vap}^{\text{air}}) \tag{4}
\]

where \(\alpha_{w,vap}^{\text{air}} = [P_{w,vap}/P_{w,sat}(T)] = (\text{relative humidity})/100\) is the activity of the water vapor in the air, assuming ideality. At equilibrium (stable or metastable), we have

\[
\mu_{w,\text{liq}}^{\text{void}} = \mu_{w,vap}^{\text{air}} \tag{5}
\]

where \(\mu_{w,\text{liq}}^{\text{void}}\) and \(\mu_{w,vap}^{\text{air}}\) are given by eqs 3 and 4, respectively. As in conventional osmotic equilibrium between pure solvent and solution, the imbalance in activities between the two phases is compensated by a stress; in this case, a deviation in the pressure in the liquid phase from the standard pressure. To solve for the “osmotic” pressure difference between the two phases, \(\Pi \equiv P_{\text{air}} - P_{\text{void}} = P_{\text{atm}} - P_{\text{void}}\); obtained from eqs 3, 4, and 4, we assume that the liquid is inextensible: \(V_{w,\text{liq}}(T) \sim \text{constant}\) over the range of the integral in eq 3. On the basis of the extrapolations of two equations of state of water (HGK41 and Speedy47), this assumption is accurate to within 1% at room temperature for 0.1 MPa \(\geq P_{\text{void}} \geq -25\) MPa. With this assumption, we find

\[
\Pi = P_{\text{atm}} - P_{\text{void}} = -\frac{RT}{V_{w,\text{liq}}} \ln\left(\frac{\alpha_{w,vap}^{\text{air}}}{\alpha_{w,\text{liq}}^{\text{void}}}\right) \tag{6}
\]

Importantly, eq 6 predicts that the pressure of the liquid within the void decreases rapidly as the degree of saturation of the vapor increases: for pure liquid water \((\alpha_{w,\text{liq}}^{\text{void}} = 1)\), \(P_{\text{void}} = P_{\text{atm}} - \Pi < 0\) for \(\alpha_{w,vap}^{\text{air}} < 0.99925\), at room temperature. We also note the expression for the osmotic pressure in eq 6 is the same is that found for two solutions with solvent activities \(\alpha_{w,1}\) and \(\alpha_{w,2}\) in conventional osmosis (\(\Pi = -RTV_{w,\text{liq}} \ln(\alpha_{w,1}/\alpha_{w,2})\)).

From a dynamic perspective, the equilibrium between a liquid at reduced pressure and a subsaturated vapor arises as follows: water evaporating from the surface of the membrane into the subsaturated atmosphere is replenished by liquid water drawn from the void. As the volume of liquid water in the void decreases,

the adhesion between molecules of water and molecules of the hydrogel material surrounding the water causes the void to contract (isotropically in the case of a spherical void). A restoring force exerted by the membrane material resists this contraction, and as a result, the pressure in the liquid, \( P_{\text{void}} \), decreases below \( P_{\text{atm}} \). Once equilibrium is reached, the transfer of water from the void to the air ceases, and a mechanical balance between the reduced pressure in the liquid in the void, \( P_{\text{void}} = P_{\text{atm}} - \Pi \) (solid red arrows in Figure 1C), and the restoring force exerted by the hydrogel material (dashed red arrows in Figure 1C) prevents the further collapse of the void.

Characteristics of Osmotic Membranes for Vapor–Liquid Equilibrium. We consider two limiting cases of membrane structures that can mediate equilibrium between a liquid and a subsaturated vapor in this context: First, a homogeneous, molecular-scale mixture of polymer and water (illustrated in the left-hand inset of Figure 1B), as described by Flory. Such a material cannot be fully invaded by air without phase separation of the water and the polymer to form pores through which the gas could pass. For this case, a balance of the chemical potential of...
water in each of the three phases—air, membrane, and void—describes equilibrium: \( \mu_{w,\text{air}} = \mu_{w,\text{gel}} = \mu_{w,\text{vap}} \), where
\[
\mu_{w,\text{gel}} = \mu_0(T) + RT \left[ \ln(1 - \phi_p) + \phi_p + \chi \phi_p^2 + \frac{V_{w,\text{liq}} G}{RT} \left( \frac{\phi^{1/3} - \phi_p}{2} \right) \right]
\]  

An advantage of this perspective is that the thermodynamic behavior of water within a hydrogel can be predicted using eq 7 and independently measured values of \( \gamma \) and \( G \); this capability provides a means of selecting appropriate hydrogel materials a priori.

Second, a porous material with distinct solid and water phases with pores sufficiently small to prevent menisci from receding into the material once reduced pressures are present in the water (illustrated in the right-hand inset of Figure 1B). Such a wettable porous solid with its associated menisci can act as a semipermeable “membrane” in its role as a mediator of equilibrium between the water in the nanoscale pores required to generate negative pressures in the air is described by the Kelvin–Young–Laplace equation:
\[
\ln(\alpha_{w,\text{vap}}) = \left( \frac{V_{w,\text{liq}} G}{RT} \right) \frac{2 \cos \theta}{r_p} = \left( \frac{V_{w,\text{liq}} G}{RT} \right) P_{\text{cap}}
\]

where \( \sigma \) [N m\(^{-1}\)] is the surface tension of water, \( \theta \) [rad] is the contact angle of water with the pore wall, \( r_p = d/2 \) [m] is the radius of the pore, and \( P_{\text{cap}} \) is the Laplace pressure difference across the meniscus. We note that this treatment ignores the possibility of corrections due to disjoining pressures at the liquid–pore interface and of changes in the surface tension relative to its macroscopic value in nanoscale pores. Thus, the primary disadvantage of this perspective is that the equilibrium behavior of water in the nanoscale pores required to generate negative pressures may not be accurately described by the Kelvin–Young–Laplace equation. Nonetheless, hydrogels have been treated both as porous materials and as molecular-scale mixtures in the literature. We therefore consider both perspectives when discussing hydrogels in this study.

Kinetic Theory of Homogeneous Nucleation of Cavitation. In this section, we summarize the kinetic theory of homogeneous nucleation and the use of this theory to obtain a prediction of the kinetic stability limit of water from experiments that measure the probability of cavitation in VCVs of volume $V$ [m$^3$] after a fixed interval of time $\tau$ [s]. We follow the development presented by Herbert et al.\textsuperscript{15} (also presented, in more detail than below, in the Supporting Information of ref 6): the homogeneous nucleation of vapor nuclei occurs in the bulk of the liquid phase from a population of vapor nuclei that forms when the liquid is superheated. The size of each individual nucleus in this population fluctuates due to thermal perturbations of the system. Once the size of an individual nucleus reaches a critical value it will continue to expand and cavitation will occur. To induce cavitation, a thermal fluctuation of sufficient energy to overcome a barrier of activation must occur; this barrier is associated with the work required to expand the surface of a nucleus to a critical size and is given by

$$E_b(P_{\text{void}}) = \frac{16\pi\alpha^3}{3(p_{w,\text{sat}} - P_{\text{void}})^2}. \quad (9)$$

The probability that a cavitation event will occur during an experiment performed in volume $V$ and over time $\tau$ is given by

$$\Sigma(P) = 1 - \exp\left\{-\ln 2 \exp\left[\xi \left(\frac{P_{\text{void}}}{P_{\text{cav}}} - 1\right)\right]\right\} \quad (10)$$

where the steepness factor of the curve, $\xi$, is given by

$$\xi = 2\ln \left(\frac{\Gamma_0 V \tau}{ln 2}\right) \quad (11)$$

$\Gamma_0$ [s$^{-1}$ m$^{-3}$] is the product of the number density of nucleation sites and the frequency of nucleation attempts and can be approximated by

$$\Gamma_0 = \left(\frac{4}{3}\pi R_C^3\right)^{-1} k_B T \quad (12)$$

where $T$ is the absolute temperature, $k_B$ is Boltzmann’s constant, $\hbar$ is Planck’s constant, and $R_C$ is the critical radius of a vapor bubble at which the bubble will continue to grow spontaneously.

The probability of cavitation reaches 1/2 at the cavitation pressure

$$P_{\text{cav}} = p_{w,\text{sat}} - \left(\frac{16\pi\alpha^3}{3k_B T \ln(\Gamma_0 V \tau/ln 2)}\right)^{1/2}. \quad (13)$$

To determine the cavitation pressure of water in VCVs, eqs 11 and 12 were used to calculate $\xi$, with $V$ taken to be the volume of a void and $\tau$ taken to be the time of equilibration. Data from cavitation probability experiments were then fit to eq 10, using $P_{\text{cav}}$ as the only adjustable parameter. We note the logarithmic dependence of $P_{\text{cav}}$ on $\Gamma_0 V \tau$; because of this weak dependence, the use of approximate values for these constants does not significantly impact our analysis.

Results and Discussion

Purity of Water in VCVs. The spectra displayed in Figure 6A are from samples of water removed from the soaking vessel after 3 h, 1 day, and 2 days of soaking. The increase in the height of the peaks from 3 h to 1 day indicates an increase in the concentration of extracted solute over this period of soaking. The peak height of the spectra for 1 and 2 days are roughly the same, indicating that minimal extraction occurred after day 1. From this indication of equilibrium, we concluded that the concentration of solutes in the soaking water and in the water within VCVs were equal after 1 day of soaking.

The presence of peaks in the spectra of the soaking water that were absent from the spectrum of deionized water (shown in Figure 6B) suggests the presence of a solute. The presence of solute in the water within VCVs would lower the chemical potential of the water and thus modify the prediction of the pressure in the void based on eq 6. For $a_{w,\text{void}} < 1$, the magnitude of osmotic pressure, $\Pi$, would be reduced relative to the value of $\Pi$ predicted for pure liquid in the void ($a_{w,\text{void}} = 1$) by $-RT/P_{\text{void}} \ln(a_{w,\text{void}})$, resulting in a higher (less negative) predicted value of $P_{\text{void}}$ in eq 6. The solute that was most likely to be present at concentrations that were high enough to affect the chemical potential of water within the voids was unreacted monomer (HEMA) because its initial concentration was highest. However, the differences in the peaks observed in the spectra of soaking water and those of 0.1 and 1 vol % solutions of HEMA in deionized water (shown in Figure 6B) indicate that other solutes, such as short polymer chains or ethylene glycol (formed by the hydrolysis of HEMA ester bonds during boiling), may also have been present.

The mass conversions of monomer for the polymerization reaction were 0.98 for formulation A, 0.97 for formulation B, and 0.98 for formulation C. During the filling/extraction step of the VCV fabrication process, ~1 g of hydrogel sample (corresponding to five 1 cm x 1.5 cm samples containing spherical voids or one sample containing microchannel voids) was boiled in water at a time. Using this mass of hydrogel as a basis, a conversion of 0.97 would result in 0.03 g of unreacted monomer. Assuming the molecular weight of the unreacted monomer is on the order of 100 g/mol (the molecular weight of HEMA is 130 g/mol and the molecular weight of MAA is 86 g/mol), the amount of unreacted monomer is $\sim 3 \times 10^{-3}$ mol. Assuming that the concentration of solute within VCVs has equilibrated after 2 days of boiling, this amount of monomer is diluted by 1 L of water (the volume of soaking water used to fill the VCVs), giving a mole fraction $x_{\text{solute}} = 5.4 \times 10^{-6}$ mol of solute/total moles. Further assuming that the concentration behaves ideally such that $a_{w,\text{void}} = 1 - x_{\text{solute}}$, the extent to which the presence of this mole fraction of solute reduces the magnitude of the negative pressure generated in experiments, relative to the prediction of eq 6, is $-7.3 \times 10^{-4}$ MPa. From this calculation, we conclude that the concentration of unreacted monomer is too low to significantly affect the predicted pressures generated in our experiments.

Stability of Water at Negative Pressure in VCVs. The probability of cavitation of water in spherical VCVs fabricated using hydrogel formulation A, and equilibrated with the water vapor activities established by several saturated salt solutions, is shown in Figure 7. The pressures corresponding to each water vapor activity, calculated with eq 6, are shown in the top, horizontal-axis. Near $a_{w,\text{vap}} = 0.849 \pm 0.005$ (eq 6), the probability of cavitation undergoes an abrupt transition. The shape of this transition suggests consistency with the prediction of the kinetic model of homogeneous nucleation (eq 10); eq 10 was fit to the data to generate the solid trend line, with cavitation pressure $P_{\text{cav}} = -22.01$ MPa as a best fit value of the only free parameter. Because of the paucity of data near the cavitation threshold it was not possible to obtain well-defined values of $\xi$ through a two-parameter fit of eq 10. Therefore, eqs 11 and 12 were used to calculate $\xi = 151.17$, with the following values: $R_C = 1$ nm, $T = 294.5$ K, $V = 5.24 \times 10^{-13}$ m$^3$ (calculated using the order of magnitude of the diameter of the voids, 100 $\mu$m), and $\tau = 604800$ s (corresponding to the 1 week
period of equilibration). The observed conformity of the data to the kinetic model, in particular the abruptness of the threshold, indicates that cavitation in the VCVs is consistent with thermally activated nucleation of the vapor phase in the bulk of the liquid or at its boundaries. Cavitation due to the presence of impurities, such as dissolved molecules, surfactants, and pre-existing nuclei, seems unlikely because, in those cases, one would expect dependence of the cavitation pressure imposed by these impurities on concentration or size distribution. The variability in concentration and size distribution of impurities inherent to most systems would result in a less abrupt cavitation transition (see Mechanism (iii): Nucleation by Pre-Existing Vapor Nuclei). A plot of eq 10 using the values for $\xi$ and $P_{\text{cav}}$ obtained by Herbert et al. is also shown in Figure 7 for comparison. The value of the cavitation pressure obtained in VCVs is within 10% of the cavitation pressure obtained by Herbert et al. However, it is significantly less negative than the stability limits for homogeneous nucleation predicted by eq 13 ($\sim 184$ MPa) and other theories and the stability limit calculated by Zheng et al., based on the isochoric cooling of liquid water entrapped in quartz inclusions. We proceed, therefore, to consider other mechanisms of cavitation that could result in the less negative stability limit.

Other Mechanisms of Cavitation. In the following sections, we discuss other mechanisms that could potentially disrupt the stability of liquid water in VCVs and lead to the observed emptying of the voids. These mechanisms can result in cavitation at negative pressures above the homogeneous, kinetic stability limit (estimated by eq 13). The mechanisms of cavitation we consider in this study are illustrated in Figure 2A–C. They include (i) heterogeneous nucleation of the vapor phase facilitated by hydrophobic moieties at the hydrogel–water interface, (ii) nucleation of the vapor phase facilitated by solutes or gases dissolved in the liquid, (iii) growth of the vapor phase from a pre-existing vapor nucleus trapped in a crevice in the wall of the VCV or on a suspended particle, and (iv) entrance of air into the VCV due to the invasion of a meniscus through the membrane and into the void.

Mechanism (i): Heterogeneous Nucleation. This mechanism can occur if the local or global surface chemistry of the wall of the VCV is such that molecules in the hydrogel interact less strongly with water molecules than water molecules interact with each other. This situation will occur if the walls of the VCV, or patches on the walls (Figure 2A), are not sufficiently hydrophilic (the contact angle of water with the surface is too large) due to the presence of hydrophobic moieties. Negative pressures in the liquid will facilitate the failure of adhesion between the liquid phase and the wall, resulting in the formation of vapor nuclei that can initiate cavitation if they reach a critical size, as in homogeneous nucleation. Although the hydrogel materials used in VCV systems are hydrophilic (equilibrium contact angle, $\theta_{\text{eq}} < 90^\circ$), the use of organic polymers in their synthesis guarantees that some hydrophobic groups (e.g., ethyl groups in HEMA) will be present in the system. This assumption is supported by the nonzero contact angles of water measured on the hydrogels (Table 2).

The kinetic theory for homogeneous nucleation can be extended to describe the heterogeneous nucleation of the vapor phase at a smooth rigid surface, as described by Blander and Katz. The energy required to form a vapor bubble at such a surface, $E_{\text{het}}$, is given by

$$E_{\text{het}}(\beta, \theta) = \frac{4}{3} \pi \beta^2 \alpha F - \frac{4}{3} \pi \beta^3 F (\rho_{\text{sat}} - P_{\text{void}})$$

where $\beta$ is the radius of curvature of the bubble, $\sigma$ is the surface tension of the liquid–vapor interface, and $F = (2 + 3 \cos \theta - \cos^3 \theta)/4$, where $\theta$ [deg] is the equilibrium contact angle of water on the surface. Assuming mechanical equilibrium (i.e., that the Laplace equation holds), the energy barrier for heterogeneous nucleation, $E_{\text{het}}(P_{\text{void}})$, is

$$E_{\text{het}}(P_{\text{void}}) = \frac{16\pi \alpha^3 F}{3(\rho_{\text{sat}} - P_{\text{void}})^2}$$

This energy barrier differs from the energy barrier for homogeneous nucleation (eq 9) only by the factor $F$. The threshold for heterogeneous cavitation is

$$P_{\text{cav, het}} = \rho_{\text{w, sat}} - \left(\frac{16\pi \alpha^3 F}{3k_B T \ln(V_{\text{het}}/V_{\text{void}})}\right)^{1/2}$$

where $V_{\text{het}}$ is the volume of water available for heterogeneous nucleation. For spherical voids in this study, we approximate $V_{\text{het}}$ as the surface area of a void with a diameter of $100 \mu$m multiplied by the assumed value of the critical nucleus, $R_C = 1$ nm.

Qualitatively, eq 16 predicts that if heterogeneous nucleation is the dominant mechanism of cavitation, then the observed threshold for cavitation should decrease (become more negative) with increasing contact angle. To investigate this prediction, we measured the probability of cavitation in VCVs formed in three hydrogel materials (Table 1): formulation A with $\theta = 40.3 \pm 3.6^\circ$ (already presented in Figure 7), formulation B with $\theta = 44.6 \pm 4.5^\circ$, and formulation C with $\theta = 13.4 \pm 1.8^\circ$. Figure 8 shows the probability of cavitation for water in all three formulations. The cavitation threshold in all cases was the same, to within our resolution (the uncertainty in the calculations of pressure, $P_{\text{void}}$, for activities near the threshold, approximately $\pm 0.7$ MPa). On the basis of the following argument, this observation suggests that the heterogeneous mechanism described by eq 16 was not dominant in any of the formulations: formulation B, with the highest contact angle, should have been most prone to heterogeneous cavitation. If the heterogeneous mechanism dominated in this case, then we would have expected to observe lower (more negative) thresholds for formations A and C given their lower contact angles.

Quantitatively, eq 16 predicts $P_{\text{cav, het}} = -195$ MPa for $\theta = 44.6^\circ$, the equilibrium contact angle of the least hydrophilic hydrogel material (formulation B). This prediction is clearly much lower than the observed threshold, $P_{\text{cav}} = -22.01$ MPa. Furthermore, this threshold is lower than that predicted for homogeneous cavitation with eq 13, $P_{\text{cav, hom}} = -184$ MPa, due to the small relative magnitude of the volume that we assumed was available for the heterogeneous mechanism versus the homogeneous mechanism ($V_{\text{het}} \ll V_{\text{hom}}$). Equation 16 predicts $P_{\text{cav, het}} = -22$ MPa for a contact angle, $\theta = 151.5^\circ$. Again, on the basis of macroscopic equilibrium contact angles (Table 2), our observations suggest that cavitation in VCVs was not due to the heterogeneous mechanism expressed by eq 16.

We note that both the qualitative and quantitative predictions of this simple model of heterogeneous nucleation could be reconciled with our observations in the following scenario: The VCVs formed in all formulations could have presented highly hydrophobic ($\theta \approx 151.5^\circ$) patches or impurities that were large enough to accommodate the critical nucleus ($\sim 1$ nm) but small enough and at sufficiently low density to have had a weak impact on the macroscopic contact angle. We cannot exclude this scenario with our current experiments; thus, we conclude that

there exists the possibility that cavitation in our system was due to heterogeneous nucleation.

**Mechanism (ii): Nucleation by Dissolved Impurities.**
This mechanism can play a role if water containing dissolved gas or solutes is used in experiments.\(^{15,20,21}\) These impurities could be of two types: (1) surfactants that reduce the surface energy associated with the formation of the liquid–vapor interface, and thus effectively reduce the activation barrier for thermally activated cavitation (eq 9), and (2) dissolved molecules that change the structure of water by disrupting the hydrogen-bond network. For the case of dissolved gas, this mechanism has been modeled as the formation of voids in the liquid that aggregate to form a vapor nucleus and as the formation of gas clusters that grow through the aggregation of gas molecules in solution and become a vapor nucleus upon reaching a critical size.\(^{54}\) It is possible to determine the likelihood that cavitation occurs due to the presence of dissolved gas or solutes by comparing experiments with different levels of purity of the water present in VCVs.

The presence of dissolved gas in the water within VCVs was inevitable in the current experimental setup; hydrogel samples were exposed to air which could diffuse into the liquid filling the VCVs. Additionally, comparison of the UV-vis spectra of samples of soaking water, after a soaking period of 2 days (the time required to fill VCVs with water), to the spectrum of deionized water (Figure 6B) indicated that solute is present in the water within the voids immediately after fabrication (see Purity of Water in VCVs section). While the solute may have been present at concentrations that were too dilute to significantly affect the negative pressures generated during equilibration with subsaturated vapors (see Purity of Water in VCVs section), its presence may nevertheless have affected the stability limit. To determine the effect of the solute on the cavitation threshold, we determined the cavitation probability for water in the same voids used to generate the data in Figure 7 after the hydrogel samples in which these voids were formed had been boiled ~5 times, used in five cavitation probability experiments, and stored at room temperature in deionized water between experiments over a period of ~5 months. After this extraction process, the UV-vis spectrum of the soaking water obtained from a final boiling for 2 days is identical to that of degassed, deionized water, indicating the reduction of the concentration of solute that was present immediately after fabrication to undetectable levels.

In Figure 9, the cavitation probability data for water in voids formed within hydrogel material \(A\), shown previously in Figure 7 (i.e., in samples immediately after fabrication, when solute may have been present), is compared to the cavitation probability for water in the same hydrogel samples after several months of soaking in water (i.e., in the same samples for which the UV-vis spectrum of the soaking water indicated that an undetectable concentration of solute was present). The transition in the cavitation probability for water after 5 months of soaking occurred at the same activity as for water in which solute was observed by UV-vis spectroscopy. These observations suggest several possibilities: (1) The solutes responsible for the peaks observed in the UV-vis spectrum have a negligible effect on the stability of water; for if they did, we would expect that the observed cavitation threshold would occur at a lower pressure for the samples that had been soaked for 5 months. (2) Alternatively, these solutes induce cavitation even at concentrations that are undetectable by UV-vis spectroscopy. (3) Some other solutes, such as dissolved gases, induce cavitation at the observed threshold. For possibility (2) and (3) the clean, uniform thresholds observed in the cavitation probability data indicate that, if there are impurities present, then these impurities are ubiquitous and uniform, so that the limit of stability is virtually the same in every void. Because of the above possibilities, we cannot discount the possibility of heterogeneous nucleation caused by dissolved impurities.

**Mechanism (iii): Nucleation by Pre-Existing Vapor Nuclei.** This mechanism can occur if pockets of gas are trapped in crevices in the wall of a VCV or on particulate impurities in the voids during the filling process. To consider this mechanism, we follow Apfel’s treatment of gas trapped in idealized, conical crevices (Figure 2A);\(^{19}\) while refinements of Apfel’s model have been shown to be important for acoustic experiments,\(^{55}\) his treatment is reasonable for our quasi-static application of tension. These pre-existing nuclei can expand when the pressure in the liquid drops, resulting in the emergence of a macroscopic gas phase, i.e., cavitation. The pressure at which the nuclei will expand is controlled by the geometry of the crevice (its radius, \(r_0\), and its half-angle, \(\beta\)), the receding and advancing contact angles of water with the wall of the crevice (\(\theta_{\text{rec}}\) and \(\theta_{\text{adv}}\)) and the maximum, positive pressure to which the system has been exposed, \(P_{\text{max}}\).\(^{9,23}\) Such crevices can stabilize a pocket of gas (air and water vapor) with respect to perturbations in the pressure in the liquid away from the equilibrium gas pressure \((P_{\text{atm}} = 1\, \text{atm})\) in our experiments if the following condition holds:

\[
\theta_{\text{rec}} < \beta + \frac{\pi}{2} < \theta_{\text{adv}}
\]

(17)

If the first inequality in eq 17 fails, the gas pocket would spontaneously expand; if the second inequality fails, the gas in the pocket would spontaneously disappear by dissolution and condensation. Apfel predicts the threshold pressure in the liquid, \(P_T\), required to cause cavitation by this mechanism for four cases:\(^{19}\)

\[
P_T = \begin{cases} 
\frac{P_{\text{atm}} - (P_{\text{max}} - P_{\text{atm}})}{[\cos(\theta_{\text{adv}} - \beta)]} & \text{for } r_0 > r_c \text{ and } \theta_{\text{rec}} < \beta \text{ (case 1)} \\
\frac{P_{\text{atm}} - (P_{\text{max}} - P_{\text{atm}})}{[\cos(\theta_{\text{adv}} - \beta)]} & \text{for } r_0 > r_c \text{ and } \theta_{\text{rec}} > \beta \text{ (case 2)} \\
\frac{P_{\text{atm}} - 2\sigma}{r_0} & \text{for } r_0 < r_c \text{ and } \theta_{\text{rec}} < \beta \text{ (case 3)} \\
\frac{P_{\text{atm}} - 2\sigma [\cos(\theta_{\text{rec}} - \beta)]}{r_0} & \text{for } r_0 < r_c \text{ and } \theta_{\text{rec}} > \beta \text{ (case 4)} 
\end{cases}
\]

(18)

where \(\sigma\) is the surface tension of water and \(r_c\) is the largest radius of a crevice for which the meniscus remains caught at the rim as the pressure in the liquid is raised to the maximum pressure, \(P_{\text{max}}\):

\[
r_c = \frac{2\sigma[\cos(\theta_{\text{adv}} - \beta)]}{P_{\text{max}} - P_{\text{atm}}}
\]

(19)

The following observations are important for the analysis of our experiments: For cases 1 and 2 (“large” crevices), eq 18 predicts that the prepressurization of VCVs should affect the observed stability threshold if cavitation occurs due to pre-existing nuclei (i.e., \(P_{\text{cov}} = P_T\)): if the same threshold is observed for two experiments run with different \(P_{\text{max}}\), then we can exclude

the existence of cases 1 and 2. For nuclei in “small” crevices of case 3, eqs 18 and 19 imply that the observed threshold due to pre-existing nuclei cannot be smaller in magnitude than the prepressure: $P_{\text{cav}} = P_T < -P_{\text{max}}$. Finally, case 4 allows for an interesting scenario in which a crevice of arbitrarily small size could lead to a threshold pressure anywhere in the range between $P_{\text{atm}}$ and $-2\sigma / r_c$ depending on the values of $\theta_{\text{rec}}$ and $\beta$ and independently of the prepressure; we cannot use prepressurization to exclude the possibility that “calibrated” crevices of case 4 set the observed threshold pressure. We note, though, that for the prepressure used in experiments with spherical VCVs, $P_{\text{max}} = 54$ MPa, eq 19 indicates that $r_c \geq 2.7$ nm; this dimension is smaller than the radius of the critical nucleus at the observed cavitation threshold ($P_{\text{cav}} = -22$ MPa), $R_c = 2\sigma / (P_{\text{atm}} - P_{\text{cav}}) = 6.5$ nm.

To investigate the possibility that the presence of pre-existing nuclei caused the cavitation of water in VCVs, we consider experiments measuring cavitation probability in voids with and without prepressurization and make use of the model of ideal, conical crevices developed above (eq 18). We begin with the discussion of microchannel VCVs (Figure 10). These VCVs had a higher surface area to volume ratio than spherical VCVs and were fabricated with a method that was more likely to leave structural defects (e.g., crevices) and particulates within the voids (e.g., fragments of silicone from the PDMS mold; see Fabrication of Microchannel VCVs). On the basis of the reeding and advancing contact angles measured for each formulation (see Table 2), the second inequality of eq 17 fails for each hydrogel material used in experiments; conical crevices in the hydrogel wall of a VCV should not stabilize pockets of gas. Any stable nuclei would need to be either on foreign materials with appropriate contact angles or exist on a scale at which the measured macroscopic contact angles of the hydrogel are not valid.

The cavitation probability data for nonpressurized microchannel VCVs, shown in Figure 10, illustrate what one would expect when pre-existing nuclei are present in crevices with $r_0 > r_c$ (cases 1 and 2) or with $r_0 < r_c$ and $\theta_{\text{rec}} > \beta$ (case 4): (1) The absence of a clean threshold (cavitation occurred for a broad range of negative pressures and the probability of cavitation was highly variable for each pressure, as is shown by the large error bars). This scatter can be interpreted as arising due to the fact that the pressure at which a trapped nucleus escapes from a crevice, resulting in the emptying of the void, is dependent on the size and geometry of the crevice. A clean threshold would only be observed if the size, geometry, and wetting character of all crevices in all surfaces of the voids were uniform. (2) Sensitivity to prepressurization, as predicted by eq 18 for cases 1–3: as indicated in Figure 10, water in the microchannel voids was more stable in samples pressurized to $P_{\text{max}} = 18$ MPa (filled circles) than in unpressurized samples ($P_{\text{max}} = P_{\text{atm}}$ for open circles). These observations suggest that the nucleation of the vapor phase in the liquid within microchannel VCVs occurred, at least in part, due to the presence of pre-existing vapor nuclei in crevices of cases 1–3: pressurization forced the pre-existing nuclei either completely into solution, or deeper into the crevices in which they resided, such that prepressurized samples exhibit a cleaner, more negative cavitation threshold relative to unpressurized samples. In the first case, the nuclei would be completely eliminated from the system; in the second case, the vapor nuclei would be trapped through contact angle hysteresis and would not attain the critical size required to nucleate cavitation until the magnitude of negative pressure in the water was roughly the same as or greater than the magnitude of the positive pressure employed during pressurization, depending on crevice geometry and the reeding and advancing contact angles (eq 18).

In contrast, cavitation in spherical VCVs showed no sensitivity to pressurization: the same sharp, threshold was observed for no prepressurization ($P_{\text{max}} = P_{\text{atm}}$) and for $P_{\text{max}} = 54$ MPa. This insensitivity excludes crevices of cases 1–3 identified in eq 18. Nuclei could have existed in “calibrated” crevices of case 4. However, this situation appears unlikely because (1) cavitation would occur by the expansion of gas pockets that are smaller than the critical nucleus size for the observed threshold and (2) it would require that all VCVs had crevices of identical size, geometry, and wettability. On the basis of these arguments, we conclude that it is unlikely that cavitation in spherical VCVs occurs due to pre-existing nuclei.

**Mechanism (iv): Invasion of Air.** To address the possibility of dry out of the liquid in the voids via invasion of air through pores, we consider the possibility that liquid water exists in discrete pores within the polymer network. At equilibrium between the liquid phase (in the void and extending to the surface of the membrane via pores) and a subsaturated vapor phase, a reduced hydrostatic pressure in the void balances the subsaturated water activity and the meniscus in the pore will assume a negative curvature (see eq 8). For a cylindrical pore as in Figure 1B, the meniscus will retrace into the pore, and the void will dry out once the contact angle reaches the receding contact angle of water at the pore surface. In this scenario, the maximum stress in the liquid that can be accommodated by the membrane is

$$\Pi_{\text{max}} = \frac{2\sigma \cos \theta_{\text{rec}}}{\rho_p}$$

In a porous material with a nonuniform distribution of pore sizes, the largest, continuously connected pore between the surface and the void will determine the maximum negative pressure that is obtainable. Equation 20 and measurements of the receding contact angle of water on the surface of the hydrogels reported in Table 2 ($\theta_{\text{rec}} < 25^\circ$) can be used to estimate the dimensions of the largest pore able to remain filled at the lowest pressure we observed in the voids, $P_{\text{void}} = -22$ MPa. Results of this calculation predict that menisci should recede into the membrane, allowing the invasion of the air into the VCV, if the diameters of the pores or mesh sizes of the hydrogel materials were 11.9 nm or larger.

To estimate the mesh size of each of the three hydrogel materials used in cavitation experiments, we use the theory developed by Canal and Peppas, experimentally determined values of the Flory interaction parameter of the three hydrogels when saturated with water, i.e., in equilibrium with $a_{w,\text{vap}} = 1$ ($\chi_S$ in Table 2), and the volume fractions of polymer in the relaxed state (just after polymerization), $\phi_{S,R}$, and in the swollen state (after soaking in water), $\phi_{S,S}$. The volume fractions were obtained as described in the Determination of $\chi_S$ section. These parameters were used to first calculate the number-average molecular weight between cross-links, $\bar{M}_c$, using the following equation:

$$1 \bar{M}_c = \frac{2}{\bar{M}_n} \left\{ \frac{1}{\bar{M}_c} \ln(1 - \phi_{S,P} + \phi_{S,S} + \chi_S \phi_{S,s} \phi_{S,P} \phi_{S,S}) \right\} \left( \frac{\phi_{S,R}}{\phi_{S,R} - \phi_{S,S}} \right)^{1/3}$$

where $\bar{M}_n$ is the number-average molecular weight of the uncross-linked polymer and $\bar{V} = 1.24$ is the specific density of HEMA. This equation applies to loosely cross-linked networks where the number of repeating units between cross-links is large enough so that the chains can be represented by a Gaussian
distribution. Since both polymerization of the monomer and the cross-linking reaction occur simultaneously, it is impossible to measure \( M_n \). We use \( M_n = 75 \text{,000 g mol}^{-1} \) for the calculation, the same value used by Canal and Peppas; Canal and Peppas state that 75000 g mol\(^{-1}\) is a reasonable value for \( M_n \) for a polymer network that is formed by simultaneous polymerization of monomer and cross-linking of polymer chains and also show that increasing \( M_n \) above 10000 g mol\(^{-1}\) has no significant effect on calculations of \( M_c \). Increasing \( M_n \) above 10000 g mol\(^{-1}\) in our calculations also had no significant effect on values of \( M_c \).

The volume fraction of polymer in the relaxed state is taken to be the total volume fraction of monomer (HEMA), cross-linking agent (EGDMA), and additive (AA or MAA) present in the prepolymer solution of each hydrogel, thereby assuming a conversion of 100%. This assumption was shown to be reasonable by the findings for monomer conversion discussed in the section Purity of Water in VCVs: conversions of ~98% were determined for all hydrogel formulations.

With all variables of eq 21 measured or calculated, the mesh size of the polymer network, \( d \) [nm], is found via

\[
d = \frac{\phi_p S^{-1/2}}{\left(2 c_n M_p^{1/2} M_c^{-1/2}\right)}
\]

where \( C_n = 6.9 \) is the Flory characteristic ratio, or rigidity factor, of the pHEMA chain, \( l \) is the length of a carbon–carbon bond (1.54 Å), and \( M_c [130 \text{ g mol}^{-1}] \) is the molecular weight of the HEMA monomer. Results of this calculation for our formulations are presented in Table 2. These results represent an upper bound on the mesh size of the hydrogel materials, since the polymer network contracts as the hydrogel material loses water during equilibration with subsaturated water vapor activities. In addition, the estimate of \( M_c \) obtained from eq 21 may be high if, in fact, \( M_c < 10000 \text{ g mol}^{-1} \). Calculation of \( d \) using this overestimate also tends toward values of \( d \) that are too large; this circumstance is consistent with the statement that values for \( d \) are upper bounds. Calculations for \( \chi \) and \( d \) may not be valid for materials made from formulation B as this material had a hazy appearance when saturated with water. This appearance is attributed to the possible existence of discrete water and polymer phases; this assumption was shown to be reasonable by the findings for monomer conversion discussed in the section Purity of Water in VCVs: conversions of ~98% were determined for all hydrogel formulations.

The mesh sizes calculated using this approach (eq 22) are displayed in Table 2 and show that all three materials have pore sizes smaller (\( d < 2.5 \text{ nm} \)) than the maximum pore size as calculated from eq 20 (\( d_{\text{max}} = 11.9 \text{ nm} \)). On the basis of this result, we conclude that the decrease in meniscus and subsequent invasion of air into the hydrogel materials were not responsible for the observed stability limits. Furthermore, as stated earlier in this section, the largest pore is most likely to determine the threshold pressure at which a VCV will dry out. The consistent nature of the dry out behavior observed for over 300 VCVs in five samples for each formulation (i.e., the sharp transition at \( d_{\text{w,vap}} = 0.85 \) would require that each void had exactly the same maximum pore size—an unlikely circumstance.

Conclusions

In this study, we explored the origins of the observed limit of stability of liquid water in vapor-coupled voids formed in hydrogel membranes. Experiments revealed that the liquid phase persisted at equilibrium with vapors of activity down to 0.85 before cavitation; this activity corresponds to predicted negative pressures of approximately ~22 MPa. The behavior of the cavitation probability of water in VCVs as a function of predicted negative pressure was compatible with the kinetic theory of homogeneous nucleation. The observed stability limit (~22 MPa) was comparable to previous experimentally observed stability limits but was also considerably smaller in magnitude than the stability limit predicted by homogeneous nucleation theory and obtained in quartz inclusions by Zheng et al.

On the basis of experiments and analysis designed to determine the likelihood of other possible mechanisms of cavitation, we exclude the possibility of nucleation by pre-existing nuclei and by the invasion of air through the membrane. We cannot exclude other mechanisms; our observations are compatible with heterogeneous nucleation of the vapor phase on hydrophobic patches on the surface of VCVs or on ubiquitous impurities and with nucleation facilitated by dissolved solutes in the water within the VCVs (e.g., dissolved air or undetectable concentrations of monomer).

It may be possible to extend the range of negative pressures generated in VCVs if greater care is taken to avoid sources of cavitation. To avoid dissolved air, samples could be equilibrated with pure subsaturated water vapor under vacuum. To avoid dissolved solutes, processes such as thermal or UV treatment could be performed to break down molecular impurities. To avoid the presence of hydrophobic patches, composite structures could be developed in which bulk liquid water is in direct contact with a highly hydrophilic, inorganic surface (e.g., silica), rather than with an organic material. Such a system could be created using hydrogel coated silica sol–gels in which bubbles are trapped during gelling.

In addition to providing a new tool for exploring the stability limit, the vapor-coupled void could potentially provide a platform for (1) the study of the link between the molecular structure of water at negative pressures and the anomalous properties of water, for example, via Raman spectroscopy, (2) the exploration of the negative pressure region of the phase diagram of water for the purpose of generating an equation of state (this mapping would require the direct measurement of a third state variable such as \( P–T \) and \( \mu \) are known), and (3) the measurement of the dynamic properties (e.g., viscosity, self-diffusivity) of water at negative pressures (the system required for this measurement could be fabricated by connecting two VCVs via a microchannel and equilibrating one VCV with a higher activity of water vapor, establishing flow from one VCV to the other, similarly to vapor-to-vapor transport in the synthetic tree of ref 6). These directions are currently being pursued in our laboratory.

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