Impacts of non-ideality and the thermodynamic pressure work term pΔv on the Surface Energy Balance

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Abstract. Present day eddy covariance based methods for measuring the energy and mass exchange between the earth's surface and the atmosphere often do not close the surface energy balance. Frequently the turbulent energy fluxes (sum of sensible and latent heat) underestimate the available energy (net incoming radiation minus the soil conductive heat flux) by 10 to 20% or more. Over the last three or four decades several reasons for this underestimation have been proposed, but nothing completely

5   definitive has been found. This study examines the contribution of two rarely discussed aspects of atmospheric thermodynamics to this underestimation: the non-ideality of atmospheric gases and the significance the water vapor flux has on the sensible heat flux, an issue related to the pressure work term $p\Delta v$. The results were not unexpected, i.e., these effects are too small to account for all of the imbalance between the sum of the turbulent fluxes and the available energy. Together they may contribute 1-3% of the difference (or 10 to 15% of the percentage imbalance).

1   Introduction

The microclimate at any given location on the earth's surface is determined by a balance between the incoming and outgoing energy. Documenting and measuring these energy flows is fundamental to micrometeorology and to the understanding of

15   the functioning of the earth's ecosystems (e.g., (Geiger et al. , 2003). In its simplest form the surface energy balance (SEB) is composed of four terms: $R_n = L_v E + H + G$; where R_n (Wm^{-2}) is net radiation (= incoming radiation minus reflected and outgoing infrared radiation), $L_v E$ (Wm^{-2}) is the latent heat flux or the energy required to evaporate (and transpire) moisture, H (Wm^{-2}) is the sensible heat flux associated with heated air currents as they move upward and away from the surface, and G (Wm^{-2}) is the heat conducted into the components of the surface (soil, tree branches and trunks, ...). For the

20   purposes of the present study all other terms of the SEB, which tend to be small, can be ignored. But despite decades of effort micrometeorologists worldwide have not been able to achieve a fully satisfactory level of closure to the SEB (Twine et al. , 2000; Oncley et al. , 2007; Leuning et al. , 2012, e.g.,).

There have been many studies that have proposed explanations for the often observed imbalance, but the present study focuses on only two (Paw U et al. , Appendix C| 2000| and Kowalski | 2018(@|), which are centered exclusively on L_vE and H. The authors of both of these studies seek at least a partial "solution" to the energy imbalance problem by suggesting that the pressure work term, $p\Delta v$ (Jkg^{-1}), that part of the first law of thermodynamics that accounts for the work done on a system or by a system during the physical expansion or compression of that system, has not been incorporated correctly into micrometeorological theory underpinning the measurements of L_vE and H. Kowalski (2018(@|) argued (incorrectly) that the enthalpy of vaporization, L_v (Jkg^{-1}), did not include $p\Delta v$ and so he proposed a small adjustment to L_v. In turn this adjustment led to an increase in the water vapor flux (L_vE) by about 3-4% due to the additional contribution to L_v by $p\Delta v$. But as pointed out by the reviewers and commenters on Kowalski's study $p\Delta v$ is, by construction and definition, a component of L_v and so it is inappropriate to assume that it is separate from L_v.

Paw U et al. (2000, Appendix C)| , on the other hand, take a different approach to the $p\Delta v$ term. They do not apply their correction directly to L_vE in the SEB equation. Rather they apply their correction to the heat flux, H, based on a change in density of an air parcel associated with mixing newly transpired or evaporated water vapor with the air contained within that air parcel. They pose their correction in terms of an equivalent temperature perturbation, such that after evaporation has occurred the (turbulent + diffusive) transport-driven expansion of the water vapor into the atmosphere surrounding the source of water vapor (e.g., plant stomatal pores and the porous soil) results in a change in the atmospheric density that is associated with a concomitant change in the atmospheric temperature. So in effect Paw U et al. (2000)| are using the first law of thermodynamics (expressed in terms of atmospheric processes and the pressure work term) to argue that H should be adjusted to include a small term that is proportional to the mass flux of water vapor, E (kgm^{-2}s^{-1}).

The purpose of the present paper is to examine the methods and conclusions of these two papers from the perspective of "classical" thermodynamics and to quantify these issues relating to the subtleties of the first law of thermodynamics and the pressure work term and to show that any related corrections are much smaller than either Kowalski (2018(@|) or Paw U et al. (2000)| propose. Although it is true that what we develop herein is not necessarily "new" science, some of the theory we employ may well be new to the general environmental and geo-biophysical communities. The present study discusses Kowalski | and commenters ?| first and Paw U et al. (2000)| second. The intent of this study is to clarify the issues that these two disparate authors are addressing. In the case of Kowalski | and commenters ?| I take an indirect approach by examining and quantifying how mixing of air and water vapor as non-ideal (or real) gases, rather than as ideal gases, can have on L_v and the specific heat of moist air, and ultimately the SEB. In the case of Paw U et al. (2000)| the first law of thermodynamics is employed to derive the influence of water vapor has on potential temperature, which in turn gives rise to an expression, different from Paw U et al.'s (2000) expression, relating how the kinematic heat flux is influenced by the mass flux of water vapor, E.

2 Non-ideal gases

The next three sections are a purely theoretical argument intended to estimate the influence that a mixture of non-ideal gases (water vapor and dry air) can have on the SEB near Standard Pressure and Temperature (STP) by comparing the enthalpy of

vaporization of water and the specific heat of moist air associated with ideal gases and non-ideal gases. Here "near STP" will be understood as pressures between about 70 kPa and 105 kPa and temperatures between about 0 C and 100 C or so – or an atmospheric state typical of near-surface conditions on earth.

2.1 Enthalpy of Vaporization

5   The enthalpy of vaporization for pure water into an atmosphere of pure water vapor, see either Wagner and Pruess (2002)| or Harvey and Friend (2004)|, is expressed as

$$L_v^* = h_v^* - h_l^* \tag{1}$$

where L_v^* (Jkg^{-1} or Jmol^{-1}) is the enthalpy of vaporization for pure water into an atmosphere of pure saturated water vapor, h_v^* (Jkg^{-1} or Jmol^{-1}) is the specific enthalpy of saturated vapor, and h_l^* (Jkg^{-1} or Jmol^{-1}) is the specific enthalpy of pure
10   water. Note (a) that the asterisk superscript (*) will be used to denote a pure quantity (as opposed to a mixture which will not be superscripted) and (b) that the researchers cited above essentially employ the Clausius-Clapeyron equation to determine $h_v^* - h_l^*$. Of course, liquid water under near-earth-surface conditions will not be composed solely of pure liquid water. Rather it will be a mixture of pure liquid water and, e.g., dissolved atmospheric gases (O_2, CO_2, CH_4, etc) and possibility any number of dissolved organic and inorganic compounds (e.g., mineral salts, organic acids, etc). But for the present study, it is
15   unnecessary of consider this additional complexity. Figure 1 includes plots of L_v^* as a function of temperature, T_K (degrees K), computed using the formulations of Wagner and Pruess (2002)| (blue line) and the first-order ideal gas approximation to it (red line) over the plotted temperature range. NOTE: (1) The red line (linear approximation) overlays the blue line and masks it almost completely. (2) This figure also displays other terms associated with the enthalpy of vaporization, i.e., the change in internal energy, du^*, and the pressure work term, $p^* \Delta v^*$, and an approximation to it, RT_K/M_w, all of which are included for
20   completeness. But these results do indicate that $p^* \Delta v^* \approx L_v^*/15$, meaning that $p^* \Delta v^*$ is a relatively small component of L_v^*.

Next, consider a system at temperature T_K (273.15 K $< T_K \leq$ 373.15 K) composed of N_d mols of dry air at pressure p_d (Pa) above a non-evaporating body of N_l mols of liquid water also at temperature T_K. Further assume (A) that this dry air/liquid water system is isolated, i.e., it cannot exchange mass or energy or interact mechanically with its surroundings, and (B) the liquid water is the dominant component of the system, i.e., $N_d \ll N_l$. The total enthalpy of this system is $N_d h_d^* + N_l h_l^*$ (J).
25   This will now be considered the initial state of the system.

The final state of the system occurs after N_v mols of liquid have evaporated and diffused throughout the volume of dry air to the point of saturation, where of course $N_v \leq N_d \ll N_l$. This later inequality is further strengthened (principally for convenience) to the overarching assumption that $N_d + N_v \ll N_l$, in essence requiring that the liquid water reservoir always be the dominant component of the system. Note: It is possible to calculate N_v, because $N_v = N_{v,sat}$, but for the present purposes
30   this is not necessary. The final pressure of the water vapor is $p_{v,sat} = p_{v,sat}(T_K)$ (Pa) and there are N_d mols of dry air, $N_l - N_v$ mols of liquid water and N_v mols of water vapor. The total pressure of the composite moist air is now $p_a = p_d + p_{v,sat}$ and the total enthalpy of the final state of the system is $(N_d + N_v) h_a + (N_d - N_v) h_l^*$; where h_a (Jmol^{-1}) is the specific enthalpy

of resulting moist air. But, because of evaporative cooling the temperature of the final state of the system is less than T_K. Nonetheless, as shown in the appendix this difference, $\delta T < 0$, is likely to be quite small whenever the liquid water reservoir is the dominant component of the system. For example, the appendix shows that $\delta T \approx -1.4(N_v/N_l)T_K$ and that $|\delta T| < 0.0005$ K for $N_v/N_l < 10^{-6}$. For so small a δT it is reasonable to assume that the temperature of the final state of the system is the

5   same as the initial temperature, T_K.

With this last simplification in mind, the change in total enthalpy of the system, $\mathcal{H}_s$ (J), is

$$\mathcal{H}_s = (N_d + N_v)h_a + (N_l - N_v)h_l^* - (N_d h_d^* + N_l h_l^*) \tag{2}$$

where $h_a = \chi_d h_d^* + \chi_v h_v^* + I_B$ (e.g., Hyland and Wexler , 1983)| and $\chi_d = N_d/(N_d+N_v) = p_d/p_a$ is the dry air molar fraction (molmol^{-1}) of the moist air, $\chi_v = N_v/(N_d+N_v) = p_{v,sat}/p_a$ is the vapor molar fraction (molmol^{-1}) of the moist air, and

10   I_B is the excess enthalpy of mixing (e.g., Wormald et al. , 1977; **?**)| that arises because of the non-ideality of the gases (e.g., Hyland and Wexler , 1983)|.

Note: a more precise definition of the molar fractions of dry air and water vapor should include an enhancement factor, $f = f(T_K, p_a)$. For example, Hyland and Wexler (1983)|, citing Goff (1949)|, include f as follows: $\chi_d = 1 - fp_v/p_a$ and p_v (Pa) is the ambient vapor pressure (which for the purposes of this definition does not necessarily have to be $p_{v,sat}$). As with

15   I_B, f allows for the departure from the non-ideal behavior of the constituent gases. But $1 < f < 1.006$ near STP (Hyland and Wexler , 1983; Nelson and Sauer , 2004)|, so for the purposes of this study $f \equiv 1$ can be assumed.

After some algebraic manipulation the following simplified expression for $\mathcal{H}_s$ results:

$$\mathcal{H}_s = N_v(h_v^* - h_l^*) + (N_v + N_d)I_B \tag{3}$$

or after dividing by N_v

20   $$L_v \equiv \frac{\mathcal{H}_s}{N_v} = L_v^* + \frac{I_B}{\chi_v} \tag{4}$$

At this point it is important to note that except for the non-ideality of water vapor and dry air the enthalpy of vaporization of water would be completely independent of the presence of dry air, i.e., $L_v \equiv L_v^*$. In other words, if not for the non-ideal behavior of these gases L_v would be the sole property of water and would otherwise not be influenced by the present or absence of dry air.

25   In general I_B is expressed in terms of the second and third virial coefficients (Hyland and Wexler , 1983; Wagner and Pruess , 2002)|. For this study it is sufficient to consider only the second virial coefficients. The general expression for I_B (e.g., **?**Wormald et al. , 1977)| is

$$\frac{I_B}{\chi_v} = p_a \chi_d \left[2\left(B_a - T_K \frac{dB_a}{dT} \right) - \left(B_d - T_K \frac{dB_d}{dT} \right) - \left(B_v - T_K \frac{dB_v}{dT} \right) \right] \tag{5}$$

where $B = B(T_K)$ (m^{3}mol^{-1}) is the second virial coefficient for moist air (subscript a), dry air (subscript d), and water vapor (subscript v) and $B_d(T_K)$ is taken from Equation (10) of **?**|, $B_a(T_K)$ is taken from Equation (15) of **?**|, and $B_v(T_K)$ is taken from Equation (6) of Harvey and Lemmon (2004)|.

The final step is to specify whether the enthalpic change occurs at a constant pressure or at a constant volume. This is equivalent to specifying p_a and p_d at the initial and final states. At a constant pressure p_a is held constant, so that p_d(final state) $= p_d$(initial state) $- p_v$(final state); where p_d(initial state) $= p_a$ and p_v(final state) $= p_{v,sat}$ and (for the sake of completeness it should also be noted that) p_v(initial state) $= 0$. In this case p_a is arbitrarily assigned a value of 101.325 kPa. To evaluate L_v^* at a constant volume p_d is held constant, so p_a(final state) $= p_a$(initial state) $+ p_v$(final state). In this case p_d is arbitrarily assigned a value of 101.325 kPa. The only difference between these two cases is that the final molar values of N_v and N_a ($= N_v + N_d$) can be different, so that the term $p_a\chi_d$ in Equation (5) can vary slightly depending on whether we are considering evaporation is occurring at a constant pressure or a constant volume. Both cases need to be considered here because any evaporation occurring on the earth's surface is going to lie somewhere between these two (boundary) cases.

The results of evaluating Equation (5) for these two different processes are shown in Figure 2. Note that beginning with this figure and henceforth ΔL_v will be used as shorthand for I_B/χ_v. These results suggests that surface energy fluxes associated with ET measured at temperatures commonly encountered with micrometeorological techniques (i.e., between about 275 and 315 K) could be underestimated by 1% to 2% solely on the basis of using an estimate for the enthalpy of vaporization, L_v^*, that does not allow for the fact that dry air and water vapor are non-ideal gases. Categorically then this underestimate is at least an order of magnitude less that the often observed surface energy imbalance mentioned in the introduction.

2.2 Specific Heat

But in many micrometeorological studies of the SEB L_vE is only half the story. There is also the sensible or convective heat flux, $H = \rho_a C_p \overline{w'T'}$; where ρ_a (kgm^{-3}) is the density of the ambient moist air, C_p (Jkg^{-1}K^{-1}) is the specific heat of moist air, and $\overline{w'T'}$ is the kinematic heat flux, which is assumed to be obtained directly from eddy covariance measurements. Here $C_p = C_p(T_K) = \chi_v C_{pv}^*(T_K) + \chi_d C_{pd}^*(T_K)$ is the weighted sum of the specific heats of pure vapor (subscript v) and pure dry air (subscript d). For the present study $C_p = C_p(T_K)$, $C_{pv}^*(T_K)$, and $C_{pd}^*(T_K)$ are obtained from Equation (6) of Bücker et al. (2003) after converting from Jmol^{-1}K^{-1} to Jkg^{-1}K^{-1} by dividing by the appropriate molecular masses.

But because $C_p \equiv dL_v/dT$ (by definition), it follows that there should be a correction, ΔC_p, that is an exact analog to $\Delta L_v \equiv I_B/\chi_v$ in Equation (5) above. In fact, $\Delta C_p \equiv dI_B/dT$, which yields:

$$\Delta C_p = -p_a \chi_d \chi_v T_K \left[2\frac{d^2 B_a}{dT^2} - \frac{d^2 B_d}{dT^2} - \frac{d^2 B_v}{dT^2} \right] \tag{6}$$

The final results for $\Delta C_p/C_p$ as a function of T_K as estimated from Equation (6) are shown in Figure 3 overlaying $\Delta L_v/L_v^*$ from Figure 2.

2.3 Consequences to the surface energy balance

Implications to the SEB of mixing the two non-ideal gases (water vapor and dry air) during evaporation can now be estimated by combining the results for $\Delta L_v / L_v^*$ and $\Delta C_p / C_p$. For example, assuming a Bowen ratio of approximately unity (i.e., the magnitude of H and $L_v E$ are approximately the same) and a temperature between say 280 K and 350 K, then the term

5 $L_v E + H$ in the SEB could be underestimated between 1% and 1.5% with micrometeorological techniques due to the non-ideality of water vapor and dry air. Allowing for different values of the Bowen ratio would imply a somewhat broader range of percentage underestimates. But even so, it is unlikely that non-ideality could cause $L_v E + H$ to be underestimated by more than 2%, which, at best, is an order of magnitude less than required to account for the imbalance of the SEB.

3 $p\Delta v$ and the Surface Fluxes of Sensible Heat and Water Vapor

10 This section examines the issue Paw U et al. (2000) address, viz., the "energy associated with evaporation into the atmosphere, necessary for the expansion of eddy parcels against an approximately constant pressure". In essence the authors are proposing a correction to eddy covariance measurements of turbulent temperature fluctuations (T') that account for the density change of an air parcel associated with the mixing of a relatively dense fluid (ambient air), with a relatively less dense fluid (water vapor). The following is a slight reformulation of their approach.

15   For an adiabatic process the first law of thermodynamics can be expressed as

$$c_v dT + p_a dv_a = 0 \tag{7}$$

where c_v (Jmol^{-1}K^{-1}) is the molar specific heat of moist air at constant volume and v_a (m^{3}mol^{-1}) is the specific volume of air, which by definition is the reciprocal of the molar air density, ϱ_a (molm^{-3}). Switching from differential notation to perturbation notation, Equation (7) can be written as $c_v T' + p_a v_a' = 0$. By definition $v_a = 1/\varrho_a$ so it also follows that $v_a' = -\varrho_a'/\varrho_a^2$, which

20 combined with the ideal gas law $p_a v_a = RT_K$ (where R (Jmol^{-1}K^{-1}) is the universal gas constant) yields the following equivalent expression for Equation (7):

$$T_e' + \frac{RT_K}{c_v}\frac{v_a'}{v_a} = 0 \quad \text{or} \quad T_e' = \frac{RT_K}{c_v}\frac{\varrho_a'}{\varrho_a} \tag{8}$$

where T_e' is temperature correction proposed by Paw U et al. (2000). Next they assume that the change in molar air density, ϱ_a', is due to the mol per mol displacement of moist air by water vapor, so that for present purposes $\varrho_a' = -\varrho_v'$, from which is

25 follows that

$$T_e' = -\frac{RT_K}{c_v}\frac{\varrho_v'}{\varrho_a} \equiv -\frac{\mu RT_K}{c_v}\frac{\rho_v'}{\rho_a} \tag{9}$$

where the second expression on the right is expressed in mass units (kg) rather than mols, i.e., $\mu = 1.609$ is the ratio of the molecular mass of dry air to the molecular mass of water vapor, ρ_v (kgm^{-3}) is the mass density of water vapor, and ρ_a (kgm^{-3}) is the mass density of the ambient atmosphere. Equation (9) is a rephrasing of the principal result of Appendix C of Paw U et al. (2000).

5   The remaining portion of this study assesses the validity of this displacement assumption and the resulting expression for T'_e, but from a very different approach, again in the hopes of clarifying the issue of the work term and whether the surface sensible heat flux includes a water vapor term similar to that suggested by Equation (9). We begin with the time dependent version of the first law of thermodynamics expressed as the conservation law for potential temperature, θ (K), for an incompressible atmospheric process:

10
$$\frac{d\theta}{dt} = \frac{\partial\theta}{\partial t} + \nabla(\mathbf{u}\theta) = \frac{1}{c_p}\frac{\theta}{T_K}\frac{dq}{dt} \tag{10}$$

where dq/dt represents the heat flow associated with diabatic atmospheric processes, $\mathbf{u}$ (ms^{-1}) is the atmospheric velocity, ∇ is the vector gradient operator, and the vector dot product has been dropped for convenience. Equation (10) is very well known and in and of itself is not novel. Nonetheless it does imply an important take away: which is that the turbulent surface sensible heat flux is more correctly expressed in terms of potential temperature, $\overline{w'\theta'}$, rather that in terms of temperature, $\overline{w'T'}$. This
15   is principally because $\overline{w'\theta'}$ explicitly includes the effects of any change in ambient pressure and the concomitant work done on or to the atmosphere during turbulent atmospheric processes. NOTE: for the sake of completeness w (ms^{-1}) is the vertical velocity and the $'$ notation is standard and refers to Reynolds averaging. Having identified potential temperature as the key variable for discussion the next step is to examine the influence moisture has on θ.

Including the effects of water vapor on potential temperature yields the following relation (e.g., Curry and Webster , 1999).

20   $$\theta = T_K \, (p_{00}/p_a)^{\kappa(1-0.33q_v)} \equiv T_K \, (p_{00}/p_a)^{\kappa} \, e^{-0.33\kappa q_v \log(p_{00}/p_a)} \tag{11}$$

where $p_{00} = 100$ kPa is a constant reference pressure; $\kappa = R_d/C_{pd}$, for which R_d is the specific gas constant for dry air and C_{pd} is the specific heat for dry air and consequently $\kappa = 2/7$ is an extremely good approximation; and $q_v = \rho_v/\rho_a$ (kgkg^{-1}) is the specific humidity of moist air. Note: that the 0.33 coefficient modifying q_v corrects an error in Equation (2.66) and related expressions in (Curry and Webster , 1999). Equation (11) clearly indicates that θ is dependent on moisture. Although this
25   dependency is extremely weak, the purpose here is to assess the influence of ρ'_v on the θ' using Equation (11) and to compare the result with Equation (9). A sketch of the derivation follows.

Linearize Equation (11) first by noting that near-surface atmospheric conditions (i.e., $q_v < 0.04$ and $\log(p_{00}/p_a) < 0.35$ or $0.33q_v < 0.014$ and $\kappa \log(p_{00}/p_a) < 0.1$) are sufficient to guarantee that $0.33\kappa q_v \log(p_{00}/p_a) < 0.33q_v \ll 1$ and second by

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assuming that the perturbation quantities are small compared to their background levels (which will be denoted by an overbar). This yields:

$$\frac{\theta'}{\overline{\theta}} = \frac{T'}{\overline{T_K}} - \kappa \frac{p_a'}{\overline{p_a}} - \alpha' \tag{12}$$

where $\alpha = 0.33 \kappa q_v \log(p_{00}/p_a)$, $\alpha' = -0.33 \kappa \overline{q_v} (p_a'/\overline{p_a}) + 0.33 \kappa \log(p_{00}/\overline{p_a}) q_v'$, and for later use $\overline{\alpha} = 0.33 \kappa \overline{q_v} \log(p_{00}/\overline{p_a})$.

5 Substituting α' into Equation (12) yields

$$\frac{\theta'}{\overline{\theta}} = \frac{T'}{\overline{T_K}} - (1 - 0.33\overline{q_v})\kappa \frac{p_a'}{\overline{p_a}} - \gamma q_v' \tag{13}$$

where $\gamma = 0.33 \kappa \log(p_{00}/\overline{p_a}) < 0.034 \ll 1$. Next is the evaluation of q_v' by expanding and linearizing $q_v = \rho_v/\rho_a$ in terms of ρ_v' and ρ_a'. This yields $q_v' = \rho_v'/\overline{\rho_a} - \overline{q_v}(\rho_a'/\overline{\rho_a})$. The ideal gas law for ambient air yields $\rho_a'/\overline{\rho_a} = p_a'/\overline{p_a} - T'/\overline{T_K}$ and therefore, $q_v' = \rho_v'/\overline{\rho_a} - \overline{q_v}(p_a'/\overline{p_a}) + \overline{q_v}(T'/\overline{T_K})$. Substituting this last expression for q_v' into Equation (13) yields:

10 $$\theta' = \overline{\theta}(1-\overline{\alpha})\frac{T'}{\overline{T_K}} - \overline{\theta}(1-\beta)\kappa \frac{p_a'}{\overline{p_a}} - \overline{\theta}\left(\gamma \frac{\rho_v'}{\overline{\rho_a}}\right) \tag{14}$$

or

$$\theta' = \overline{\theta}\left(\frac{T'}{\overline{T_K}} - \kappa \frac{p_a'}{\overline{p_a}}\right) - \overline{\theta}\left(\overline{\alpha}\frac{T'}{\overline{T_K}} - \beta\kappa \frac{p_a'}{\overline{p_a}}\right) - \overline{\theta}\left(\gamma \frac{\rho_v'}{\overline{\rho_a}}\right) \tag{15}$$

where $\beta = 0.33\overline{q_v}[1 + \log(p_{00}/\overline{p_a})] < 0.018 \ll 1$. At this point it is important to reiterate that for near-surface conditions $\alpha < 0.33\overline{q_v} < \beta < 0.018 \ll 1$.

15 Equation (15) suggests that water vapor contributes two different "corrections" to the kinematic heat flux. First, the middle term on the right hand side of this equation, is due to the overall presence of water vapor, $\overline{q_v}$, and the second, the last term on the right hand side of Equation (15) and the term of interest in this study, results from fluctuations in water vapor, ρ_v'. Although Equations (9) and (15) have somewhat different definitions of heat flux, it is still possible to assess the appropriateness of the displacement assumption made by Paw U et al. (2000)| by numerically comparing the dimensionless coefficient $\mu R/c_v$ in

20 Equation (9) with γ in Equation (15). Noting that $R/c_v = 2/5$, then $\mu R/c_v \approx 0.644 \approx 19\gamma$. In other words $\gamma \ll \mu R/c_v$ and therefore, the approach followed by Paw U et al. (2000)| predicts significantly more turbulent heat flux associated with the water vapor flux than does the approach based on potential temperature (initiated above with Equation (10)). Even allowing for the difference between potential temperature and T_K does not really change this result by more than 10% because $(p_{00}/p_a)^\kappa < 1.1$ for conditions being considered here.

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This difference between Paw U et al. (2000) and the present result is made more explicit by comparing the next two expressions. The first expression derives from combining Equation (9) for T_e' with the equivalent heat flux, $H_e = \overline{\rho_a} C_p \overline{w' T_e'}$ from Paw U et al. (2000). This yields the following generalization of Paw U et al. (2000) result:

$$H_e = -\frac{\mu C_p}{c_v}\left(\frac{R T_K}{L_v}\right) L_v E \approx -\frac{9}{4}\left(\frac{R_d T_K}{L_v}\right) L_v E \approx -(0.07 - 0.10)\, L_v E \tag{16}$$

where $R_d \approx 287$ Jkg^{-1}K^{-1} is the gas constant for dry air. The second expression results by identifying the equivalent potential temperature, θ_e', associated with the water vapor perturbation, ρ_v', in Equation (15), i.e., $\theta_e' = -\overline{\theta}(\gamma \rho_v'/\overline{\rho_a})$ and combining it with the expression for the equivalent heat flux, H_e, appropriate to Equation (10), i.e., $H_e = \overline{\rho_a} C_p \overline{w'\theta_e'}$. This yields

$$H_e = -\left(\frac{\gamma C_p}{L_v}\overline{\theta}\right) L_v E \approx -\frac{3}{25}\left(\frac{R_d T_K}{L_v}\right) L_v E \approx -(0.0037 - 0.0053)\, L_v E \tag{17}$$

It is not possible to reconcile these two expressions, which brings into question the validity of the displacement assumption of Paw U et al. (2000) (i.e., $\varrho_a' = -\varrho_v'$), on which Equation (16) is based. To truly assess the cogency of this assumption and any enthalpic changes associated with mixing of the dry air and water vapor requires a better description of the physical processes and the initial and final states involved than Paw U et al. (2000) provide. But since they are addressing evapotranspiration, it seems reasonable to assume they are envisioning the final state of the evaporative process. In this case the work done to/by the atmosphere associated with the expansion of water vapor into the atmosphere is appropriately included in the enthalpy of vaporization as previously discussed and, consequently, the displacement assumption would result in over-counting the work term. On the other hand, if they are describing the enthalpic changes associated with rising plumes of warm moist air associated with density differences between very moist air near the surface and drier and therefore, denser air above the near-surface, then the methods and results outlined by Equations (10), (11), and (17) above are more appropriate.

4 Conclusions

The present study has explored some of the issues involving the surface energy balance (SEB) and the thermodynamics of evaporation of water into the atmosphere. Specifically I have looked at (1) the influence that molecular interactions between water vapor and dry air (non-ideality of atmospheric gases) could have on estimates of L_v and C_p and the SEB and (2) the impact that fluctuations of atmospheric water vapor could have on the surface heat flux. At typical atmospheric temperatures (285-325 K), the influence of the first affect is probably on the order of about 1% and the second is about 0.5%. Consequently, these phenomena acting either independently or in consort are far too small to be of any real significance in explaining the lack of closure of the SEB. This result should not be surprising, but because these issues may not be well known to the micrometeorological and geo-biophysical communities it seemed worthwhile to attempt to verify this supposition quantitatively.

Code and data availability. The computer code used in this study was developed using MatLab version 2017b and will be publicly available along with any output data upon publication of this manuscript. Otherwise the code and any output is also freely available from the author.

Appendix A: A

This appendix derives the relation $\delta T / T_K \approx -1.4 N_v / N_l$ for the temperature drop, δT, associated with evaporative cooling.

5 Achieving this requires an approach similar to that used when calculating the wet bulb temperature (e.g., Curry and Webster , 1999), but for this study it is applied to the evaporative cooling that occurs with an isolated thermodynamic system that includes a large reservoir of liquid water. The formal expression for the first law of thermodynamics for the system under consideration is:

$$0 = Q_f - Q_i = (C_{ps}T_K)_f - (C_{ps}T_K)_i + (N_v M_v L_v^*)_f - (N_v M_v L_v^*)_i \tag{A1}$$

10 where the subscripts f and i refer to the final and initial states; $Q_f - Q_i$ (J) is the total heat exchanged by the system and its environment, which must be 0 since the system is isolated from its environment; C_{ps} (JK^{-1}) is the bulk heat capacity of the composite system (vapor + dry air + and liquid water) at constant pressure so that the change in heat content of the system, $(C_{ps}T_K)_f - (C_{ps}T_K)_i$, must exactly cancel the change in the enthalpy of the system $(N_v M_v L_v^*)_f - (N_v M_v L_v^*)_i$, which is expressed here in terms of the water vapor component. L_v^* assumes that water vapor is ideal gas (an assumption that is

15 sufficient for the present purposes) and M_v (kgmol^{-1}) the molecular mass of water vapor. Simplifying this expression begins by identifying

$$T_{Kf} = T_{Ki} + \delta T \tag{A2}$$

and

$$C_{ps} = N_d M_d c_{pd} + N_v M_v c_{pv} + (N_l - N_v) M_l c_{pl} \equiv N_d M_d c_{pd} + N_l M_v c_{pl} + N_v M_v (c_{pv} - c_{pl}) \tag{A3}$$

20 where N refers to the number of mols of any particular component (subscript d for dry air; v for vapor, and l for liquid); M refers to the molecular mass of that component; c_p (Jkg^{-1}K^{-1}) refers to the specific heat at constant pressure of that component; and $M_l = M_v$ has been used for the right hand side of the last expression.

Combining these last two expressions with $N_{vi} = 0$ and after dividing the resulting expression by $N_l M_v$ yields;

$$\left(\frac{N_d M_d}{N_l M_v} c_{pd} + c_{pl} + \frac{N_v}{N_l} (c_{pv} - c_{pl}) \right) \delta T = -\frac{N_v}{N_l} (c_{pv} - c_{pl}) T_K - \frac{N_v}{N_l} L_v^* \tag{A4}$$

25 where the δT term on the left hand side and the term $(N_v / N_l) L_v^*$ on the right hand side are evaluated at T_{Kf} and the first term on the right hand side, $-(N_v / N_l)(c_{pv} - c_{pl}) T_K$, is evaluated at $T_{Ki} = T_K$. The order of magnitude calculation is facilitated

by dividing the last expression $c_{pl}T_K$, by noting that $c_{pl} \approx 2c_{pv} \approx 4c_{pd}$, and by ignoring the relatively weak temperature dependency of the various c_p's. This yields:

$$\left(0.25\frac{M_d}{M_v}\frac{N_d}{N_l} + 1 - 0.5\frac{N_v}{N_l}\right)\frac{\delta T}{T_K} = \left(0.5 - \frac{L_v^*}{c_{pl}T_K}\right)\frac{N_v}{N_l} \tag{A5}$$

Basic to the final result is the assumption that the system contains a large reservoir of liquid water. In terms of the ongoing

5   order of magnitude calculation this means that $N_d + N_v \ll N_l$, thereby also implying $N_v \ll N_l$. From this it follows that the coefficient on the left hand side of this last expression, $0.25(M_d/M_v)(N_d/N_l) + 1 - 0.5(N_v/N_l)$, can be approximated by 1. Furthermore, ignoring the temperature dependency of L_v^* on the left hand side implies $L_v^* \approx 2.5 \times 10^6$ Jkg^{-1}. And finally for the temperature range 295 K $\leq T_K \leq$ 325 K, $c_{pl} \approx 4.186 \times 10^3$ Jkg^{-1}K^{-1} and $c_{pl}T_K \approx (1.24 - 1.36) \times 10^6$ Jkg^{-1}. These last conditions yield the final result:

10
$$\frac{\delta T}{T_K} \approx -(1.43 \pm 0.09)\frac{N_v}{N_l} \tag{A6}$$

which leads to the conclusion that as long as the dominant component of the isolated thermodynamic system discussed in this study is liquid water, e.g., $N_v/N_l < 10^{-6}$ implies $|\delta T| < 0.0005$ K, then evaporative cooling will have a negligible effect on the final temperature of the system. Therefore, for all present intent and purposes, one could claim that evaporation is very nearly isothermal for the thermodynamic system under consideration here and that the temperature of the final state is not

15   significantly different from its initial state.

Author contributions. W. J. Massman is the sole author of this paper.

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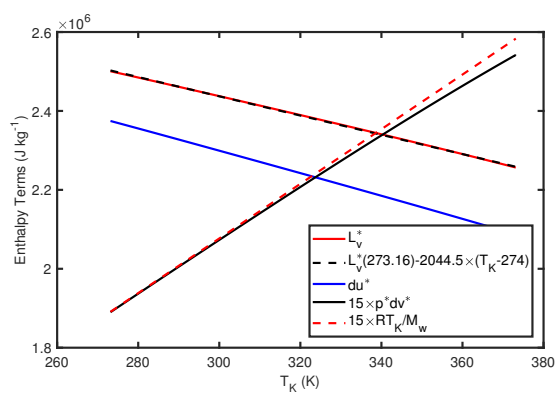
Figure 1. The solid red line is the enthalpy of vaporization of pure water, L_v^*, from Wagner and Pruess (2002), and the dashed black line is a linear approximation to it; where $L_v^*(273.16K) = 2.50054 \times 10^6$ Jkg^{-1}. The solid blue line is the thermodynamic change in internal energy, du^*, associated with L_v^*. The other two lines are $p^*\Delta v^*$ (solid black) and RT_K/M_w (dashed red) after multiplication by a factor of 15 for ease in plotting and visualization. Here T_K is the temperature in degrees K, R (Jmol^{-1}K^{-1}) is the universal gas constant, and $M_w = 0.0180153$ kgmol^{-1} is the molecular mass of water vapor.

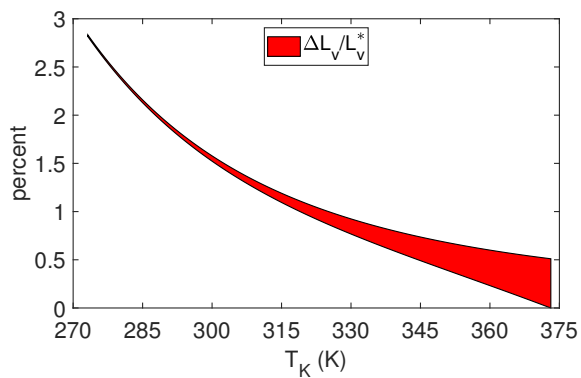**Figure 2.** % change in L_v^* according to Equation (5), where ΔL_v on the y-axis label is used in place of I_B/χ_v. The upper curve bounding the red shaded area is $\Delta L_v/L_v^*$ for a process occurring at constant volume and the lower boundary is for a isobaric process.
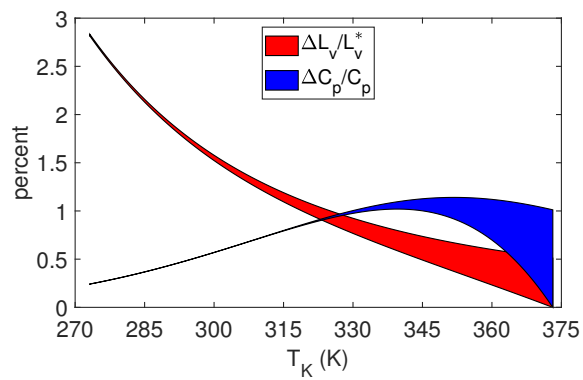
Figure 3. % change in C_p from Equation (6) along with (overlaying) the results for $\Delta L_v/L_v^*$ as shown in Figure 2. The upper curve bounding the blue shaded area is $\Delta C_p/C_p$ for a process occurring at constant volume and the lower boundary is for a isobaric process.