



AFRL-AFOSR-VA-TR-2022-0002

Plant-Mimetic Functional Materials for Thermal Management and Suppression of Freezing

**Stroock, Abraham
CORNELL UNIVERSITY
341 PINE TREE RD
ITHACA, NY, 14850
USA**

**10/10/2021
Final Technical Report**

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
Air Force Office of Scientific Research
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 10-10-2021	2. REPORT TYPE Final	3. DATES COVERED (From - To) 15 Jun 2018 - 14 Jun 2021
--	--------------------------------	--

4. TITLE AND SUBTITLE Plant-Mimetic Functional Materials for Thermal Management and Suppression of Freezing	5a. CONTRACT NUMBER
	5b. GRANT NUMBER FA9550-18-1-0345
	5c. PROGRAM ELEMENT NUMBER 61102F

6. AUTHOR(S) Abraham Stroock	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) CORNELL UNIVERSITY 341 PINE TREE RD ITHACA, NY 14850 USA	8. PERFORMING ORGANIZATION REPORT NUMBER
--	---

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AF Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203	10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR RTB2
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-VA-TR-2022-0002

12. DISTRIBUTION/AVAILABILITY STATEMENT
A Distribution Unlimited: PB Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Aeronautical technologies must operate under extreme dynamic and environmental conditions that challenge conventional systems for the management of thermal loads and make exposed surfaces prone to the accumulation of ice. Desirable solutions for addressing these challenges should involve a minimum of components and active elements, allow for multi-functional deployment within structural materials, and operate effectively over a wide range of environmental conditions. In developing new technologies to accomplish these tasks, we have adapted strategies observed in vascular plants. These organisms have evolved elegant, largely passive methods to manage fluxes of mass and energy to maintain hydration, provide thermal regulation, and control phase transitions to avoid damage due to cavitation and freezing. These plant strategies bring together micro- and nano-structured materials with metastable states of liquid water (both supercooled and superheated). In this project, we have designed and fabricated synthetic devices that capture the features of plant vascular physiology. We have exploited these systems to elucidate the fundamental physico-chemistry of phase equilibrium and transport involving metastable liquids. Further, we will use these platforms and our acquired knowledge of them to develop new technologies for heat transfer and control the formation of ice at supercooled temperature. In parallel, we have investigated the physiological features that allow plants to operate with metastable liquid states. Together, these studies provide a foundation of concepts and techniques to build high performance, multi-functional materials for current and future Air Force applications.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON BYUNG LEE
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (Include area code) 426-8483
U	U	U	UU	9	

Title: Plant-Mimetic Functional Materials for Thermal Management and Suppression of Freezing

P.I.: Abraham Stroock, Chemical and Biomolecular Engineering, Cornell University

Co-P.I.: N. Michelle Holbrook, Organismic and Evolutionary Biology, Harvard University

Contract #: FA9550-18-1-0345

PM: Byung Lip Lee

Abstract:

Aeronautical technologies must operate under extreme dynamic and environmental conditions that challenge conventional systems for the management of thermal loads and make exposed surfaces prone to the accumulation of ice. Desirable solutions for addressing these challenges should involve a minimum of components and active elements, allow for multi-functional deployment within structural materials, and operate effectively over a wide range of environmental conditions. In developing new technologies to accomplish these tasks, we have adapted strategies observed in vascular plants. These organisms have evolved elegant, largely passive methods to manage fluxes of mass and energy to maintain hydration, provide thermal regulation, and control phase transitions to avoid damage due to cavitation and freezing. These plant strategies bring together micro- and nano-structured materials with metastable states of liquid water (both supercooled and superheated). In this project, we have designed and fabricated synthetic devices that capture the features of plant vascular physiology. We have exploited these systems to elucidate the fundamental physico-chemistry of phase equilibrium and transport involving metastable liquids. Further, we will use these platforms and our acquired knowledge of them to develop new technologies for heat transfer and control the formation of ice at supercooled temperature. In parallel, we have investigated the physiological features that allow plants to operate with metastable liquid states. Together, these studies provide a foundation of concepts and techniques to build high performance, multi-functional materials for current and future Air Force applications.

Report:

I. Summary: Under this award, we have focused on maturation of tools with which to manipulate a characterize metastable phase equilibria. These phase equilibria generate stresses (Fig. 1A) that can be exploited to drive transport processes, as in heat transfer applications (Fig. 1B) and control phase behavior. In our previous reports, we have discussed the following developments: elucidation of the impact of large negative pressures on the solubility molecular oxygen in liquid water;¹ capture of a plant-inspired process for the refilling of cavitating vessels with osmotic potentials;² quantification of impact of solutes on wetting of nanoporous solids;³ design and operation of a new form of osmometer based on a plant-mimetic MEMS tensiometer;⁴ quantification of the coupling between thermal gradients and chemical potential with a plant-mimetic tensiometer;⁵ and characterization structure-function relationships in the transport of sap in phloem.⁶⁻⁸ In this report, we highlight: i) the development of a powerful new tool for the measurement of stresses within plant tissues and ii) the application of this tool for the characterization of local dynamics within leaves that open onto exciting opportunities for multi-functional materials.

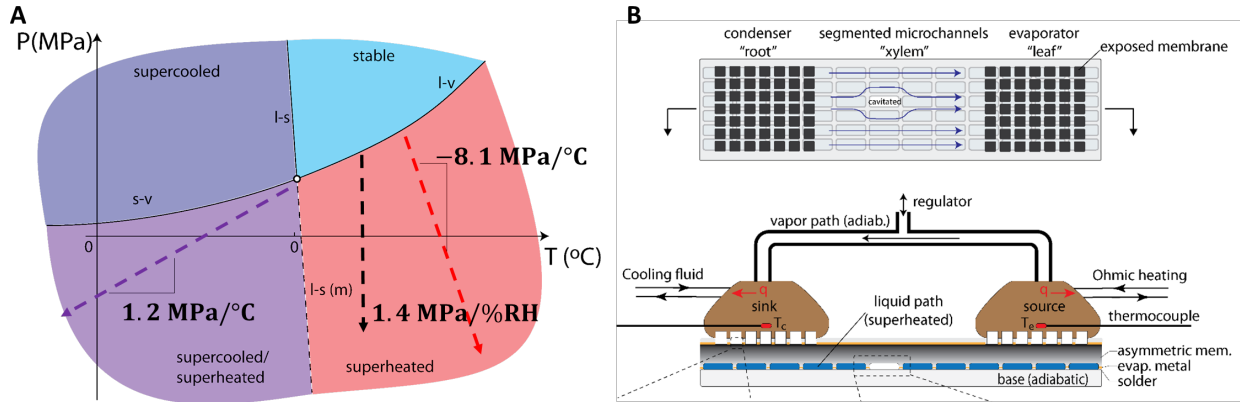


Fig. 1: Autonomic stresses generated in metastable extensions of phase diagram of water. (A) Pressure-temperature phase diagram of water showing triple point (white circle), the stable (blue), superheated (pink), supercooled (dark purple), and doubly metastable supercooled/supercooled liquid regions. Three trajectories of metastable equilibrium are shown: Kelvin effect (black dashed line) describes the stress that emerges under isothermal conditions between a dry vapor atmosphere and a wetted porous solid; the psychrometric effect describes the difference in water potential associated with a difference in temperature; and the Gibbs-Thompson effect predicts the stress a confined liquid in equilibrium with sub-cooled ice. G-T is usually expressed as the suppression of the melting temperature. **(B)** Plant-inspired system for the manipulation of metastable liquids for the efficient transfer of heat (shown) and management of freezing (not shown).

II. Objectives:

1. Fundamental studies of the thermodynamics and transport phenomena implicated in plant's strategies for the manipulation of metastable liquids.
2. Development of new strategies for the fabrication of plant-mimetic systems for the manipulation of metastable liquids.
3. Construction and characterization of superheated loop heat pipes.
4. Construction and characterization of surfaces that provide active management of the deposition and accumulation of ice.
5. Characterize the biology of deeply supercooling trees with the aim of identifying new molecules that provide dramatic stabilization of metastable liquid water.

III. Progress: In the following, we focus on recent developments that have opened unprecedented opportunities to dissect the mechanisms by which plants manipulate liquids, phase change, and exchange with the environment. Here, we provide an overview of our new approaches, the new observations they have enabled, and the opportunities these observations create relative to the design of multi-functional materials.

A. Overview. In this period, we have developed a second plant-inspired tool with which to study the fundamental thermodynamics and physiology associated with metastable liquids. The first tool, a MEMS tensiometer, that we developed with AFOSR support provides access to the state and dynamics of water stress (water potential, Ψ [MPa]) in macroscopic phases and full plants;⁴⁻⁵ this tool has recently been commercialized by a start-up out of Cornell (www.florapulse.com). Complementary to this macroscopic operation, the second tool, a fluorescence nanoreporter, AquaDust, provides a local measurement of water potential via optical interrogation.⁹

B. Design and function of AquaDust. Fig. 2a presents the design of an AquaDust particle. Building on insights from our labs about the functional responses of hydrogel in the xylem

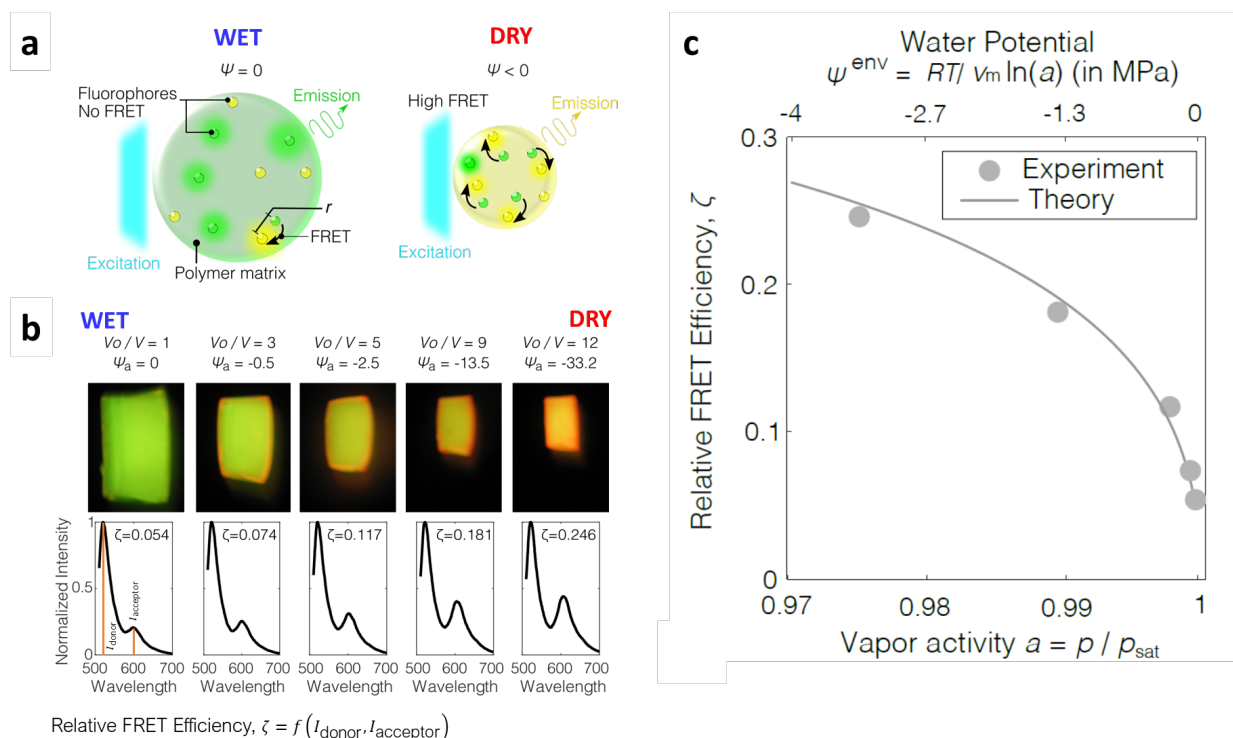


Fig. 2: Fluorescent nanoreporters of water potential, AquaDust. (a) Schematic diagram of AquaDust, nanoparticles of hydrogel with two types of fluorescent dyes – donor in green and acceptor in yellow – covalently linked to matrix. As the particles shrink with decreasing water potential, the average inter-dye spacing decreases, leading to an increase in the Förster Resonance Energy Transfer (FRET). (b) Characterization of macroscopic gels form with the composition as in (a). The photos show the simultaneous change in color and size with decreasing water potential (Ψ_a). The emission spectra show the corresponding changes in the donor (left) and acceptor (right) peak heights. The relative FRET efficiency, ζ is calculated from these peak heights. (c) Variation of relative FRET efficiency of gels in (b) (grey circles) with vapor activity (bottom axis) and equivalent water potential (top axis) with comparison to theory (grey curve).

vascular system of plants,¹⁰⁻¹¹ we exploit gels’ strong change in volume as a function of the local water potential to actuate Förster Resonance Energy Transfer (FRET) within the AquaDust particle: We covalently link two complementary fluorescence dyes (Fig. 2a – green and yellow circles) to the hydrogel backbone during emulsion polymerization of the particles; at high water potential (“wet”), the gel is swollen, the separation between the dyes is large, and FRET is weak; and at low water potential (“dry”), the gel shrinks, the separation between the dyes decreases and FRET is strong. The series of photographs **Fig. 2b** show the evolution of the size and color of a macroscopic gel as it responds to the lowering of water potential; the associated fluorescence spectra show the changes in the emission peaks of the two dyes. From these spectra, we can extract a relative FRET efficiency, ζ . **Fig. 2c** shows how ζ varies with Ψ . Importantly, we have developed a theory that couples the thermodynamics of the gel with the photophysics of FRET; this theory matches the measured $\zeta(\Psi)$ with a single adjustable parameter. The robustness of this theory allows us to calibrate AquaDust’s response with a single measurement (e.g., at saturating conditions, i.e., $\Psi = 0$).

C. Local transport processes in leaves. AquaDust opens an opportunity to characterize the movement of water in plant tissues in unprecedented ways. Of particular interest are the terminal tissues through which transpiration of water occurs, from the xylem vessels within the mid-plane

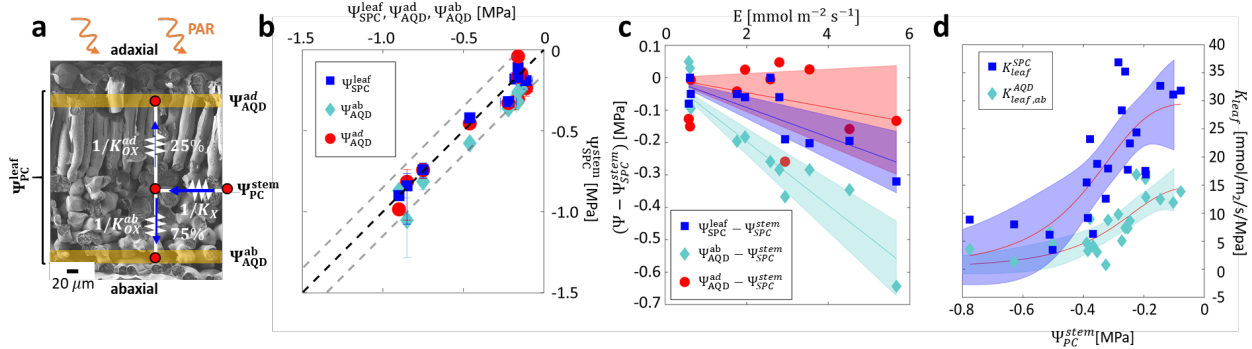


Figure 3: Interrogation of leaf hydraulics with aquadust. (a) Local flows and resistances in the cross-section of tomato leaf. We used the Schölander Pressure Chamber (SPC) to measure stem (Ψ_{SPC}^{stem}) and whole leaf (Ψ_{SPC}^{leaf}) potentials, and aquadust (AQD) to measure adaxial (Ψ_{AQD}^{ad}) and abaxial (Ψ_{AQD}^{ab}) potentials in the near epidermal region (yellow bands) to extract information about the conductances of the xylem (K_X) and the outside xylem paths to the adaxial (K_{OX}^{ad}) and abaxial (K_{OX}^{ab}) surfaces. (b) Correspondence of Ψ_{SPC}^{leaf} (squares), Ψ_{AQD}^{ab} (diamonds), and Ψ_{AQD}^{ad} (circles) with Ψ_{SPC}^{stem} for dark adapted leaves with low transpiration rate ($E < 0.7$ mmol/m²/s) (replicates). Black, dashed line is one-to-one; gray, dashed lines show uncertainty in calibration of aquadust (± 0.15 MPa). (c) Deviation of Ψ_{SPC}^{leaf} (squares), Ψ_{AQD}^{ab} (diamonds), and Ψ_{AQD}^{ad} (circles) from Ψ_{SPC}^{stem} as a function of E in well-watered tomato ($\Psi_{SPC}^{stem} = -0.3 \pm 0.14$ MPa). Slopes of linear fits (lines) and 95% confidence intervals (shaded zones): leaf [-0.046 (-0.058, -0.037)]; abaxial [-0.098 (-0.114, -0.083)]; and adaxial [-0.023 (-0.046, +0.001)] in MPa m² s/mmol. (d) Variation of effective leaf conductance with stem potential based on SPC leaf potential (K_{leaf}^{SPC} , squares) and abaxial AQD potential ($K_{leaf,ab}^{AQD}$, diamonds).

of the leaf to the top and bottom surfaces of the leaf from which water vapor escapes through stomates (openings in cuticle and epidermis – Fig. 3a). This tissue, the leaf mesophyll, hosts critical life functions, most notably photosynthesis, and has been proposed to present the largest resistance to the flow of water from root to atmosphere despite its small dimension (~ 100 μ m). The mesophyll, with its porous structure and interweaving of wetted tissues and vapor spaces, also shares important characteristics with porous structures of importance in technologies such as heat pipe. Upon infiltration into a leaf, AquaDust lines the cells adjacent to the vapor spaces within the mesophyll. When interrogated optically, the collected FRET spectrum from AquaDust comes from a region localized within the first ~ 10 μ m beneath the epidermis (yellow-shaded bands in Fig. 3a). This limitation results from the adsorption and scattering of both the excitation and emission light. While limiting, this localization allows us to measure the water potential at the extreme end of the transpiration pathway such that we can assess the gradients of water potential in this critical zone.

Fig. 3b-c present water potentials measured with AquaDust (Ψ_{AQD}) with two types of measurements performed with the conventional, macroscopic tool (Schölander Pressure Chamber - Ψ_{SPC}). We take one measurement of Ψ_{SPC} with the leaf exposed to the atmosphere and transpiring (Ψ_{SPC}^{leaf}); this value represents an average of the whole leaf tissue. We take another measurement on an adjacent leaf that has been stored in a plastic bag to inhibit transpiration; the bagged leaf's potential approaches that of the stem (Ψ_{SPC}^{stem}). In Fig. 3b, we present measurements take on leaves near equilibrium (small rates of transpiration) for which we expect weak gradients of water potential within the leaf. The strong, one-to-one relationship between Ψ_{AQD} , Ψ_{SPC}^{stem} , and Ψ_{SPC}^{leaf} demonstrates the accuracy of AquaDust for these in-situ measurements.

Fig. 3c presents the variation of the potential differences from stem to leaf potential as a function of transpiration rate, E . The potential differences were measured by the SPC ($\Psi_{SPC}^{leaf} - \Psi_{SPC}^{stem}$ - blue squares) and by AquaDust to the lower, abaxial side of the leaf ($\Psi_{AQD}^{ab} - \Psi_{SPC}^{stem}$ - light blue diamonds) and to the upper, adaxial side ($\Psi_{AQD}^{ad} - \Psi_{SPC}^{stem}$ - red circles); the majority of transpiration occurs through the abaxial side. We observe linear trends in the growth of the potential differences as a function of transpiration rate; the slopes of these trends provide a measure of leaf resistance or inverse of leaf conductance, K_{leaf} . Importantly, we see that the trend is significantly stronger when assessed by AquaDust than by the conventional method (red circles vs. blue squares). This observation suggests that the conventional method (SPC), which provides an average value of potential, misses a substantial component of the potential drop that occurs within the leaf. In contrast, the localization of our measurements with AquaDust at the extreme end of the pathway provides us with a more accurate assessment of the full potential drop across the leaf tissue.

We have further applied this approach in leaves with different levels of equilibrium stress (i.e., stress with no transpiration) in the stem (Ψ_{SPC}^{stem}) by drying down the soil. **Fig. 3d** presents the variation of the effective leaf conductance, K_{leaf} assessed as in Fig. 3c with Ψ_{SPC}^{stem} as assessed with the SPC (blue squares) and with AquaDust (light blue diamonds). We make the following two interesting observations: i) by both measurement techniques, the effective conductance of the leaf varies in a sigmoidal fashion with the level of stress (Ψ_{SPC}^{stem} near zero), passing from a plateau, maximum value at low stress through a steep decline as stress increases (more negative values of Ψ_{SPC}^{stem}). This variation suggests an autonomic response by which the plant tissue may protect the upstream vascular network from dangerous levels of stress that could, for example, lead to irreversible cavitation in the xylem. This mechanism could complement the mechanism of vascular collapse that we elucidated recently and have reported on under our AFOSR project.¹² We will revisit this hypothesis in the next sub-section. ii) As discussed in relation to Fig. 3c, we see conductance assessed by AquaDust (light blue diamond) is substantially lower than that measured by the conventional method (blue squares). This observation reinforces our conclusion that AquaDust provides us access to a more accurate measurement of the full variation of potential within leaves.

D. Extreme levels of stress in leaf tissue. As mentioned above in relation to Fig. 3d, the observed loss of conductance as stress increases could serve as a protective mechanism for the xylem: a loss of conductance in the terminal end of the transpiration path will tend to lower the potential at the sites of evaporation within the leaf; in turn, this lowering of potential will decrease the rate of transpiration throughout the vascular system and thus limit gradients of water potential in upstream components of the vascular system. In short, this loss of conductance could serve as a safety valve that isolates the xylem and other upstream tissues from the dryness (low water potential) of the atmosphere. For this mechanism to be effective, the potential at the evaporative surface would need to drop significantly relative to the typical potentials in the atmosphere, outside the leaf. Typical water potentials of water vapor in the atmosphere are -10 to -100 MPa, corresponding to relative humidities from 90 to 50%. To date, using conventional tools, no one has reported sufficiently large stresses (i.e., ~ -10 MPa) in leaves to support this mechanism. Indeed, a pervasive assumption in plant physiology is that the stomates always present a limiting resistance and regulate their conductance to avoid ever allowing for large stress inside leaves. With the access provided by AquaDust to potentials within the terminal tissues along the transpiration pathway, we have begun to address the intriguing possibility that

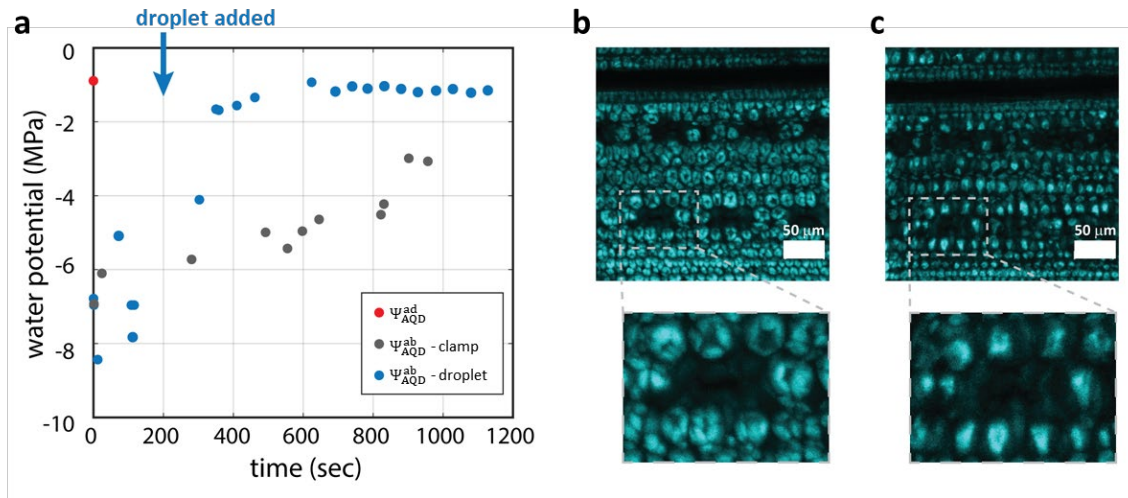


Figure 4: Response to high evaporative demand in maize. (a) Evolution of abaxial measurements of aquadust water potential with optical fiber clamp only (Ψ_{AQD}^{ab} – grey circles) and with a droplet of water added beneath clamp after 200 seconds (Ψ_{AQD}^{ab} – blue circles). The measured region of the leaf had its adaxial side covered.

plants may have the capacity to limit transpiration internally by allowing for large negative potentials inside their leaves.

Fig. 4a presents a preliminary example of a measurement of stress relaxation in a maize leaf that had been exposed to hot dry conditions for times, $t < 0$. At time, $t = 0$, we attached the clamp containing a fiber optic probe for the measurement of the AquaDust spectrum in three configurations: i) on the transpiring abaxial side (grey circles), ii) on the transpiring abaxial side with a water droplet within the probe (blue circles), and iii) on the adaxial side on which the transpiration had been obstructed with an impermeable film (red circle). In cases (i) and (ii) for the abaxial side of the leaves that had been transpiring in hot, dry conditions (grey and blue circles), we see that the initial water potential measured by AquaDust, $\Psi_{AQD}^{ab} = -6$ to -8 MPa. At the same moment, the non-transpiring side of the leaf was at a mild potential (red circle): $\Psi_{AQD}^{ad} = -0.8$ MPa. Subsequent measurements show a fast relaxation of Ψ_{AQD}^{ab} toward Ψ_{AQD}^{ad} with the presence of a water droplet (blue circles) and a slow relaxation with the clamp without a droplet (grey circles). In maize, the typical minimum reported value of Ψ_{SPC}^{leaf} based on the SPC is ~ -2 MPa; at such values of Ψ_{SPC}^{leaf} , stomates are closed. Our measurements with AquaDust indicate the existence of a massive gradient through the thickness of the leaf, from the transpiring adaxial side (-6 to -8 MPa) to the non-transpiring abaxial side (-0.8 MPa) and thus suggest that transpiration continued (stomates open) on the abaxial side despite the fact that a portion of leaf's interior was experiencing enormous stress. These observations disrupt the current understanding of leaf physiology in several important ways: i) potentials within the interior of leaves can drop sufficiently (i.e., -8 MPa) that could have a non-negligible impact on the gradient from the internal evaporative surfaces to the outside atmosphere. This mode of regulating transpiration breaks with conventional thinking in which stomates alone provide this regulation. Further, this effect could provide a functional link between the autonomic regulation of conductance seen in Fig. 3d, its role in the regulation of transpiration, and the protection of upstream tissues from extreme stresses. ii) Conventional methods of assessing stress provide a

tissue-averaged value that fails to capture the full range of stress within the leaf's interior. This limitation has may have led researchers to conclude that stomatal regulation is more conservative than it actually is, i.e., that stomates close at less negative internal potentials. Our measurements suggest a new, non-stomatal mode of regulation that can allow the stomates to remain open under conditions of extreme water demand. By maintaining open stomates under these conditions, the plant can continue photosynthesis (by continuing to access carbon dioxide). If borne out with subsequent experiments, this new mechanism would have major implications for our understanding of the drought physiology of plants and for our ability to breed and engineer plants for hot, dry conditions.

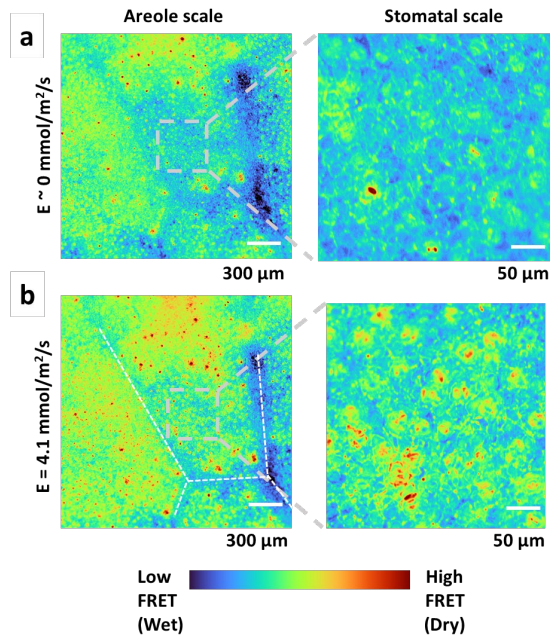


Fig. 5: Direct imaging of local variations in mesophyll water potential. (a-b) Intensity-based FRET images of AquaDust water potential in coffee leaves at two magnifications (areole and stomatal scales) and low (a) and high (b) rates of transpiration (E). Variations in FRET efficiency from wet (blue) to dry (red) are associated with the underlying vascular elements (demarcated with white, dashed lines in (b) and with stomatal pores (discrete points of red).

These observations of extreme stress within leaves also challenges our understanding of leaf physiology in other ways. Most importantly, one expects that the living cells within the leaf mesophyll should collapse (lose turgor) when exposed to such potentials. **Fig. 4b-c** present fluorescence confocal micrographs of mesophyll cells under moderate (4b) and extreme stress (4c) conditions; the green regions in these images correspond to chloroplasts within the cells. We note a strong change in the configuration of the chloroplast in the stressed (4c) versus the non-stressed (4b) case. We note that we did not observe any macroscopic loss of turgor in these leaves. These observations provide a preliminary indication that the mesophyll cells adjacent to the epidermis may undergo highly localized loss of turgor to accommodate the extreme stress to which they can be exposed. This behavior would represent a second autonomic adaptation of the mesophyll structure to manage the transport processes within this critical tissue.

Taken together, the methods we have developed with AquaDust and the observations in Figs. 3 and 4 open onto exciting new areas for discovery and onto new insights that we hope to exploit in the design of synthetic, multi-functional materials.

E. Direct imaging of distribution of water potential. In the proceeding sub-sections, we have discussed application of AquaDust reporters in which we probe a single macroscopic lateral area with an optical fiber probe connected to a light source and a spectrometer. Recently, we have developed two methods of quantifying the AquaDust signal in imaging mode on a scanning confocal microscope. The first method directly follows from the spectral method described in Fig. 2b: we capture a coarsely resolved spectrum with narrow-band filters at each pixel interrogated by the scanning microscope. The second method takes advantage of the dependence of fluorescence lifetime on the FRET. In this case, we use a pulsed excitation and a picosecond

photon counter to measure fluorescence decay at each scanned pixel. **Fig. 5** presents an example of our ability to capture maps of AquaDust FRET at high spatial resolution. We note the ability to resolve individual cells (“stomatal scale”) and changes in the distribution of water potential upon increasing the rate of transpiration from near zero (5a) to an elevated value (5b). *This unprecedented capability opens exceptional opportunities to characterize local transport and thermodynamic processes in complex living and synthetic systems.*

IV. Future Directions

A. Outstanding questions, challenges, and opportunities. As discussed in the previous section, the development of AquaDust has allowed us to perform a variety of new measurements and uncover new phenomena. Our work under this project has opened a number of interesting questions and opportunities:

1. Within the context of water stress physiology of leaves, the results in Figs. 3-5 require significant additional exploration in a variety of directions. The first is to characterize the physics further of the water and energy transport in the mesophyll in which we and others have predicted an important interplay between tissue structure, phase equilibrium, and the movement of heat and mass.¹³ Second, our preliminary work has challenged conventional understanding of the biological mechanisms and functional importance of transport through the mesophyll. We must still probe the limits and generality of the effects (e.g., extreme negative potentials) that we have elucidated.
2. Both our methodological advances and physiological discoveries point to interesting opportunities for translation into synthetic systems. Firstly, AquaDust provides a powerful new tool for the study of transport processes within materials for multi-phase heat and mass transfer. Notably, our ability to interrogate AquaDust with optical wavelengths allow us to image the spatial and temporal dynamics of water potential in ways (e.g., with high resolution microscopy – Fig. 5) that are not possible with IR imaging of distributions of temperature. Given the strong coupling of water potential and temperature in multiphase systems, this capability provides a new route to characterize materials and systems designed for heat and mass transfer with phase change. Secondly, our new views into the functional characteristics of the leaf mesophyll suggest exciting design concepts for multi-functional materials for autonomic control of heat and mass transfer.

B. Future directions. Under our up-coming award from this AFOSR program, we will take advantage of the tools developed under this award to pursue the concept of “synthetic mesophyll” for the design of highly tunable thermal metamaterials. In parallel, we will continue to look to plants for additional insights and inspiration.

VI. Bibliography

1. Lidon, P., Marker, S.C., Wilson, J.J., Williams, R.M., Zipfel, W.R. and Stroock, A.D. Enhanced oxygen solubility in metastable water under tension. *Langmuir*, 34(40), pp.12017-12024 (2018).
2. Vincent, O., Zhang, J., Choi, E., Zhu, S. and Stroock, A.D. How solutes modify the thermodynamics and dynamics of filling and emptying in extreme ink-bottle pores. *Langmuir*, 35(8), pp.2934-2947 (2019).
3. Jain, P., Vincent, O. and Stroock, A.D. Adsorption, desorption, and crystallization of aqueous solutions in nanopores. *Langmuir*, 35(11), pp.3949-3962 (2019).

4. Black, W. L., Santiago, M., Zhu, S. & Stroock, A. D. Ex Situ and In Situ Measurement of Water Activity with a MEMS Tensiometer. *Analytical Chemistry* 92, 716-723 (2019).
5. Lidon, P., Perrot, E. and Stroock, A.D. Nonisothermal effects on water potential measurement in a simple geometry. *Physical Review Fluids*, 6(2), p.023801 (2021).
6. Rockwell, F.E., Gersony, J.T. and Holbrook, N.M. Where does Münch flow begin? Sucrose transport in the pre-phloem path. *Current opinion in plant biology*, 43, pp.101-107 (2018).

7. Clerx, L.E., Rockwell, F.E., Savage, J.A. and Holbrook, N.M. Ontogenetic scaling of phloem sieve tube anatomy and hydraulic resistance with tree height in *Quercus rubra*. *American journal of botany*, 107(6), pp.852-863 (2020).
8. Gersony, J.T., Hochberg, U., Rockwell, F.E., Park, M., Gauthier, P.P. and Holbrook, N.M. Leaf carbon export and nonstructural carbohydrates in relation to diurnal water dynamics in mature oak trees. *Plant Physiology*, 183(4), pp.1612-1621 (2020).
9. Jain, P., Liu, W., Zhu, S., Chang, C.Y.Y., Melkonian, J., Rockwell, F.E., Pauli, D., Sun, Y., Zipfel, W.R., Holbrook, N.M. and Riha, S.J. A minimally disruptive method for measuring water potential in planta using hydrogel nanoreporters. *Proceedings of the National Academy of Sciences*, 118(23) (2021).
10. Zwieniecki, M. A., Melcher, P. J. & Holbrook, N. M. Hydrogel control of xylem hydraulic resistance in plants. *Science* 291, 1059-1062 (2001).
11. Wheeler, T. D. & Stroock, A. D. Transpiration at negative pressures in a synthetic tree. *Nature* 455, 208-212 (2008).
12. Zhang, Y. J., Rockwell, F.E., Graham, A.C., Alexander, T. & Holbrook, N. M. Reversible leaf xylem collapse: a potential "circuit breaker" against cavitation. *Plant Physiology* **172**, 2261-2274 (2016).
13. Rockwell, F. E., Holbrook, N. M. & Stroock, A. D. The Competition between Liquid and Vapor Transport in Transpiring Leaves. *Plant Physiology* **164**, 1741-1758 (2014)