Supplemental Text S2: Expanded derivation for the competition between liquid and vapor transport in leaves

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January 19, 2014

Non-isothermal water vapor and liquid transport in leaves

Conservation of thermal energy and molecules in leaf tissue and air space

The flux of thermal energy $\boldsymbol{E}$ in the presence of a molecular flux $\boldsymbol{J}$ is given by the sum of the heat flux due to conduction $\boldsymbol{q}$ and the convection of enthalpy ($\bar{h}$, enthalpy per molecule) due to the net transport of molecules,

$$\boldsymbol{E} = \boldsymbol{q} + \boldsymbol{J}\bar{h}. \tag{1}$$

Conservation of energy then requires no local accumulation at steady state, leading to

$$\nabla \cdot \boldsymbol{E} = 0, \tag{2}$$

which says that the divergence, or local change, in the heat flux at steady state must be zero. In the presence of a local volumetric heat source, $\dot{Q}$, the conservation statement becomes,

$$0 = -(\nabla \cdot \boldsymbol{E}) + \dot{Q}, \tag{3}$$

which says that the divergence of the heat flux must balance the local production of heat. The combination of (1) and (3), and then expanding the divergence of the convective term, leads to,

$$0 = -(\nabla \cdot \boldsymbol{q}) - (\nabla \cdot (\boldsymbol{J}\bar{h})) + \dot{Q}, \tag{4}$$

$$0 = -(\nabla \cdot \boldsymbol{q}) - (\bar{h}\, \nabla \cdot \boldsymbol{J} + \boldsymbol{J} \cdot \nabla \bar{h}) + \dot{Q}. \tag{5}$$

The first part of the expanded term represents the change in the rate of local energy accumulation due to a change in the molecular flux, while the second accounts for the change due to a change in the enthalpy of the molecules in flux. In order to understand the physical meaning of these terms, it is helpful to recall the definition of the enthalpy of a substance as its internal energy U, plus the work required to make room V for it within an environment at some pressure P, or $H = U + PV$. The molar enthalpy recasts this relation in terms of quantities per mole, $\bar{h} = \bar{u} + p\bar{v}$. The differential form is then given by,

$$\mathrm{d}\bar{h} = \mathrm{d}\bar{u} + p\mathrm{d}\bar{v} + \bar{v}\mathrm{d}p = c_p(T)\,\mathrm{d}T + \left[\bar{v} - T\left(\frac{\partial \bar{v}}{\partial T}\right)_p\right]\mathrm{d}p. \tag{6}$$

For an ideal gas, substituting in the gas law shows that the term in brackets vanishes, and the $\bar{h}$ is a function of temperature only. Treating the liquid phase as incompressible over the range of temperatures and pressures of interest, the change in enthalpies of the two phases can be written,

$$\mathrm{d}\bar{h}_v = c_{p,v}(T)\,\mathrm{d}T, \qquad \mathrm{d}\bar{h}_l = c_{p,l}(T)\,\mathrm{d}T + \bar{v}\,\mathrm{d}p_l. \tag{7}$$

Here p_l refers to the pressure in a pure phase of the liquid. For an impure phase, such as water inhabiting the cellular solid fraction, we can regard p_l as a pressure potential, or the pressure in a pure phase that would bring it into equilibrium with the cellular water. We can then write this pressure in terms of an isothermal change in chemical potential due to pressure, $\bar{v}\,\mathrm{d}p_l = [\mathrm{d}\mu]_T$, or, following the convention in plant water relations, use the definition of water potential ψ, $\mu = \bar{v}\psi$, to describe the variations in enthalpy due to changes in the pressure potential of the liquid as,

$$\mathrm{d}\bar{h}_l = c_{p,l}(T)\,\mathrm{d}T + \bar{v}\,\mathrm{d}\psi. \tag{8}$$

In defining ψ in this way, we are ignoring temperature induced variation in water potential, which is reasonable for variations in temperature of a few degrees or less, as for an impure phase the temperature sensitive term ($\bar{v}\,RT\ln a$) depends only on the absolute temperature, and not the gradient.

We now apply these ideas to a representative volume composed of a continuous, porous liquid-filled elastic solid (liquid phase) interspersed with a continuous air space (the vapor phase). We consider that over the expected range of potential changes the volume changes of the cells (the liquid phase) are small, a few percent, and so neglect changes of dimension. With $\mathcal{A}$ as the area fraction of a phase, and the subscripts l and v referencing the liquid and vapor phases respectively, conservation of thermal energy (5) becomes,

$$\begin{aligned} 0 = -\mathcal{A}_l(\nabla\cdot\boldsymbol{q}_l) - \mathcal{A}_v(\nabla\cdot\boldsymbol{q}_v) - \mathcal{A}_l(\bar{h}_l\,\nabla\cdot\boldsymbol{J}_l + \boldsymbol{J}_l\cdot(c_{p,l}\nabla T + \bar{v}\,\nabla\psi)) \\ - \mathcal{A}_v(\bar{h}_v\,\nabla\cdot\boldsymbol{J}_v + \boldsymbol{J}_v\cdot c_{p,v}\nabla T) + \dot{Q}. \end{aligned} \tag{9}$$

Conservation of the number of water molecules in steady state requires that the divergence of the total flux be zero (the flux into a representative volume balances the flux out). In terms of the individual phases,

$$0 = -(\nabla\cdot\boldsymbol{J}_{total}) = -\mathcal{A}_l(\nabla\cdot\boldsymbol{J}_l) - \mathcal{A}_v(\nabla\cdot\boldsymbol{J}_v), \tag{10}$$

$$\mathcal{A}_l(\nabla\cdot\boldsymbol{J}_l) = -\mathcal{A}_v(\nabla\cdot\boldsymbol{J}_v). \tag{11}$$

This last equation says that in steady state, water molecules may change phase, but conservation of the total number of water molecules requires that an increase in the flux of molecules in one phase is equal to a decline of the flux in the other. Using (11) we can then write (9) as,

$$\begin{aligned} 0 = -\mathcal{A}_l(\nabla\cdot\boldsymbol{q}_l) - \mathcal{A}_v(\nabla\cdot\boldsymbol{q}_v) + \mathcal{A}_l(\nabla\cdot\boldsymbol{J}_l)(\bar{h}_v - \bar{h}_l) \\ - (\mathcal{A}_l c_{p,l}\boldsymbol{J}_l + \mathcal{A}_v c_{p,v}\boldsymbol{J}_v)\cdot\nabla T - \mathcal{A}_l\boldsymbol{J}_l\bar{v}\cdot\nabla\psi + \dot{Q}. \end{aligned} \tag{12}$$

The difference in enthalpy between the two phases, $(\bar{h}_v - \bar{h}_l)$, accounts for the thermal energy required to move water molecules from the liquid to the vapor phase. For an isobaric phase change, across the coexistence line for the pure liquid and vapor with a flat interface, this energy difference defines the molar heat of vaporization at constant pressure $\bar{\lambda}_p$,

$$\bar{\lambda}_p = \int_0^T \left(c_{p,v}(T) - c_{p,l}(T)\right)\,\mathrm{d}T. \tag{13}$$

When the pressure in the liquid deviates from the vapor pressure at the coexistence line, the difference in enthalpy becomes,

$$\bar{\lambda} = \int_0^T \left(c_{p,v}(T) - c_{p,l}(T)\right)\,\mathrm{d}T - \bar{v}\,(p_l - p_{sat}(T)) = \bar{\lambda}_p - \bar{v}(p_l - p_{sat}(T)). \tag{14}$$

Here, $p_{sat}(T)$, is the pressure in a pure vapor and liquid given by the coexistence line for a given temperature (i.e., saturated vapor pressure, as given by Lemmon et al. (2013)). Given that $p_{sat}(T)$ is on the order of kpa, for p_l on there order of a MPa, we can simplify (14) by evaluating the temperature dependent saturated reference pressure term at some reference temperature that characterizes the system, $p_o = p_{sat}(T_o)$.

However, for many purposes the pressure correction will be small and may as well be neglected. For many leaves, $\psi \bar{v}$ is on the order of tens of J mol^{-1}, while $\bar{\lambda}_p$ is 44 kJ mol^{-1} at 25 $°C$, and it will suffice to let $\bar{\lambda} \approx \bar{\lambda}_p$.

Reduction of dimensions: local equilibrium between liquid and vapor

In order to reduce the transport equations to one dimension in the principal direction of the flux (i.e., from the vascular plane through the leaf thickness to the upper and lower leaf surfaces), we idealize the vasculature as a continuous plane of delivery, and stomatal conductance as smoothly distributed across an epidermis. With these assumptions, in steady-state we can then expect that the vapor and liquid phases are in 'local equilibrium' within-plane (i.e., in planes normal to the leaf thickness), and the only gradients in temperature, water potential and vapor pressure are through the leaf thickness in z. Under these conditions, the standard boundary conditions of thermal and chemical equilibrium at a liquid-vapor interface extends throughout planes normal to the flux. To find the vapor pressure in the pore space, we begin by integrating the Clausius-Clapeyron from a known point (T_o, p_o) on the vapor-liquid coexistence line for pure water (Kittel & Kroemer 1980), to find the saturated vapor pressure p_{sat} at some temperature T,

$$p_{sat}(T) = p_{sat}(T_o)\ \exp\left[-\frac{\bar{\lambda}_p(T_o)}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right]. \tag{15}$$

On the coexistence line for a pure substance described by Clausius-Clapeyron, the pressure in the fluid and the pressure in vapor are the same. In general, we are interested in the situation where the vapor pressure is a partial pressure, and the gas phase as a whole is in mechanical equilibrium with the liquid phase, at atmospheric pressure. Setting the chemical potentials of the liquid and gas phase equal (as for co-existent phases),

$$\mu_l = \mu_v = \mu^*(T) + RT \ln\left(\frac{p}{p_{sat}(T)}\right), \tag{16}$$

where p is now exclusively the vapor pressure. Re-arragement yields a general form of the Kelvin equation for the reduction in vapor pressure above a fluid due to an isothermal deviation in the chemical potential from a reference state defined by the coexistence line (Pickard 1981; Wheeler & Stroock 2009);

$$p(\mu_l, T) = p_{sat}(T) \exp\left[\frac{[\Delta\mu_l]_T}{RT}\right], \qquad [\Delta\mu_l]_T = \mu_l - \mu^*(T). \tag{17}$$

We can then combine (15) and (17), divide both sides by p_{atm}, and define the reference mole fraction $\chi_o \equiv p_{sat}(T_o)/p_{atm}$. The resulting form we will refer to as the Clausius-Clapeyron-Kelvin equation for the mole fraction of water vapor, χ, in a gas held at atmospheric pressure and in local equilibrium with a liquid phase,

$$\chi(\mu_l, T) = \chi_o \exp\left[-\frac{\bar{\lambda}_p(T_o)}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) + \frac{[\Delta\mu_l]_T}{RT}\right], \qquad \chi_o \equiv \frac{p_{sat}(T_o)}{p_{atm}}. \tag{18}$$

The definition of the chemical potential for an incompressible liquid phase,

$$\mu_l = \mu^*(T) + (p_l - p_{sat}(T))\,\bar{v} + RT\ln a_l = \psi\bar{v}, \tag{19}$$

referenced to the coexistence line, leads to equivalent forms of (18) in terms of the pressure (for a pure liquid), or more generally the water (or pressure) potential, ψ,

$$\chi(p_l, T) = \chi_o \exp\left[-\frac{\bar{\lambda}_p(T_o)}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) + \frac{(p_l - p_{sat}(T))\bar{v}}{RT}\right] \tag{20}$$

$$\chi(\psi, T) = \chi_o \exp\left[-\frac{\bar{\lambda}_p(T_o)}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) + \frac{[\Delta\psi]_T\,\bar{v}}{RT}\right] \tag{21}$$

The inconvenience of having the reference state as a function of temperature motivates the approximation $p_o \equiv p_{sat}(T_o) \approx p_{sat}(T)$, justified whenever the isothermal deviations in liquid pressure are large in magnitude relative to $p_o - p_{sat}(T)$. Observing the convention of taking atmospheric pressure as the reference pressure for water potential, and with the understanding that ψ represents isothermal departures in water potential from that reference state, we arrive at,

$$\chi(\psi, T) = \chi_o \exp\left(-\frac{\bar{\lambda}_p}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) + \left(\frac{(\psi + p_{atm} - p_o)\bar{v}}{RT}\right)\right). \tag{22}$$

With ψ=0 Pa, the above equation provides the mole fraction of water vapor in air at atmospheric pressure in equilibrium with pure water across a flat interface. With respect to the energy conservation equation (12), the form of the difference in molar enthalpies between the two phases consistent with (20) is given by (14), and for (18, 21, 22) by:

$$\bar{\lambda} = \bar{\lambda}_p - [\Delta\mu_l]_T\,, \tag{23}$$

$$= \bar{\lambda}_p - [\Delta\psi]_T\,\bar{v}, \tag{24}$$

$$\approx \bar{\lambda}_p - (\psi + p_{atm} - p_o)\bar{v}. \tag{25}$$

As noted above, for leaves, the difference between $\bar{\lambda}_p$ and $\bar{\lambda}$ will be only 1% or less. An approximate form of (22) can then be written with the reference mole fraction of water vapor defined for air spaces at atmospheric pressure (tabulated in Nobel, 2005),

$$\chi(\psi, T) = \chi_o(T_o, p_{atm}) \exp\left(-\frac{\bar{\lambda}}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) + \left(\frac{\psi\bar{v}}{RT}\right)\right). \tag{26}$$

Linearization of the dependence of vapor mole fractions on temperature and potential

For a leaf, the gradients in temperature and liquid phase potential within a leaf are expected to be less than 2°C and 2 MPa (Yianoulis & Tyree 1984), and under these conditions we can linearize the partial derivatives of χ with respect to temperature and potential with an expected error of less than 1%. Linearizing about the reference state temperature T_o and the characteristic potential ψ_o, we denote the constant partial derivatives as χ_ψ and χ_T,

$$\chi_\psi \equiv \frac{\partial\chi}{\partial\psi}\Big|_{T_o,\psi_o} = \frac{\chi(T_o,\psi_o)\bar{v}}{RT_o}, \tag{27}$$

$$\chi_T \equiv \frac{\partial\chi}{\partial T}\Big|_{T_o,\psi_o} = \frac{\chi(T_o,\psi_o)\bar{\lambda}}{RT_o^2}. \tag{28}$$

where we have used (25) evaluated at ψ_o to define the latent heat. The gradient in water vapor mole fraction through the leaf thickness can then be expressed,

$$\frac{\partial\chi}{\partial z} \approx \chi_\psi \frac{\partial\psi}{\partial z} + \chi_T \frac{\partial T}{\partial z}. \tag{29}$$

Alternatively, (22) may be linearized for small variations by taking logs of both sides, and approximating the natural log as the argument minus one,

$$\ln\left(\frac{\chi(T,\psi)}{\chi_o}\right) \approx \left(\frac{\chi(T,\psi)}{\chi_o}\right) - 1 \tag{30}$$

$$\frac{\chi(T,\psi)}{\chi_o} \approx 1 - \frac{\bar{\lambda}_p}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) + \frac{(\psi + p_{atm} - p_o)\bar{v}}{RT}, \tag{31}$$

Taking the partial derivatives and evaluating them as before leads to,

$$\frac{\partial\chi}{\partial T}\Big|_{(T_o,\psi_o)} \approx \frac{\left(\bar{\lambda}_p - (\psi_o + p_{atm} - p_o)\bar{v}\right)\chi_o}{RT_o^2} \approx \frac{\bar{\lambda}\chi_o}{RT_o^2}, \qquad \frac{\partial\chi}{\partial\psi}\Big|_{T_o} \approx \frac{\chi_o\bar{v}}{RT_o}, \tag{32}$$

where we have again used (25) to define $\bar{\lambda}$. Comparing (32) to (27) and (28) shows they have same form, differing only in that the χ that appears in the former is a function of the temperature only - it is the χ given by the coexistence line of pure water liquid and vapor- whereas the former takes into account the (potential) pressure of the liquid phase being something other than the vapor pressure. At 25°C, and -1 MPa, the difference in the two representations of the partial derivatives is less than 1%. Here we proceed using (27) and (28).

Flux descriptions

We now turn to description of the fluxes of vapor, liquid and heat. The appropriate one dimensional form of Fick's law for the non-isothermal flux of species a diffusing in species b at constant pressure is given by (Bird et al. 1960),

$$J_a = -c(T)D_{ab}(T)\frac{\partial\chi_a}{\partial z} + \chi_a(J_a + J_b). \tag{33}$$

where J_a is the total flux of a, and the first term on the RHS describes the diffusive flux and the second term the convective flux, the mole fraction of a times the total molecular flux. Ignoring the depletion of CO_2 by photosynthesis in the cells, we regard the air as a stagnant gas with zero total flux ($J_b = 0$), which with water vapor as species a and all the components of dry air as species b leads to,

$$J_v = -\frac{c(T)D_v(T)}{(1-\chi)}\frac{\partial \chi}{\partial z}. \tag{34}$$

The nonlinearity in (34) arises from the fact that the evaporation of water molecules into stagnant air results in a small convective flux. From the perspective of the air molecules, in steady state convection balances the equi-molar diffusive flux of air opposite to the water vapor diffusive flux, such that the net movement of air molecules is zero. The error in the vapor flux arising from neglecting convection is proportional to the mole fraction of water vapor itself, such that at $20°C$ the error is only about 2%, rising to almost 6% at $35°C$. In addition, the temperature dependencies of c and D_v are partly compensating, such that their product varies by less than 3% between 20 and $30°C$. Neglecting convection, with c and D_v as constant about T_o, and with the linearization in (29), we can now write the flux of water vapor through the leaf thickness in terms of the potential and temperature of the liquid phase with which it is in local equilibrium as,

$$J_v = -cD_v\left(\chi_\psi \frac{\partial \psi}{\partial z} + \chi_T \frac{\partial T}{\partial z}\right). \tag{35}$$

The flux of liquid water J_l through the cells can be written in a form analogous to Darcy's law, with k_l the combined hydraulic conductivity of the cell wall and symplast (Molz & Ferrier 1982; Rockwell et al. 2014). Here we are neglecting temperature effects on liquid phase transport that might arise due to viscosity, fluid density, and osmotic potentials, as these are negligible for the expected variations in temperature within a leaf of less than 1 °C. The conductive heat flux in both phases follows Fourier's law, with k^T the thermal conductivity of the respective phase,

$$J_l = -k_l \frac{\partial \psi}{\partial z}, \tag{36}$$

$$q_l = -k_l^T \frac{\partial T}{\partial z}, \qquad q_v = -k_v^T \frac{\partial T}{\partial z}. \tag{37}$$

Inserting these expressions for the fluxes into (12), and with z aligned through the thickness of the leaf, energy conservation in the composite of air and cells has the form,

$$\begin{aligned} 0 = {} & (\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T)\frac{\partial^2 T}{\partial z^2} - \mathcal{A}_l \bar{\lambda} k_l \frac{\partial^2 \psi}{\partial z^2} + \mathcal{A}_l \bar{v} k_l \left(\frac{\partial \psi}{\partial z}\right)^2 \\ & + \left[\mathcal{A}_l\, c_{p,l}\, k_l \frac{\partial \psi}{\partial z} + \mathcal{A}_v\, c_{p,v}\, cD_v\left(\chi_\psi \frac{\partial \psi}{\partial z} + \chi_T \frac{\partial T}{\partial z}\right)\right]\frac{\partial T}{\partial z} + \dot{Q}. \end{aligned} \tag{38}$$

Non-dimensionalization

In order to organize our thinking about the relative importance of the various terms in (38), it is helpful to re-scale the derivatives to order 1. To do so, we express temperature and potential in reference to their values at the course boundary for water and their characteristic gradients. The precise form of the latter is unknown at this stage, but will be defined by the problem. For a tissue of length L in the z direction, the new variables are,

$$Z = \frac{z}{L}, \qquad \Theta = \frac{T - T_o}{\Delta T_c}, \qquad \Psi = \frac{\psi - \psi_o}{\Delta \psi_c}. \tag{39}$$

Inserting the change of variables into (38) and re-arranging, we find

$$\begin{aligned} 0 = \frac{\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T}{\mathcal{A}_l \bar{\lambda} k_l} \frac{\Delta T_c}{\Delta \psi_c} \frac{\partial^2 \Theta}{\partial Z^2} - \frac{\partial^2 \Psi}{\partial Z^2} + \left(\frac{c_l^T \Delta T_c}{\bar{\lambda}} + \frac{\mathcal{A}_v c_v^T c D_v \chi_\psi \Delta T_c}{\mathcal{A}_l \bar{\lambda} k_l} \right) \frac{\partial \Psi}{\partial Z} \frac{\partial \Theta}{\partial Z} \\ + \frac{\mathcal{A}_v c_v^T c D_v \chi_T}{\mathcal{A}_l \bar{\lambda} k_l} \frac{\Delta T_c^2}{\Delta \psi_c} \left(\frac{\partial \Theta}{\partial Z} \right)^2 + \frac{\bar{v} \Delta \psi_c}{\bar{\lambda}} \left(\frac{\partial \Psi}{\partial Z} \right)^2 + \frac{\dot{Q} L^2}{\mathcal{A}_l \bar{\lambda} k_l \Delta \psi_c}. \end{aligned} \tag{40}$$

By construction, the derivatives are all order one, scaled by non-dimensional groupings of parameters. Both the mixed and squared derivative terms, which arise from convection of enthalpy with the molecular flux, are multiplied by the ratio of heat capacity (vapor or liquid) or the characteristic chemical potential difference $\bar{v}\Delta\psi_c$ to the heat of vaporization: the first is a very small quantity (< 0.002), and the second is likely to be small for physiologically relevant range of ψ. At his juncture, we will assume we can neglect these terms; once the forms of the characteristic gradients are known, the convective terms and this assumption can be evaluated.

Turning to the conservation of molecules, with the above change of variables (11) becomes,

$$\frac{\mathcal{A}_l k_l \Delta \psi_c}{L^2} \frac{\partial^2 \Psi}{\partial Z^2} = - \frac{\mathcal{A}_v c D_v \chi_\psi \Delta \psi_c}{L^2} \frac{\partial^2 \Psi}{\partial Z^2} - \frac{\mathcal{A}_v c D_v \chi_T \Delta T_c}{L^2} \frac{\partial^2 \Theta}{\partial Z^2}. \tag{41}$$

Re-arrangement leads directly to an expression relating the divergences of the gradients in Θ and Ψ,

$$- \left(\frac{\mathcal{A}_l k_l + \mathcal{A}_v c D_v \chi_\psi}{\mathcal{A}_v c D_v \chi_T} \right) \frac{\partial^2 \Psi}{\partial Z^2} = \frac{\Delta T_c}{\Delta \psi_c} \frac{\partial^2 \Theta}{\partial Z^2}. \tag{42}$$

The left hand side of (42) can be substituted into (40), which with the neglect of the convective terms leads to,

$$0 = - \left(1 + \frac{\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T}{\mathcal{A}_v \bar{\lambda} c D_v \chi_T} + \frac{\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T}{\mathcal{A}_l \bar{\lambda} k_l} \frac{\chi_\psi}{\chi_T} \right) \frac{\partial^2 \Psi}{\partial Z^2} + \frac{\dot{Q} L^2}{\mathcal{A}_l \bar{\lambda} k_l \Delta \psi_c}. \tag{43}$$

This equation governs the steady state potential field. In the absence of any energy loading, (43) simplifies to linear function. To the extent that the thermal load ($\dot{Q}L$) is consumed by local evaporation of a liquid flux ($\mathcal{A}_l \bar{\lambda} k_l \Delta\psi_c / L$), their ratio on the RHS of (43) will approach one. The parenthetical non-dimensional groups tell us how any energy that is loaded will tend to move. As the whole equation must balance, and the derivative term is order one, for local evaporation to consume the whole thermal load requires that the parenthetical term evaluate to one. This in turn requires that the combined heat transport due to conduction in both phases must be negligible relative to the transport of latent heat due to temperature driven gradients in vapor concentration, as well as relative to the potential latent heat in liquid transport, scaled by the ratio of the sensitivity of vapor concentrations to changes in potential and temperature (the latter ~ 0.1).

We can also find an equation for the temperature field by again combining (42) and (40), while normalizing energy loading by the characteristic conductive flux,

$$0 = \left(1 + \frac{\mathcal{A}_l \bar{\lambda} k_l}{\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T} \frac{\chi_T}{\chi_\psi} \frac{\mathcal{A}_v c D_v \chi_\psi}{\mathcal{A}_l k_l + \mathcal{A}_v c D_v \chi_\psi}\right) \frac{\partial^2 \Theta}{\partial Z^2} + \frac{\dot{Q} L^2}{\left(\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T\right) \Delta T_c}. \tag{44}$$

The analysis is similar, in that the derivative is $O(1)$ by construction, and the larger the parenthetical term, the smaller the proportion of loaded energy removed by conduction. For convenience, we label the parenthetical terms scaling the derivatives in (43) and (44) Π_ψ and Π_T,

$$\Pi_\psi \equiv 1 + \frac{\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T}{\mathcal{A}_v \bar{\lambda} c D_v \chi_T} + \frac{\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T}{\mathcal{A}_l \bar{\lambda} k_l} \frac{\chi_\psi}{\chi_T} \tag{45}$$

$$\Pi_T \equiv 1 + \frac{\mathcal{A}_l \bar{\lambda} k_l}{\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T} \frac{\chi_T}{\chi_\psi} \frac{\mathcal{A}_v c D_v \chi_\psi}{\mathcal{A}_l k_l + \mathcal{A}_v c D_v \chi_\psi}. \tag{46}$$

Π_T offers a different view of the behavior of the system than Π_ψ, but contains no new information on the relative importance of conduction versus evaporation. As Π_ψ and Π_T balance the proportions of conductive and evaporative dissipation of a thermal load, with the neglect of internal heat transfer by convection and radiation, their inverses must sum to one,

$$\Pi_\psi^{-1} + \Pi_T^{-1} = 1, \tag{47}$$

which may be readily confirmed with the aid of a computer (the algebra is tedious). We can now complete the analysis of the governing equations by defining the characteristic gradients in order to satisfy our claim that the derivative terms are order one;

$$\Delta T_c = \frac{\dot{Q} L^2}{\Pi_T \left(\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T\right)}, \quad \Delta \psi_c = \frac{\dot{Q} L^2}{\Pi_\psi \mathcal{A}_l \bar{\lambda} k_l}. \tag{48}$$

These quantities can then be used to check whether the neglect of convection from (40) on is justified, given the magnitude of a typical thermal load $\dot{Q}$. With these choices of the characteristic gradients, the governing equations become,

$$0 = -\frac{\partial^2 \Psi}{\partial Z^2} + 1. \tag{49}$$

$$0 = \frac{\partial^2 \Theta}{\partial Z^2} + 1. \tag{50}$$

The above forms will be convenient for solving, but all of the information on the relative importance of conduction and local evaporation for dissipating a thermal load is now contained in (48). While these two non-dimensional groups describe the inherent properties of a composite formed of liquid and vapor phases, the behavior of the solution in any real system will depend on the conditions that exist on its boundaries as well.

Boundary conditions and solution for a non-transpiring leaf surface

We first consider a 1D domain of leaf tissue bounded on one side by the vascular plane, and on the other by a non-transpiring epidermis (e.g., the upper epidermis of an hypostomatous leaf). We fix the origin at the vascular plane, and let L be the distance to the epidermal surface. As there is no flux of water from this surface, steady state molecular conservation, the flux of vapor and liquid from the interior sums to zero at the surface,

$$(\mathcal{A}_l J_l + \mathcal{A}_v J_v)\big|_{z=L} = 0, \tag{51}$$

$$-\mathcal{A}_l k_l \frac{\partial \psi}{\partial z}\big|_{z=L} - \mathcal{A}_v c D_v \left(\chi_\psi \frac{\partial \psi}{\partial z}\big|_{z=L} + \chi_T \frac{\partial T}{\partial z}\big|_{z=L} \right) = 0. \tag{52}$$

For the thermal energy balance, conduction from the interior plus the enthalpy of the vapor and liquid fluxes must be balanced by conduction of sensible heat to the surrounding air and the net long wave radiation flux,

$$\left(\mathcal{A}_l q_l + \mathcal{A}_v q_v + \mathcal{A}_l J_l \bar{H}_l + \mathcal{A}_v J_v \bar{H}_v\right)\big|_{z=L} = (q_c + q_r)\big|_{z=L}. \tag{53}$$

Here we are neglecting cuticular transpiration, as well as the possibility that the epidermal leaf temperature could fall below the dew point, leading to condensation of external water vapor on the leaf surface. The latter could be accounted for by adding enthalpy transport terms to the RHS, and an additional molecular conservation statement summing external liquid and vapor fluxes to zero. However, as condensation on the outer surface falls outside the typical regime of transpiring conditions that is our principal interest, it will not be explored further. Making use of the requirement from molecular conservation that at the surface $\mathcal{A}_l J_l = -\mathcal{A}_v J_v$ leads again to a latent heat term,

$$\left(\mathcal{A}_l q_l + \mathcal{A}_v q_v + \mathcal{A}_l J_l \left(\bar{H}_l - \bar{H}_v\right)\right)\big|_{z=L} = (q_c + q_r)\big|_{z=L}, \tag{54}$$

$$\left(\mathcal{A}_l q_l + \mathcal{A}_v q_v - \mathcal{A}_l J_l \bar{\lambda}\right)\big|_{z=L} = (q_c + q_r)\big|_{z=L}, \qquad \bar{\lambda} = \bar{H}_v - \bar{H}_l. \tag{55}$$

Here the latent heat term accounts for the energy involved in a liquid flux evaporating on the internal boundary of the surface and diffusing back toward the center of the leaf, or a vapor flux condensing on the internal surface and flowing backward as liquid.

For the moment, we will avoid writing the outward sensible and radiative fluxes in terms of their dependence on leaf temperature at the surface, as the radiative term is proportional to temperature to the fourth power, a non-linearity that prohibits finding a simple closed form solution. That is, we will first find and analyze the structure of the solution to the general problem with the external fluxes regarded as known, and later add-in explicit representations of the external fluxes to assemble a system of simultaneous equations that can be solved numerically.

For the boundary conditions at the vascular plane, we simply label the potential and temperature that exist there. These quantities will link together the solutions for the upper and lower domains of our leaf, and indeed have already been identified as properties of the 'source region' in our analyses of the governing equations for the temperature and potential fields; the particular values will be solved for later. The boundary conditions are then,

$$\psi(z=0) = \psi_o, \qquad T(z=0) = T_o. \tag{56}$$

While this completes the specification of the boundary conditions, they are not yet in a useful form for solving (49, 50); we need expressions that prescribe the values of the gradients in ψ and T at the surface. Adopting the same change of variables as before (39) and substituting in the expressions for the individual fluxes (36, 37, 35), molecular conservation at the surface (52) leads to,

$$\frac{\partial \Theta}{\partial Z}\Big|_{Z=1} = -\frac{(\mathcal{A}_l k_l + \mathcal{A}_v c D_v \chi_\psi)}{\mathcal{A}_v c D_v \chi_T}\frac{\Delta\psi}{\Delta T}\frac{\partial \Psi}{\partial Z}\Big|_{Z=1}. \tag{57}$$

Whereas in the body molecular conservation lead to a relationship between the divergences of the temperature and potential field (42), at the boundary the gradients are related by the requirement that if a gradient in potential drives a flow to the boundary, the temperature gradient has to be large enough to drive an equivalent molar flux as vapor away from the boundary. Note that $\Delta\psi$ and ΔT are defined as before, by (39) and (48). Turning to thermal energy conservation (55), the change of variables leads to,

$$\frac{\partial \Psi}{\partial Z}\Big|_{Z=1} = \frac{L(q_c + q_r)}{\bar{\lambda}\mathcal{A}_l k_l} + \frac{(\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T)}{\bar{\lambda}\mathcal{A}_l k_l}\frac{\Delta T}{\Delta\psi}\frac{\partial \Theta}{\partial Z}\Big|_{Z=1}. \tag{58}$$

Combining (57) and (58) so as to eliminate either the Θ or Ψ derivative yields the sought for boundary conditions, which simplify to just the ratio of the surface heat fluxes to the absorbed load. The complete boundary conditions for solving (49) and (50) are given by,

$$\frac{\partial \Psi}{\partial Z}\Big|_{Z=1} = \frac{(q_c + q_r)}{\dot{Q}L}, \qquad \Psi(Z=0) = 0, \tag{59}$$

$$\frac{\partial \Theta}{\partial Z}\Big|_{Z=1} = -\frac{(q_c + q_r)}{\dot{Q}L}, \qquad \Theta(Z=0) = 0. \tag{60}$$

The solution follows easily from two integrations and application of the boundary conditions:

$$\Psi(Z) = \frac{Z^2}{2} + \left[\frac{(q_c + q_r)}{\dot{Q}L} - 1\right] Z, \tag{61}$$

$$\Theta(Z) = -\frac{Z^2}{2} - \left[\frac{(q_c + q_r)}{\dot{Q}L} - 1\right] Z. \tag{62}$$

Returning to the original variables results in,

$$\psi(z) = \psi_o + \frac{\dot{Q}L^2}{\Pi_\psi \bar{\lambda}\mathcal{A}_l k_l}\left[\frac{z^2}{2L^2} - \frac{z}{L}\right] + \frac{L(q_c + q_r)}{\Pi_\psi \bar{\lambda}\mathcal{A}_l k_l}\frac{z}{L}, \tag{63}$$

$$T(z) = T_o - \frac{\dot{Q}L^2}{\Pi_T\left(\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T\right)}\left[\frac{z^2}{2L^2} - \frac{z}{L}\right] - \frac{L(q_c + q_r)}{\Pi_T\left(\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T\right)}\frac{z}{L}. \tag{64}$$

In the above solutions, area fractions, surface fluxes, and the solar radiation load are quantities specific to the particular domain of interest.

Boundary conditions and solution for a transpiring leaf surface

In the presence of a transpirational flux of water vapor E from the leaf surface to the surrounding air, molecular and thermal energy conservation at the surface become,

$$\left(\mathcal{A}_l J_l + \mathcal{A}_v J_v\right)\big|_{z=L} = E\big|_{z=L}, \tag{65}$$

$$\left(\mathcal{A}_l q_l + \mathcal{A}_v q_v + \mathcal{A}_l J_l \bar{H}_l + \mathcal{A}_v J_v \bar{H}_v\right)\big|_{z=L} = \left(E\bar{H}_v + q_c + q_r\right)\big|_{z=L}. \tag{66}$$

Substituting (65) into (66) again leads to a latent heat term; after accounting for molecular conservation the energy conservation statement has the same form as the non-transpiring surface case (55),

$$\left(\mathcal{A}_l q_l + \mathcal{A}_v q_v - \mathcal{A}_l J_l \bar{\lambda}\right)\big|_{z=L} = \left(q_c + q_r\right)\big|_{z=L}. \tag{67}$$

After the change of variables and insertion of the expressions for the individual fluxes as above, substitution and re-arrangement of (65) and (67) again yield the necessary conditions on the gradients in Ψ and Θ at the surface, while the boundary conditions at the vascular plane are unchanged from the previous case, leading to,

$$\frac{\partial \Psi}{\partial Z}\Big|_{Z=1} = \frac{(q_c + q_r)}{\dot{Q}L} - \frac{\bar{\lambda}E}{\dot{Q}L}\frac{\left(\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T\right)}{\bar{\lambda}\mathcal{A}_v c D_v \chi_T}, \qquad \Psi(Z=0) = 0, \tag{68}$$

$$\frac{\partial \Theta}{\partial Z}\Big|_{Z=1} = -\frac{(q_c + q_r)}{\dot{Q}L} - \frac{\bar{\lambda}E}{\dot{Q}L}\frac{\mathcal{A}_l k_l}{\left(\mathcal{A}_l k_l + \mathcal{A}_v c D_v \chi_\psi\right)}, \qquad \Theta(Z=0) = 0. \tag{69}$$

Solving the non dimensional potential and temperature fields (49) and (50) subject to (68) and (69) respectively results in,

$$\Psi(Z) = \frac{Z^2}{2} + \left[\frac{(q_c + q_r)}{\dot{Q}L} - 1 - \frac{\bar{\lambda}E}{\dot{Q}L}\frac{\left(\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T\right)}{\bar{\lambda}\mathcal{A}_v c D_v \chi_T}\right] Z, \tag{70}$$

$$\Theta(Z) = -\frac{Z^2}{2} - \left[\frac{(q_c + q_r)}{\dot{Q}L} - 1 + \frac{\bar{\lambda}E}{\dot{Q}L}\frac{\mathcal{A}_l k_l}{\left(\mathcal{A}_l k_l + \mathcal{A}_v c D_v \chi_\psi\right)}\right] Z. \tag{71}$$

Returning to dimensional variables, the solutions for the temperature and potential fields in a domain between the vascular plane and transpiring epidermis are,

$$\psi(z) = \psi_o + \frac{\dot{Q}L^2}{\Pi_\psi \bar{\lambda}\mathcal{A}_l k_l}\left[\frac{z^2}{2L^2} - \frac{z}{L}\right] + \left[\frac{L(q_c + q_r)}{\Pi_\psi \bar{\lambda}\mathcal{A}_l k_l} - \frac{LE}{\Pi_\psi \bar{\lambda}\mathcal{A}_l k_l}\frac{\left(\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T\right)}{\mathcal{A}_v c D_v \chi_T}\right]\frac{z}{L}, \tag{72}$$

$$\begin{aligned} T(z) = T_o &- \frac{\dot{Q}L^2}{\Pi_T\left(\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T\right)}\left[\frac{z^2}{2L^2} - \frac{z}{L}\right] \\ &- \left[\frac{L(q_c + q_r)}{\Pi_T\left(\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T\right)} + \frac{L\bar{\lambda}E}{\Pi_T\left(\mathcal{A}_l k_l^T + \mathcal{A}_v k_v^T\right)}\frac{\mathcal{A}_l k_l}{\left(\mathcal{A}_l k_l + \mathcal{A}_v c D_v \chi_\psi\right)}\right]\frac{z}{L}. \end{aligned} \tag{73}$$

Appendix A: Neglect of the radiative flux through the pore space

The radiative flux across the air spaces in the leaf can be written

$$q_r^{oe} = \sigma_{sb} F (T_o^2 + T_e^2)(T_o + T_e)(T_o - T_e) \tag{74}$$

For any given temperature difference $T_o - T_e$ over a length L, the quantity $\sigma_{sb} F (T_o^2 + T_e^2)(T_o + T_e)$ represents an effective conductance due to radiative transfer that may be compared in magnitude to the conductance due to thermal conduction in the airspace k_v^T/L. At $25C$, for distances as large as on the order of 100 microns, the above comparison shows that conduction in the airspace is still 43 times that of radiative transfer. Given that clear views between cells will be less than 100 microns in internal airspaces, and that liquid phase conduction exceeds that of the airspace by an order of magnitude, it appears safe to neglect radiative transfer within a leaf.

Appendix B: effective boundary layer thickness from licor

The Licor 6400 gives the boundary layer conductance g_{bw} in mol m^{-2} s^{-1}, which for the oak data is 1.42 (August 8 2009). The conductance is defined by the equation relating the molecular flux to the difference in mole fraction $\Delta\chi$ between the leaf surface and the free air stream an effective distance $\Delta z = \delta$ from the surface, or

$$J_v = g_{bw}\, \Delta\chi = -g_{bw}\, \delta\, \frac{\partial \chi}{\partial z} = -c D_v \frac{\partial \chi}{\partial z} \tag{75}$$

The last equality defines δ, the effective boundary layer thickness for diffusion and conduction, as

$$\delta = \frac{c D_v}{g_{bw}}. \tag{76}$$

Appendix C: Analysis of stomatal responses to increased energy loads

For the sake of simplicity, we consider a leaf as a single domain subject to a short wave load SR, with a single transpiring surface. Global energy conservation then takes the form,

$$\delta SR = \delta(\bar{\lambda} E) + \delta(q_r + q_c) \tag{77}$$

With $\Delta\chi$ the leaf to air water vapor mole fraction difference, with ambient air and surrounding temperature T_a constant, expanding the terms on the RHS leads to,

$$\bar{\lambda} \delta E = \bar{\lambda}(\delta g_T \cdot \Delta\chi + g_T \cdot \delta\Delta\chi), \tag{78}$$

$$\delta(q_r + q_c) = K_s^T (\delta T_e) \qquad K_s^T \equiv \frac{k_v^T}{\delta} + K_r = \frac{q_r + q_c}{\Delta T_{ea}}, \tag{79}$$

where K_s^T is the effective total sensible heat conductance from leaf to air, as defined by the sensible flux form the leaf divided by the leaf to air temperature difference ΔT_{ea}. Combining the above three equations, re-arranging, and using $\delta\chi = \chi_T \delta T_e$ and results in an expression for the proportional change in g_T,

$$\frac{\delta g_T}{g_T} = \frac{\delta SR}{\bar{\lambda} E} - \left(\frac{K_s^T}{\bar{\lambda} E} + \frac{\chi_T}{\Delta \chi} \right) \delta T_e. \tag{80}$$

To find δT_e, we next consider the changes in internal transport. By the assumption that stomatal aperture changes to hold a fixed epidermal potential, ψ_e is fixed, and neglecting the secondary effects of variation in the vascular potential drop due to a change in the flux, we regard the liquid flux in the leaf as well as the vapor flux due to the potential gradient as constant. With the further approximation that the internal latent and sensible fluxes are linear in the vascular plane to epidermal surface potential and temperature drops (i.e., neglecting the effects of evaporation in the spongy mesophyll), an internal energy balance leads to,

$$\delta SR = \left(\bar{\lambda} \mathcal{A}_v c D_v \chi_T + \mathcal{A}_v k_v^T + \mathcal{A}_l k_l^T \right) \frac{\delta \Delta T_{oe}}{L}. \tag{81}$$

Further, as the vascular to epidermal potential gradient is (approximately) conserved by the stomata, considering molecular conservation together with energy conservation allows shows that the responses of the internal and external latent and sensible fluxes balance separately,

$$\bar{\lambda} \delta E = \bar{\lambda} \mathcal{A}_v c D_v \chi_T \frac{\delta \Delta T_{oe}}{L}, \tag{82}$$

$$\delta (q_r + q_c) = \left(\mathcal{A}_v k_v^T + \mathcal{A}_l k_l^T \right) \frac{\delta \Delta T_{oe}}{L}. \tag{83}$$

Combining (79) with (83) to relate the internal and external sensible fluxes, and then using the result to eliminate the change on the vascular to epidermal temperature drop $\delta \Delta T_{oe}$ from (81), leads to an expression for the change in epidermal temperature δT_e, as

$$\delta T_e = \frac{\mathcal{A}_v k_v^T + \mathcal{A}_l k_l^T}{K_s^T} \left(\frac{\delta SR}{\left(\bar{\lambda} \mathcal{A}_v c D_v \chi_T + \mathcal{A}_v k_v^T + \mathcal{A}_l k_l^T \right)} \right). \tag{84}$$

With the epidermal temperature response do defined, the stomatal response (80) can be written,

$$\frac{\delta g_T}{g_T} = \frac{\delta SR}{\bar{\lambda} E} \left[1 - \frac{1}{1 + \frac{\bar{\lambda} \mathcal{A}_v c D_v \chi_T}{\mathcal{A}_v k_v^T + \mathcal{A}_l k_l^T}} \left(1 + \frac{\bar{\lambda} g_T \chi_T}{K_S^T} \right). \right] \tag{85}$$

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