

Nonisothermal effects on water potential measurement in a simple geometry

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In this paper, we investigate quantitatively the coupling between gradients of temperature and of chemical or water potential under steady-state conditions in the vapor phase. This coupling is important for the measurement and modeling of the dynamics of water in unsaturated environments such as soils and plants. We focus on a simple nonequilibrium scenario in which a gradient of temperature exists across an air-filled gap that separates two aqueous phases with no net transfer of water. This scenario is relevant for measurements of the water potential in environmental and industrial contexts. We use a tool, a microtensiometer, to perform these measurements. We observed variations of the water potential with a difference of temperature across the air gap of $-7.9 \pm 0.3 \text{ MPa K}^{-1}$, in agreement with previous measurements. Our result is close to a first-order theoretical prediction, highlighting that most of the effect comes from the variation of saturation pressure with temperature. We then show that thermodiffusion (Soret effect) coupled to natural convection could occur in our experiment and discuss how these effects could explain the small discrepancy observed between measurements and first-order theoretical predictions.

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I. INTRODUCTION

A. Water transport in nonisothermal unsaturated media

In countless natural and technological contexts, multiphase transport of a mass and heat energy occurs in the presence of gradients of both chemical potential and temperature. Many examples of this process involve water, as in unsaturated soils under arid atmospheric conditions and solar radiative forcing [1,2], the drying of porous materials [3,4], the cooking of foods [5], and the

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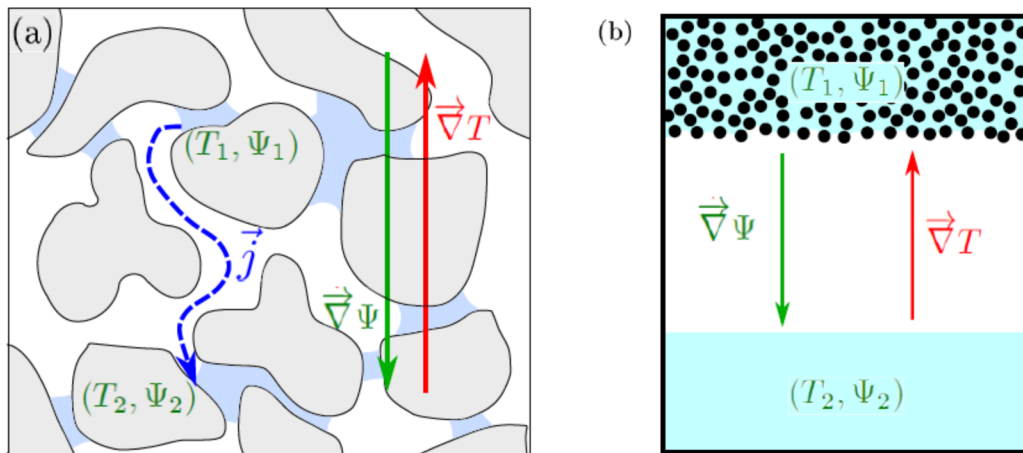


FIG. 1. Context of interest. (a) Unsaturated porous medium. Within the porous matrix, pockets of capillary condensed liquid water coexist with pockets of vapor in air. In the presence of a temperature gradient, a gradient of water potential is established which drives a net water flux \vec{j} through the medium. The gradient of water potential $\nabla\Psi$ is proportional to the gradient of temperature ∇T [see Eq. (4)]. (b) Simplified situation studied here. Aqueous phases are kept separated by a vapor gap, in a closed system ensuring that there is zero net flux of mass ($\vec{j} = \vec{0}$). An imposed stationary temperature gradient ∇T results in a steady water potential gradient $\nabla\Psi$. We focus on the special case in (b) in this study.

operation of air-breathing electrodes in fuel cells [6,7]. As presented schematically in Fig. 1(a), a porous solid hosts interspersed liquid and vapor phases in contexts such as these.

In this paper, we use the “water potential” Ψ (Pa) which is a commonly used quantity in soil and plant science to describe water status, as water fluxes are directed from areas of high water potential towards areas of low water potential. It is defined by the following equation [8],

$$\Psi(T, P) = c_\ell[\mu(T, P) - \mu_{\text{sat}}(T)], \quad (1)$$

where $\mu(T, P)$ (J mol^{-1}) is the chemical potential of water in the system, $\mu_{\text{sat}}(T) = \mu[T, P_{\text{sat}}(T)]$ (J mol^{-1}) is the chemical potential at saturation [$P_{\text{sat}}(T)$ being the vapor saturation pressure], and c_ℓ (mol m^{-3}) is the mole density of the liquid phase. Water potential thus measures the deviation from saturation in a substance containing water: From now on, we will express it in MPa which provides a typical order of magnitude of water potential in our experiments as well as in field situations. In this study, we focus our attention on water, but the phenomena explored are relevant to other substances undergoing multiphase transport within a porous host matrix, as in packed bed reactors [9,10].

The combination of various transport phenomena, local phase equilibria, and interfacial phenomena within complex geometries makes the study of such processes challenging. A strong tradition of theoretical and experimental studies of multiphase transport in porous media exists in the field of soil physics. Since the foundational theoretical work on this topic by Philip and de Vries was proposed [11–15], numerous studies have attempted to characterize the various contributions to the flux of mass and heat, e.g., vapor diffusion and convection, capillary convection, surface transport, conduction, but important uncertainties remain [16–18].

B. Coupling between temperature and water potential gradients

Perhaps surprisingly, we still lack clarity on one of the most basic seeming contributions to the flux of mass and energy: the transfer, across a volume of vapor, between two volumes of liquid at different temperatures and chemical potentials. Such a situation occurs between pockets of the condensed phase in realistic settings depicted in Fig. 1(a). Throughout this study, we focus on a

simple, steady-state realization of this scenario shown in Fig. 1(b) in which a constant difference in temperature ΔT (K) and a constant heat flux \vec{j}_q ($\text{W m}^{-2} \text{s}^{-1}$) are maintained between two condensed phases of water across air- and vapor-filled gas, with no net transfer of mass ($\vec{j} = \vec{0}$ at the boundaries of the system). We examine in detail how the steady-state difference in water potential $\Delta\Psi$ depends on this difference in temperature ΔT : In what follows, we will refer to this effect as the Ψ - T coupling. This dependence is important in the context of measurements of the water potential in complex media such as soils, plant tissues, and food stuffs [19–21].

In this situation, the water potential Ψ_ℓ of the condensed phases can vary due to differences in pressure, osmolarity, and interfacial interactions with the host matrix,

$$\Psi_\ell = [P - P_{\text{sat}}(T)] - \Pi + \Psi_{\text{matrix}}, \quad (2)$$

where P and $P_{\text{sat}}(T)$ (MPa) are the total gas pressure and saturation partial pressure of the pure liquid, Π (MPa) is the osmotic pressure due to the presence of solutes, and Ψ_{matrix} (MPa) is the contribution of specific interactions with the matrix (e.g., van der Waals interactions of an adsorbed film). In the gas phase, the water potential of the vapor Ψ_g has the form

$$\Psi_g(T, P) = c_\ell RT \ln \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{sat}}(T)} \right), \quad (3)$$

where $P_{\text{H}_2\text{O}}$ is the partial pressure of water in the gas phase, and $P_{\text{H}_2\text{O}}/P_{\text{sat}}$ is the relative humidity of the vapor. By introducing the mole fraction x of water in the gas phase and assuming the gas mixture behaves ideally, the partial pressure can be written as $P_{\text{H}_2\text{O}} = xP$. At the interfaces between the vapor and the condensed phases, we assume a local equilibrium, which imposes that $\Psi_\ell = \Psi_g$. Therefore, the nonequilibrium processes that drive the Ψ - T coupling should occur within the gas phase if we neglect all other paths (e.g., surface diffusion along solid boundaries) connecting the two reservoirs.

C. A first-order model of the Ψ - T coupling

Even in this highly simplified context, a variety of physical phenomena can come into play in defining the dependence of water potentials on the disequilibrium in temperature. These phenomena include the temperature dependences embedded in the local phase equilibria through Eqs. (2) and (3), the temperature dependences of the density and local concentrations in the mixed gas phase through which heat and mass can be exchanged between the two reservoirs, and molecular diffusion, thermodiffusion, and convection driven by variations in composition, temperature, and density within the gas. In this section, we develop a first-order model accounting only for this latter effect; we discuss the other possible contributions in the Discussion, after presenting our experimental observations.

Taking the derivative of Eq. (3) with respect to temperature, we obtain

$$\left(\frac{d\Psi}{dT} \right)^0 = c_\ell R \left(\frac{\Psi}{c_\ell RT} - \frac{T}{P_{\text{sat}}} \frac{dP_{\text{sat}}}{dT} \right). \quad (4)$$

We use the superscript 0 to refer to this simple model, where the total gas pressure P and partial vapor pressure of water $P_{\text{H}_2\text{O}}$ (or mole fraction $x = P_{\text{H}_2\text{O}}/P$) are assumed to be homogeneous in the gas-filled gap [see Fig. 1(b)]. In our experiments and many common contexts, the phases are near saturation such that $|\Psi| \ll c_\ell RT \sim 120$ MPa, so the first term in this equation is negligible. Thus, the variation of water potential with temperature is essentially due to the dependency of the saturation pressure. For the liquid-gas equilibrium, this variation is classically described by the Clausius-Clapeyron equation

$$\frac{dP_{\text{sat}}}{dT} \simeq \frac{P_{\text{sat}} \ell_{\text{vap}}}{RT^2}, \quad (5)$$

where ℓ_{vap} (J mol^{-1}) is the latent heat of evaporation of water. By using values from the International Association for Properties of Water and Steam equation of state [22] and for a temperature $T = 21^\circ\text{C}$ corresponding to our experiment, we obtain that

$$\left(\frac{d\Psi}{dT}\right)^0 = -8.33 \text{ MPa K}^{-1}. \quad (6)$$

This coupling of water potential and temperature creates the potential for a substantial driving force for water transport throughout the soil-plant-atmosphere continuum due to ambient gradients of temperature or those generated by solar radiative forcing [23–25]. It could also be exploited for heat management technologies [26]. This coupling between water potential and temperature is actually general for any phase equilibrium and can be described by similar arguments [27,28].

D. Experimental investigations with psychrometers

This Ψ - T coupling is the basis of the measurement of water potential by thermocouple-based psychrometers [29,30]. In this original approach, a single thermocouple is held in an air-filled cavity adjacent to the sample of interest. A first measurement of the air temperature provides the wet-bulb temperature. Then, an applied voltage would cool the junction by the Peltier effect until condensation occurred. The condensation temperature provides the dew point temperature. After calibration of the thermocouple junction, the measured dew point can be associated with the water potential of the system, as justified by Eq. (4). A detailed sensitivity analysis of thermocouple-based psychrometers has been proposed [31,32]. This original design with a single thermocouple assumes that the air and the sample are at thermal equilibrium and it is highly sensitive to Ψ - T coupling in the presence of thermal gradients.

Later, Dixon and others introduced a psychrometer design with two thermocouples, one in contact with the sample to measure its temperature and one operated as described above [19,33]. In this approach, one of the thermocouples is used to measure the temperature of a wetted sample of a known water potential while the second thermocouple is separated from the first (and the matrix) by an air-filled gap. This second thermocouple is used to measure the air temperature (the “dry-bulb temperature”), and then cooled until condensation occurs to define the dew point in the air (the “wet-bulb temperature”). This operation creates, transiently, the scenario depicted in Fig. 1(b).

They investigated this Ψ - T coupling in an applied perspective of correcting systematic uncertainties in water potential measurements due to a temperature difference between the sample under study and the wet bulb. Psychrometers indeed measure the water potential of the vapor surrounding the wet bulb: If it is not in thermal equilibrium with the sample of interest, the measured water potential will be biased due to the Ψ - T coupling, and the prediction of Eq. (6) shows that the associated error is significant. For example, a temperature difference of 0.1 K leads to a systematic error of 0.8 MPa on the measured water potential, which is significant for applications in soils and leaves for which the usual order of magnitude of water potentials is a few MPa. They thus purposely imposed a controlled temperature gradient in the measuring chamber: In a first study they estimated a variation of -7.77 MPa K^{-1} [19] and later, in a more systematic study with an improved setup [33], obtained values ranging between -7.53 and -7.84 MPa K^{-1} . However, they did not give any details on the measurement uncertainties (in particular, they did not discuss the sensitivity analysis proposed by Peck [32]) and they only investigated small temperature variations of about 0.1 K; their measurements appear to significantly differ from the theoretical prediction of Eq. (6) and without an uncertainty analysis it is not possible to discuss the relevance of this discrepancy.

E. Model situation of this study

As it appears from the previous discussion, despite its importance both for water transport in unsaturated porous media and for measurement of the water potential, there is no direct experimental confirmation of the theoretical prediction of Eq. (4). In particular, existing studies do not perform a

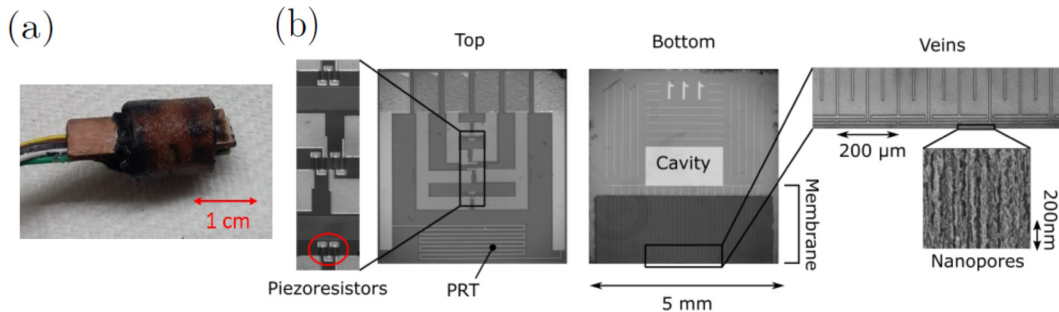


FIG. 2. Pictures of the tensiometer. (a) Global view of a packaged tensiometer with a copper strip. See Figs. 3(a) and 3(b) for a schematic diagram of the packaged device. (b) Details of the tensiometer. The top view shows the piezoresistors (an example circled in red) that constitute the strain gauge to measure deformations of the diaphragm and the platinum wire used as PRT. The bottom view shows the cavity containing bulk water and the nanoporous membrane (dark on the picture) connecting it with the outside. Microfluidic veins are etched in the membrane without linking directly the cavity and the outside in order to decrease the response time of the device. The image of the nanopores has been acquired by scanning electron microscopy and have an average pore radius $r_p = 1.7$ nm. Details on microfabrication are given in the text. [Image credit (b): Antoine Robin.]

quantitative comparison between measurements and theory, as would require a careful uncertainty analysis, and they mostly rely on measurements with thermocouple-based psychrometers which also rely on exploiting the Ψ - T coupling.

In this study, we present an experimental measurement of the Ψ - T coupling using a distinct sensing tool, a microtensiometer, with the goals of extending the measurement to a larger range of temperature and providing a thorough assessment of uncertainties. The microtensiometer (see Fig. 2) exploits distinct physics relative to the psychrometer to transduce a water potential into an electronic signal and allowed us to perform measurements at true steady states and independently of any assumption on the Ψ - T coupling. We worked in an experimental system (see Fig. 3) designed to recreate the simple scenario depicted in Fig. 1(b) as closely as possible by providing precise control of the temperature gradients, isolating the contributions of processes associated with the gas phase and vapor-liquid equilibrium, and independently varying the isothermal difference in the water potential. With this approach, we provide a complete experimental characterization of the Ψ - T coupling of which we are aware. We find a constant of proportionality $-7.9(3)$ MPa K $^{-1}$ that is compatible, within uncertainty, with that reported previously, but in limited agreement with the theoretical prediction in Eq. (6). This discrepancy motivates a discussion of other contributions to the Ψ - T coupling and the proposal of future studies.

II. MATERIALS AND METHODS

A. Microtensiometer

Despite its importance, the water potential is a challenging quantity to measure reliably and *in situ* [34]. The aforementioned thermocouple-based psychrometers have been the most relevant tool available for *ex situ* water potential measurement as they provide appropriate sensitivity to the water potential over a useful range [2]. Nonetheless, the use of psychrometers has been limited by challenges in their operation (e.g., due to microvolt-scale, transient signals) and in evaluating local temperature gradients with the air gap that must separate the sensing junction from the sample [19].

A few years ago, our group introduced a microfluidic device, called the microtensiometer and presented in Fig. 2, that allows for the local (the sensor being smaller than ~ 1 cm) and continuous (with a response time ~ 1 min) measurement of water potentials down to ~ -20 MPa [20], relevant to conditions commonly encountered in soils and plants. Such a sensor complements

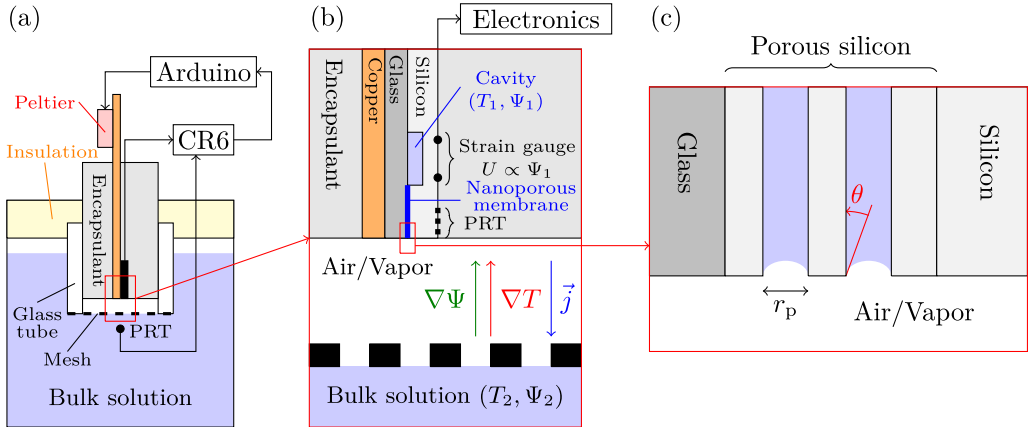


FIG. 3. Schematic diagrams of the experimental setup (not to scale). (a) Cross-sectional view of the experimental setup. The tensiometer (in black) is glued to a copper strip (in orange) and packaged in urethane (in gray). The device is capped by a glass tube (in white) closed by a porous hydrophobic mesh (dashed line) and dipped in an osmotic solution of known water potential (in blue) through a thermal insulation (in light yellow). Temperature of the tensiometer is controlled by a Peltier module (in pink) attached at the emerging end of the copper strip and powered through an Arduino-based feedback loop imposing a constant temperature difference with the solution. (b) Expanded view of the vapor gap. While the temperature of the solution T_2 is imposed by a thermostat, that of the tensiometer T_1 is controlled with a Peltier element connected to the copper strip on which the tensiometer is glued with thermal paste. When a temperature difference is imposed, there is a difference between the water potential measured by the tensiometer Ψ_1 and that of the solution Ψ_2 . The water potential in the cavity is obtained by measuring the deformation of the diaphragm with the strain gauge, giving a voltage U proportional to Ψ_1 . (c) Expanded view of the nanoporous membrane. When in contact with an unsaturated vapor, curvature of the menisci at the pore mouth decreases the pressure of the pore liquid to achieve mechanical equilibrium.

the psychrometers in that it senses the water potential by a distinct physical mechanism: It measures pressure (tension) in pure liquid water in equilibrium with the phase of interest. We recently proved it can provide users with simple and reliable measurements of water potential both *ex situ* and *in situ* for food products [21]. It thus opens an opportunity to monitor the water status within soils and plants and gives another platform to explore water fluxes in unsaturated media.

We now recall the characteristics of the microtensiometer; further details on the fabrication have been published elsewhere [21]. The microtensiometer is a microfluidic tool designed to measure the water potential in unsaturated phases. The size of the chip is of ~ 5 mm on a side and ~ 1 mm thick; when packaged, the size of the sensor is of the order of a centimeter. The internal liquid equilibrates with the external environment via the exposed edge of the porous silicon membrane; this exposed edge is ~ 5 μm thick and ~ 4 mm wide. This small size allows for local measurements.

Figure 2 presents pictures of the microtensiometers used in this study; the design is presented in more detail in Ref. [20]. The key elements of this design are as follows:

(1) An internal cavity (1 mm \times 2.5 mm \times 3 mm) is formed by dry etching in a single-crystal silicon wafer (111) and filled with liquid water in a pressure chamber (~ 3.5 MPa during ~ 10 h) before use.

(2) A strain gauge is formed of a piezoresistive polysilicon on the opposite side of the silicon wafer from the cavity. The piezoresistors form a Wheatstone bridge.

(3) A layer of porous silicon (5 μm thick) is formed by anodization on the side of the wafer that contains the cavity. This layer is filled with liquid water and provides a connected path of nanoscopic pores [average pore radius $r_p \simeq 1.7(4)$ nm] from the cavity to one edge of the device. We have characterized the hydraulic and wetting properties of this material previously [35].

(4) Microfluidic veins, also filled with liquid water, partially span the distance between the cavity and the edge within the porosified region. These veins increase the permeability of the path between the cavity and the edge.

(5) A glass wafer is anodically bonded to the side of the wafer with the cavity and veins.

(6) A platinum resistance thermometer (PRT) is formed by a thin platinum wire deposited on the backside of the wafer, over the porous membrane top side of the silicon. It provides a local measurement of the sensor's temperature.

Under isothermal conditions, corresponding to $T_1 = T_2$ in the scenario detailed in Fig. 3(b), both thermal and mass transfer equilibria are reached: The temperature of the pure liquid in the cavity T_1 equals that of the reference solution T_2 and the water potentials of the internal liquid Ψ_1 , the vapor phase Ψ_{vap} , and the reference solution Ψ_2 are equal. Given that the water potential of the bulk, pure liquid water $\Psi_1 = P_\ell - P_0$ is just the difference between its pressure P_ℓ and this of standard state P_0 and the water potential of the vapor is given by Eqs. (1) and (3), we have

$$\Psi_1 = P_\ell - P_0 = c_\ell RT \ln \left(\frac{P}{P_{\text{sat}}(T)} \right) = \Psi_{\text{vap}} = \Psi_2, \quad (7)$$

where P_ℓ is the pressure and c_ℓ the molar density of the liquid phase. This equilibrium is allowed by the curvature of the liquid/gas menisci at the mouth of the nanopores in the membrane; this curvature causes a reduction of the pressure of the liquid in the cavity, as shown in Fig. 3(c), given by the Laplace law

$$P_\ell = P_0 - \frac{2\gamma \cos \theta}{r_p}, \quad (8)$$

where γ (J m^{-2}) is the liquid/vapor surface tension of air, θ is the contact angle of the meniscus, and r_p is the pore radius ($r = r_p / \cos \theta$ being the radius of curvature of the meniscus). Equilibrium can be sustained as long as the contact angle θ of the meniscus at the pore mouth is smaller than the receding angle. Previous studies by our laboratory indicate that the Kelvin-Laplace effect captured by Eqs. (7) and (8) accurately describes the behavior of water in the porous silicon used in the tensiometer [35]. Nonetheless, the precise character of the thermodynamic interactions of water within the pores of the membrane do not affect the measurements performed here: At equilibrium, the pressure (a state variable) in the pure, bulk liquid in the internal cavity depends only on the state of the bulk, external phase (vapor or pure liquid) at the external surface of the membrane.

The internal cavity was bounded by a diaphragm of plain silicon; the pressure difference between the liquid in the cavity and the external atmosphere deforms this diaphragm. This deformation was measured with a strain gauge made of a Wheatstone bridge of piezoresistors deposited on the diaphragm [see Fig. 2(b)] and supplied with a fixed applied voltage of 0.4 V. Previous work showed that the relationship between the voltage U across the Wheatstone bridge and water potential Ψ of the water in the cavity is linear over the whole range of water potential accessible to the tensiometer [20,21,36]. After a calibration procedure, that will be described in Sec. III A, it was thus possible to obtain the water potential from the voltage across the bridge. Based on Eq. (7), the calibrated response of the tensiometer provides the water potential of the phase with which the microtensiometer is in equilibrium.

We calibrated the PRT in temperature against a commercial PRT (Omega) by placing them together in a water bath and changing its temperature stepwise. In this situation, the cavity and membranes were filled with liquid water and the voltage from the Wheatstone bridge was equal to its offset U_0 , corresponding to saturated conditions. We observe that U_0 depended slightly on temperature: This effect induced a small systematic uncertainty; it was negligible as compared to other sources of uncertainty discussed in a later section.

B. Experimental setup

The global view of the experimental system is depicted on Fig. 3(a). The microtensiometer was glued to a copper strip on its glass slide, as is visible in the expanded view in Fig. 3(b). We placed the sensor bound to the copper strip in a tube formed of resin-impregnated cardboard. The gaps around the device were filled with a curable urethane resin (UR5041, Electrolube) such that at one end the nanoporous membrane slightly protruded from the tube. In this package, the diaphragm of the tensiometer was protected from the resin so that, in the final device, it was covered by a small air pocket. This air pocket avoided deformations of the diaphragm due to thermal expansion of the urethane. We capped the end of the device with a glass tube (radius $R_0 \simeq 0.5$ cm and height $h \simeq 1$ cm) closed at the other extremity by a hydrophobic polymer mesh (Mo-Flow Ventilation, mesh size ~ 0.5 mm) and dipped it in a solution of known water potential Ψ_{ref} . This hydrophobic mesh allowed for an exchange of vapor but excluded the entry of liquid. The liquid water in the microtensiometer thus equilibrated with the solution through the vapor in the tube. This gas-filled tube volume [see Fig. 3(b)] recreates the geometry of interest from Fig. 1(b).

We controlled the temperature of the reference solution by submerging it in a temperature-controlled water bath, and we measured the temperature of the solution with a commercial PRT placed as closely as possible to the hydrophobic mesh. The bath was closed by a plate of insulating foam in which we drilled a tight hole to insert the probe assembly with the copper strip protruding. We attached a Peltier module (Digikey Electronics, 1681-1028-ND) to the exposed end of the copper strip, to control the temperature of the tensiometer.

A data logger (CR6, Campbell Research Scientific) acquired data from the tensiometer and the commercial PRT in the solution. It then delivered a voltage proportional to the difference, $\Delta T^* = T_1 - T_2$, between the temperature of the tensiometer T_1 and that of the solution T_2 to an Arduino board. A Proportional-Integral-Derivative controller programed on the Arduino switched the power supply of the Peltier module in order to impose a target temperature difference between the tensiometer and the reference solution. At steady state, this feedback loop provided a temperature difference with fluctuations of order 0.05 °C. This fluctuation constituted a random source of uncertainty on the temperature difference that was smaller than the systematic uncertainty from the PRT calibration.

Finally, this whole setup allowed us to measure the change in water potential of the liquid water in the cavity of the tensiometer for different values of the temperature difference across the vapor gap in the glass tube and for different reference water potentials. In the following, we consider experiments during which we imposed steps of measured temperature difference ΔT^* by keeping the solution at constant temperature and modifying the temperature of the tensiometer with the Peltier module. We monitored the evolution of voltage across the Wheatstone bridge continuously. In general, steps of ~ 20 min were long enough to allow for equilibration of the device.

III. RESULTS

A. Calibration of the tensiometer

As previously explained, equilibrium between liquid water in the cavity and water vapor surrounding the nanoporous membrane, described by Eq. (7), decreases the pressure in the cavity and deforms the diaphragm of the tensiometer. In this section, we explain the calibration procedure of the sensor, allowing us to estimate the water potential Ψ of the vapor at the interface of the nanoporous membrane from the voltage U measured across the Wheatstone bridge.

1. Measurement in water

First, we used de-ionized water as the reference solution: By definition [Eq. (1)], the water potential of pure water is zero at any temperature and atmospheric pressure and $\Psi_{\text{ref}} = 0$. The measurements are displayed in Fig. 4.

As seen in Fig. 4, the obtained variations of U with the measured difference of temperature ΔT^* can be divided into two parts. When the temperature of the tensiometer was lower than

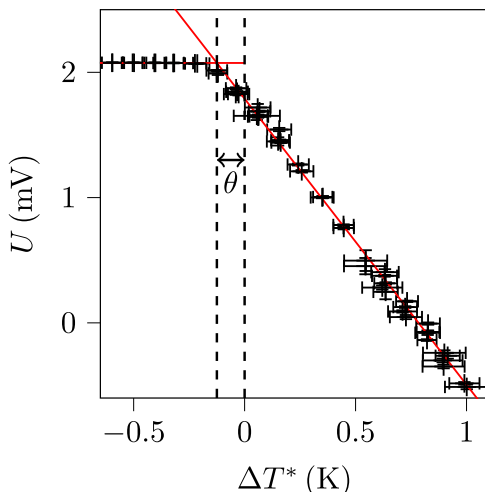


FIG. 4. Evolution of the voltage U across the Wheatstone bridge of the tensiometer with the measured difference of temperature ΔT^* between the tensiometer and pure liquid water. The red lines are linear regressions to determine the offset between the measured difference ΔT^* and the true difference $\Delta T = \Delta T^* + \theta$.

that of the solution (corresponding to negative values of ΔT^*), water vapor condensed on the nanoporous membrane (corresponding to positive values of water potential Ψ). As the membrane is hydrophilic, water then spreads; no deformation of the diaphragm was induced and the bridge voltage plateaued at its saturation value U_0 . On the contrary, when the tensiometer was hotter than the solution (corresponding to positive values of ΔT^*), water vapor in the air gap was unsaturated and the voltage U across the Wheatstone bridge evolved linearly with temperature difference.

We note, though, that the plateau voltage appeared for $\Delta T^* < 0$, while it should be reached under isothermal conditions, i.e., at $\Delta T^* = 0$. This is the sign of a systematic offset $\theta = \Delta T - \Delta T^* = 0.13 \pm 0.01$ °C between our temperature measurement ΔT^* and the actual temperature difference ΔT across the air gap. We determined this offset, with good precision, by taking the intersection between the abscissa axis, $\Psi = 0$, and a linear fit over the points of nonzero water potential in plots as in Fig. 4.

This offset corresponds to a resistance ~ 0.9 Ω for the PRT, which is smaller than the numerical resolution of our resistance measurements during temperature calibration. It could also stem from a variation of contact resistances in the tensiometer which could have changed during manipulation between the temperature calibration and the experiment. As a consequence, we use this offset θ to correct our temperature measurements and estimate the temperature difference across the vapor gap by $\Delta T = \Delta T^* + \theta$. The uncertainty in the temperature difference ΔT is mostly due to the uncertainty in the estimation of θ .

2. Measurements in osmotic solutions

We repeated this experiment with different solutions of solutes [sodium chloride, urea, PolyEthylene Glycol (PEG)] in order to have reference solutions of varying water potentials. The reference water potential Ψ_{ref} of these solutions was determined by using a chilled mirror hygrometer (WP4C, Meter Group). As we worked in dilute solutions, the water potential of the solution did not vary strongly with temperature and in most experiments the temperature of the water bath was kept at 21 °C, at which the measurement of the reference potential was performed. For each reference solution, we measured the voltage U across the Wheatstone bridge for varying temperature differences ΔT ; the results are displayed on Fig. 5.

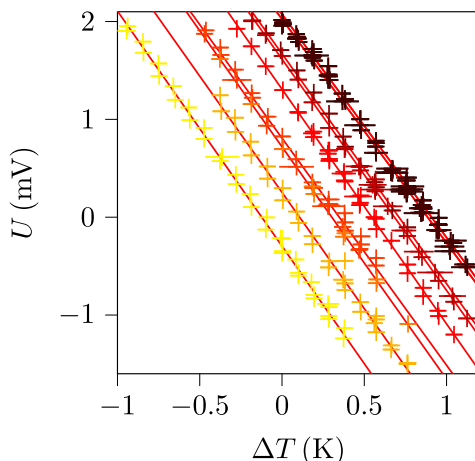


FIG. 5. Variation of bridge voltage U as a function of the (corrected) temperature difference ΔT across the air gap for several solutions of different water potential Ψ_{ref} (pure water $\Psi_{\text{ref}} = 0$ MPa; urea solutions $\Psi_{\text{ref}} = -1.16, -3.10, -3.94, -4.06, -6.13,$ and -8.88 MPa; PEG solution $\Psi_{\text{ref}} = -1.2$ MPa). Lighter colors correspond to increasing absolute water potential $|\Psi_{\text{ref}}|$. Lines are linear fits.

Results were qualitatively similar to what we observed with water (Fig. 4), except that the voltage plateaus (not displayed in Fig. 4) occur for a tensiometer colder than the solution. This shift is due to the fact that water potential of the solution in isothermal conditions Ψ_{ref} was nonzero and measurements by the tensiometer are possible as long as $\Psi \leq 0$.

As displayed in Fig. 5, we performed linear fits of the the $U(\Delta T)$ curves for the different solutions, and extracted the isothermal voltage $U(\Delta T = 0)$ for every reference. The result is displayed in Fig. 6.

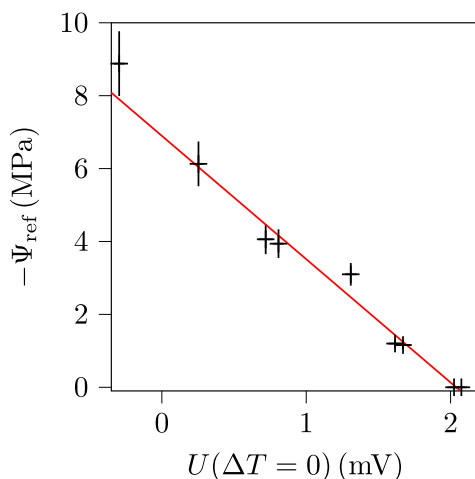


FIG. 6. Absolute water potential of the solution $-\Psi_{\text{ref}}$, determined by a chilled mirror hygrometer, as a function of the bridge voltage $U(\Delta T = 0)$ measured by the tensiometer in isothermal conditions. The red line corresponds to a linear fit according to Eq. (9).

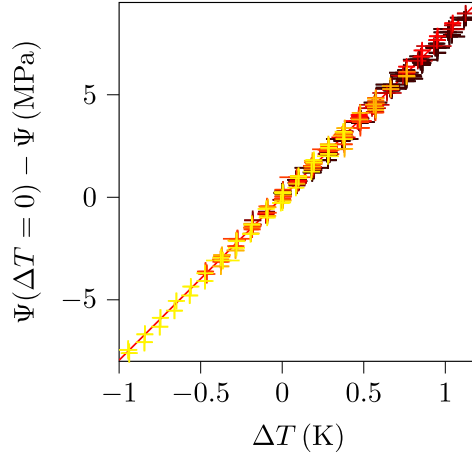


FIG. 7. Variation of water potential measured by the tensiometer relative to the value in isothermal conditions, $\Psi_{\text{ref}} - \Psi$, for several solutions of different Ψ_{ref} (pure water $\Psi_{\text{ref}} = 0$ MPa; urea solutions $\Psi_{\text{ref}} = -1.16, -3.10, -3.94, -4.06, -6.13,$ and -8.88 MPa; PEG solution $\Psi_{\text{ref}} = -1.2$ MPa). Lighter colors correspond to increasing absolute water potential $|\Psi_{\text{ref}}|$. The red line is a linear fit.

As expected, there is a linear relationship between the isothermal voltage $U(\Delta T = 0)$ and water potential of the solution Ψ_{ref} and our data can be fitted by the following equation,

$$-\Psi_{\text{ref}} = \alpha U(\Delta T = 0) + \beta, \quad (9)$$

with $\alpha = -3.4 \pm 0.2$ MPa mV $^{-1}$ and $\beta = 8.0 \pm 0.4$ MPa. By using this equation, we were able to convert the measured voltage U across the Wheatstone bridge under any condition into the water potential Ψ of the vapor at the nanoporous membrane.

3. Measurement of the Ψ - T coupling

Finally, we aggregated all data in Fig. 7 by plotting the variation of water potential $\Psi(\Delta T = 0) - \Psi = \alpha[U(\Delta T = 0) - U]$ of the vapor at the top of the air gap with respect to its value under isothermal conditions as a function of the temperature difference ΔT across the vapor gap.

We observe that, independently of the reference value of the water potential and of the nature of the reference solution, the water potential decreased linearly with the temperature difference with a constant slope,

$$\left. \frac{d\Psi}{dT} \right|_{\text{expt}} = -7.9 \pm 0.3 \text{ MPa K}^{-1}. \quad (10)$$

We performed all experiments shown in Fig. 7 at the same bath temperature, $T_{\text{bath}} = 21$ °C. We, however, reproduced the experiment for different bath temperatures between $T_{\text{bath}} = 15$ °C and $T_{\text{bath}} = 30$ °C (data not shown): We observed a trend of a decreasing (absolute) slope with increasing temperature, but the differences in slope were within our uncertainty. This trend is consistent with our simple prediction [Eq. (4)] that predicts a range of slope from -8.56 to -8.00 MPa K $^{-1}$ between 15 and 30 °C.

IV. DISCUSSION

A. Confrontation of our results with literature and model

As already discussed, the question of the coupling between gradients of temperature and water potential is of crucial importance in psychrometry and has been mostly studied in this context by Dixon *et al.*, by using their own design of a psychrometer. In a first paper [19], they observe a deviation between the water potential of plant tissues measured with a mechanical technique (the Scholander pressure chamber [37]) and measurements with their psychrometer: These deviations are related to the temperature difference between the sample and the psychrometer and they report a correction factor of -7.77 MPa K^{-1} at $T = 25^\circ\text{C}$. In a later article [33], they investigate this effect more systematically by using salt solutions of a calibrated water potential as a reference and controlling more carefully the temperature gradient. In this case, they report a variation between -7.53 and -7.84 MPa K^{-1} at $T = 25^\circ\text{C}$.

These values are compatible with our measurements [Eq. (10)] if we account for our measurement uncertainties. However, a comparison is hard to make as they do not discuss uncertainties. Moreover, they are restricted to small temperature differences below 0.1 K and small tensions below 5 MPa. Our study thus significantly extends the range of measurement of the Ψ - T coupling (with both positive and negative temperature differences over a 2° range in various solutions) and includes experimental uncertainties.

The theoretical value obtained with the simple model [-8.33 MPa K^{-1} , Eq. (4)] sits slightly outside of the experimental uncertainty of our measurements [$-7.9(3) \text{ MPa K}^{-1}$, Eq. (10)]. This discrepancy is small, in particular as uncertainties are hard to estimate with precision in such a measurement. However, it seems significant, in particular as previous measurements also report values which lie below the theoretical prediction. It is thus interesting to look for possible biases both in the experiment and in the model.

B. Possible biases in the experiment

In designing the setup and performing the experiments, we took great care to avoid possible systematic uncertainties in our measurements. However, it is never possible to guarantee their absence. A first possibility would be the presence of impurities at the liquid/vapor interfaces [27], but this effect is likely to be negligible as we took care to work with de-ionized water and did not observe any systematic evolution of our measurements when repeating the experiment.

Precise temperature control and measurement are an experimental challenge and, due to the large variations of water potential caused by the Ψ - T coupling, small errors in the measured temperature difference lead to significant errors in the Ψ - T coupling. Such errors can arise between the temperatures at the ends of the vapor gap, and these at the location of the thermometers. We already described the correction of the observed offset $\theta = \Delta T - \Delta T^*$ between the measured and actual temperature differences.

However, there is another possible source of error in temperature measurement: Due to the finite thermal conductivity of water and porous silicon, we cannot rule out the existence of temperature gradients between the on-chip PRT and the cavity in the tensiometer, and between the reference PRT and the liquid-vapor interface in the solution. These discrepancies would cause a linear relationship $\Delta T^* = \gamma \Delta T$ with $\gamma \neq 1$ and we overall expect an affine relationship $\Delta T^* = \gamma \Delta T + \theta$. As the PRT of the microtensiometer is placed at its tip and silicon is a good heat conductor, we do not expect significant errors in the measurement of the temperature on the tensiometer side. If such an error could occur, as the PRT is further from the heat source than the cavity, it would lead to an underestimation of the temperature difference and thus to an overestimation of the value of $(d\Psi/dT)$. Correction of this effect would tend to give a correction toward lower values of this coefficient and thus cannot explain the observed discrepancy with the theoretical prediction.

The measurement of the temperature at the mesh side is more difficult as we cannot place precisely the thermometer exactly at the end of the vapor gap, in contact with the mesh. To control

this possible uncertainty, we repeated the experiment without the mesh such that we could place the tip of the reference PRT inside the vapor gap. In this situation, we obtained exactly the same value for the slope $d\Psi/dT$, i.e., -7.9 MPa K^{-1} (data not shown). This makes us confident that the correction factor γ is very close to 1 and our estimations of temperature differences (corrected by the offset) were reliable.

C. Refinement of the model

Derivation of Eq. (4) relies on the assumption that both pressure and mole fraction of water are constant throughout the vapor gap. A more general relation can be obtained by differentiating Eq. (3):

$$d\Psi = c_\ell R \left[\frac{\Psi}{c_\ell RT} - \frac{T}{P_{\text{sat}}(T)} \frac{dP_{\text{sat}}}{dT} \right] dT + c_\ell RT \left(\frac{dP}{P} + \frac{dx}{x} \right) \equiv \left(\frac{d\Psi}{dT} \right)^0 dT + c_\ell RT \left(\frac{dP}{P} + \frac{dx}{x} \right). \quad (11)$$

The first term of this equation corresponds to the first-order theory presented in Sec. IC [Eq. (4)]. In this theory, we assumed pressure and composition remain homogeneous across the vapor gap. The second term in Eq. (11) quantifies the corrections to the first-order theory of Ψ - T coupling due to possible variations in pressure and mole fraction.

From the right-hand side of Eq. (11), we can get an idea of the gradients of pressure and mole fraction that would need to be present to match the discrepancy between our measurement and theory. For example, for a temperature difference of $\Delta T = 1 \text{ K}$, we have

$$\frac{\Delta P}{P} + \frac{\Delta x}{x} = \frac{\Delta\Psi - \Delta\Psi^0}{c_\ell RT} \sim 0.3\%, \quad (12)$$

where $\Delta\Psi^0 = (d\Psi/dT)^0 \Delta T$ is the prediction from the simple theory. Consequently, moderate variations of pressure or mole fraction could explain the small discrepancy between our measurements and the simple theory; in the following, we describe possible causes of such variations and the order of magnitude of their impact on Ψ - T coupling. Further details can be found in Appendix.

1. Pressure gradients

Pressure gradients are unlikely to explain the observed discrepancy. A hydrostatic pressure gradient on the small air column of height $h = 1 \text{ cm}$ we studied is completely negligible and, as detailed in Appendix A 1, pressure gradients generated by possible convection flow in the air gap would require a nonrealistic flow speed around $v \sim 10^4 \text{ m s}^{-1}$. However, it is important to note that in porous media, due to the small hydraulic permeability, significant pressure gradients could occur from flows of moderate speed.

2. Cross-diffusion effects

Mole fractions gradients can be directly created by a temperature gradient through a cross-diffusion effect called thermodiffusion or the Soret effect. This corresponds to a differential migration of species of a mixture in a temperature gradient. It was initially observed in salt solutions [38] and later gaseous and liquid mixtures [39]. In gas mixtures, it can be predicted from kinetic theory [40], while in liquids, its explanation remains elusive [41]. The Soret effect would result in a mass flux of water vapor \vec{j}_T ($\text{kg m}^{-2} \text{ s}^{-1}$) which is directly proportional to the temperature gradient. Such a flux superimposes to the regular diffusion flux given by Fick law, and equilibrium between them leads to a steady gradient of mole fraction. As detailed in Appendix A 2, the resulting variation of mole fraction across the vapor gap is given by the equation

$$\frac{\Delta x}{x} \simeq -\alpha_T \frac{\Delta T}{T}, \quad (13)$$

where α_T is a dimensionless coefficient, depending on the interactions between gas molecules.

We have not found values of the Soret coefficient α_T of water vapor in air at ambient temperature in the literature. It can be computed from kinetic theory but it requires a precise knowledge of the molecular details of the studied mixture [40]; by considering that the gaseous species are spherical with no internal structure and undergo elastic collisions, we estimated that $\alpha_T \simeq -0.20$ for a mixture of water and air at $T = 21^\circ\text{C}$. These assumptions are rough but it has been shown that this treatment gives a correct sign and order of magnitude of the coefficient α_T for mixtures of water and molecular hydrogen under large temperature gradients [42].

Qualitatively, we observe that $\alpha_T < 0$, which corresponds to an accumulation of water at hot places and a reduction of the measured absolute water potential with respect to the simple prediction; this is in qualitative agreement with our experiment. Quantitatively, we find that Soret effect induces a correction to the Ψ - T coupling leading to $(d\Psi/dT) = -8.24 \text{ MPa K}^{-1}$: The Soret effect could have an impact of about 1% on the Ψ - T coupling. This contribution would not be negligible and could bring the prediction within the uncertainty of our measurements.

Another cross-diffusion effect arises in the presence of a pressure gradient, called barodiffusion. In this case, the transport coefficient can be directly obtained from molar masses and the composition of the difference species, with no need for a detailed microscopic theory [43]. However, as argued above, pressure gradients should be very small in our experiment and barodiffusion should have a negligible impact.

3. Natural convection

Finally, in our estimate of the impact of the Soret effect, we assumed the gas was at rest. Natural convection by itself cannot generate a steady concentration gradient in the air gap. However, it can couple with the Soret effect; this could lead to an enhanced separation of the species [44], here corresponding to further accumulation of water around the tensiometer. Such an effect would further reduce the absolute water potential and could possibly explain the discrepancy between our measurement and the simple theory of Ψ - T coupling. A full (numerical) resolution of the advection-diffusion equation for water vapor accounting for the Soret effect would be required to estimate precisely the impact of convection on the Ψ - T coupling.

In most of our experiments, the temperature gradient is upwards, i.e., the gas in the tube is heated from above; this situation is stable with respect to convection and no flow should appear. In the few cases in which the temperature gradient was downwards (with osmotic solutions), temperature gradients are too small to trigger thermal convection.

However, the temperature gradient is not purely vertical in our experiment. As thermal conductivity of the glass tube is significantly larger than this of the gas inside, there should be a radial temperature gradient, with temperature decreasing from the center of the tube towards the walls. Such a situation in which the temperature gradient is orthogonal to gravity leads to convection flows without any threshold, with fluid going upwards where the temperature is higher and downwards when it is lower. In our case, we thus should have a vertical upwards flow at the center of the cell. As detailed in Appendix A 3, simple estimates lead to a maximum recirculation velocity of $v_{\text{max}} \simeq 2 \times 10^{-4} \text{ m s}^{-1}$.

V. CONCLUSION AND PERSPECTIVES

In this paper, we studied experimentally the evolution of the water potential caused by a temperature gradient across a vapor in a closed system and obtain a value of $-7.9 \pm 0.3 \text{ MPa K}^{-1}$ at 21°C , in agreement with previous experimental results. This result is close to a simple theoretical prediction, assuming the gas phase is at rest and displays no gradients of pressure and mole fraction; we conclude that most of the effect comes from the variation of saturation pressure with temperature. However, this first-order prediction lies slightly outside our experimental uncertainty and previous experiments also systematically obtained values below the theory. We thus investigated the possible source of errors both in the experiment and the modeling of the situation.

While always possible, it seems that systematic biases in the experiment (in particular regarding temperature control and measurement) cannot explain the discrepancy as these effects would tend to overestimate the real effect. However, we showed that modeling of our setup is more complex than could be thought at first sight due to the possibility of the thermodiffusion flux (Soret effect) and its coupling with natural convection occurring due to the radial component of the temperature gradient. Future experiments will improve the setup in order to decrease measurement uncertainties (in particular by using more careful calibration procedures of the microtensiometer) and should be performed with a pure water vapor gap (i.e., in an evacuated cell). In this case, there should be no Soret effect and the mole fraction should be one everywhere. If we confirm that the Soret effect is at the origin of the observed discrepancy, our setup could give an interesting method to measure the Soret coefficients of various molecules in gases as the microtensiometer can be operated with fluids other than water [36].

As confirmed by our work, the water potential varies strongly with temperature; this highlights the necessity, well known by users of psychrometers, to ensure isothermal conditions or to apply a proper correction if it is not the case. This same caution applies to the use of our microtensiometer for the measurement of the water potential in unsaturated media. Nonetheless, the design and mode of operation of the microtensiometer provides an important opportunity relative to thermocouple psychrometers: Whereas the operation of psychrometers requires that the sensing element, the thermocouple junction, be exposed to vapor that, in turn, is exposed to the medium of interest, the nanoporous membrane of the microtensiometer can be put into direct contact with the medium of interest to favor thermal equilibrium and minimize the effect characterized here. Alternatively, for situations in which direct contact could lead to contamination, a conductive element, such as the copper strip used in this study [Fig. 3(b)], can help maintain thermal equilibrium with the sample. Work in our laboratory (unpublished) with the microtensiometer embedded in the xylem tissues of woody plants indicates that good thermal contact between the tissue and the device can indeed be achieved. Finally, this strong coupling between water potential and temperature could be exploited to engineer new porous membranes for heat management [26].

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APPENDIX: DETAILS ON THERMODIFFUSION AND NATURAL CONVECTION

In this Appendix, we detail the calculations leading to the orders of magnitude of the different corrections to the first-order theory of Ψ - T coupling discussed in Sec. IV C.

1. Possible pressure gradients

Hydrostatic pressure gradients are usually accounted for in models of soil hydrology. As gas in the vapor gap of our experiment is mostly composed of air (at the considered temperature, the saturation mole fraction of water is $x_{\text{sat}} \sim 2.5\%$), we can assume its mass density is $\rho_{\text{g}} \sim 1.2 \text{ kg m}^{-3}$

which gives a pressure variation $\Delta P = \rho_g h g \sim 0.1$ Pa across the vapor gap of height $h = 1$ cm; this pressure variation is fully negligible when compared with ambient pressure.

If some convection flow occurs (see Appendix A 3), it would also be coupled with pressure gradients. A simple estimate of such gradients can be obtained by using the Poiseuille law, which links flow speed of a fluid of kinematic viscosity η (Pa) and pressure difference in a cylindrical pipe of height h and radius R_0 through

$$\Delta P = \frac{4\eta h}{R_0^2} v. \quad (\text{A1})$$

In our case, the cell has dimensions $2R_0 \simeq L \sim 1$ cm and air has a viscosity $\eta \simeq 1.8 \times 10^{-5}$ Pa s. In order to obtain a pressure variation of 0.3% of the atmospheric pressure $P = 1$ bar, a speed $v \sim 10^4$ m s⁻¹ would be required: This flow speed in the vapor gap is not realistic.

Consequently, it is legitimate to neglect pressure gradients in our experiment. However, it is important to note that in porous media in which the permeability is small, significant pressure gradients could occur.

2. Thermodiffusion

The Soret effect would result in a mass flux of water vapor \vec{j}_T (kg m⁻² s⁻¹) which is directly proportional to the temperature gradient and can be written as

$$\vec{j}_T = -\rho_g D \alpha_T c (1 - c) \frac{\vec{\nabla} T}{T}, \quad (\text{A2})$$

where ρ_g (kg m⁻³) is the average mass density of the gas, D (m² s⁻¹) is the diffusion coefficient, and α_T is a dimensionless coefficient [45].

The total mass flux of water is thus obtained by adding the Soret flux \vec{j}_T to the regular Fick law $\vec{j}_d = -\rho_g D \vec{\nabla} c$:

$$\vec{j} = -\rho_g D \left(\vec{\nabla} c + \alpha_T c (1 - c) \frac{\vec{\nabla} T}{T} \right). \quad (\text{A3})$$

As the amount of water is constant in the vapor gap, we should have $\vec{j} = \vec{0}$, so

$$\vec{\nabla} c + \alpha_T c \frac{\vec{\nabla} T}{T} = 0. \quad (\text{A4})$$

In the dilute regime, mole and mass fraction of water can be assimilated and we obtain

$$\frac{\Delta x}{x} \simeq -\alpha_T \frac{\Delta T}{T}. \quad (\text{A5})$$

The Soret effect thus induces a correction to the Ψ - T coupling given by

$$d\Psi \simeq \left[\left(\frac{d\Psi}{dT} \right)^0 - c_\ell R \alpha_T \right] dT. \quad (\text{A6})$$

The value of this coefficient can be predicted theoretically from kinetic theory for a binary mixture of spheres with a given interaction potential [40]. If we model the gas in the air gap as a binary mixture of water molecules and air (with the average molar mass and molecular size between molecular nitrogen and oxygen) and assume collisions are elastic, it is possible to obtain an expression for α_T as a function of T , leading to a value of $\alpha_T \simeq -0.20$ in saturated air at temperature $T_0 = 21$ °C. We do not claim that this value is quantitative: Our assumptions in the kinetic theory of spherical molecules, elastic collisions, and treatment of air as a pure species with average properties are indeed dubious. However, it has been shown that this treatment gives a correct

sign and order of magnitude of the coefficient α_T for mixtures of water and molecular hydrogen under large temperature gradients [42]. We thus believe that our model should give a correct order of magnitude of the impact of the Soret effect.

3. Hadley thermal convection

In the few cases in which the temperature gradient was downwards in our experiment (with osmotic solutions), we can compute the Rayleigh number $Ra = \alpha \Delta T g h^3 / \nu \kappa$, where $\alpha \sim 1/T$ is the isobaric dilation coefficient of the gas, $\nu = \eta / \rho_g$ its kinematic viscosity, and κ its thermal diffusivity. For air, $\nu \simeq 1.6 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ and $\kappa \simeq 2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, so for a temperature difference of $\Delta T = 1 \text{ K}$ across the vapor gap, the Rayleigh number is $Ra \sim 100$. The onset of convection corresponds generally to Rayleigh numbers $Ra \gtrsim 1000$ so convection is very unlikely.

However, as discussed in the main text, the horizontal component of the temperature gradient could be comparable to the vertical one. In the case of a fluid contained between two infinite vertical plates separated by a distance a , the flow resulting from a temperature difference between the plates has an analytic expression known as the Hadley flow [46]. The maximum vertical velocity in such a case is given by

$$v_\infty = \frac{\alpha g \Delta T}{9\sqrt{3}\nu} a^2. \quad (\text{A7})$$

For a cell of finite size, the flow field is generally not known. However, for a rectangular cell of height h , width a in the direction of the temperature gradient, and infinite in the third direction, approximate solutions can be found for an aspect ratio h/a close to 1 and a moderate horizontal Rayleigh number (typically $Ra < 1000$ corresponding to $\Delta T < 10 \text{ K}$ in our experiment) and give [47] a maximum vertical velocity:

$$v_{\max} = v_\infty \frac{1}{h^4 + a^4} \left(\frac{h}{2} \right)^4. \quad (\text{A8})$$

Our cylindrical geometry is different from this situation and the horizontal temperature gradient is not constant across the vapor gap in our experiment, but this expression should give at least a correct order of magnitude of the convection speed. By taking $h = 1 \text{ cm}$ and $a = R_0 = 0.5 \text{ cm}$, we obtain $v_{\max} \simeq 2 \times 10^{-4} \text{ m s}^{-1}$.

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