

Interactive comment on “Impacts of non-ideality and the thermodynamic pressure work term $p\Delta v$ on the Surface Energy Balance” by William J. Massman

William Massman

wmassman@fs.fed.us

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Response to Comments from Grant Petty dated 15 August 2019

My thanks to Grant Petty for his comments. They were helpful. My response (in italics) follow a repeat of his comment.

GP (0-a) The topic addressed by this paper is surprisingly subtle and complex, which is probably why it has not already been definitively addressed in the past. Bill Massman offers what appears to be a rather rigorous analysis that seems plausible

on its face, and it certainly leads to the conclusions one might expect, which is that the effects of second-order corrections are far too small to account for the commonly reported closure problem in surface energy budget studies.

RESPONSE (0-a) *I agree.*

GP (0-b) However, even after multiple readings, I have still not completely convinced myself that there couldn't be an error or inconsistency in assumptions buried somewhere in the analysis that affects the precise conclusions. I recommend publication anyway with the thought that (a) it may well be correct, and (b), even if not, it will at least provide a useful starting point for others who may wish to reexamine this problem in the future.

RESPONSE (0-b) *Thank you and I concur.*

GP (0-c) A number of specific issues have already been addressed by other reviewers, and Dr. Massman has already responded to many of those. Here I focus only on the things that caught my attention as I was reviewing the manuscript:

GP 1) With regard to this paper's reference to the Kowalski note, it's not completely clear to me that Massman's section 2 is even really examining the same physical issue. In particular, line 20 on p. 2 states, "The purpose of the present paper is to examine the methods and conclusions of these two papers." But Massman doesn't actually examine Kowalski's methods, as far as I can tell. And Massman is looking at the role of non-ideality, whereas my recollection of Kowalski's contribution (which was withdrawn) was that it was looking at a possibly missing contribution of pV work in the enthalpy of evaporation (I don't have the link to the Kowalski manuscript at my fingertips so can't verify). In any case, if Kowalski's unpublished (except as a discussion paper) work is referenced at all – and I'm not necessarily sure it should be, I think the physical and logical relationship between the problems Massman and

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Kowalski were considering (irrespective of the methods employed) should be made more explicit.

RESPONSE 1) *I have revised the paragraph to eliminate the suggestion that I am examining Kowalski's methods. The paragraph now reads:*

The present paper employs "classical" thermodynamics to examine (a) the influence that the non-ideality of atmospheric gases can have on the SEB and (b) the methods and conclusions of Paw U et al. (2000, Appendix C) regarding the first law of thermodynamics and the pressure work term's influence on the turbulent heat flux and ultimately the SEB as well. Although it is true that what I develop herein is not necessarily "new" science, some of the theory I employ may well be new to the general environmental and geo-biophysical communities. The present study is divided into two parts. The first examines and quantifies 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. In the second part the first law of thermodynamics is employed to derive the influence water vapor has on potential temperature, which in turn gives rise to an expression, different from that developed by Paw U et al. (2000, Appendix C), relating how the kinematic heat flux is influenced by the mass flux of water vapor, E . In summary, this study shows that any potential corrections to the SEB from either of these two sources are likely to be negligible and certainly much smaller than either Kowalski (2018) or Paw U et al. (2000) propose.

GP 2) There do seem to be some potential inconsistencies in assumptions. These may not be fatal, but the author should perhaps acknowledge them and explain why they don't undermine some of the conclusions. For example:

GP 2a) In lines 20–25 of p. 3, the system is considered to be isolated, including no mechanical interaction with the environment. By definition, this implies constant

volume, yet line 4 of p. 5 states, "The final step is to specify whether the enthalpic change occurs at a constant pressure or at a constant volume." The reality, of course, is that pressure is normally very close to hydrostatic in the boundary layer, so a constant pressure assumption seems more germane. In fact, if I were attempting the analysis myself, I might consider evaporation in a constant volume system as an intermediate stage for analytical convenience, with subsequent adiabatic expansion to the ambient pressure.

RESPONSE 2a) *I have revised the manuscript so that the paragraph above Equation (3) now reads as below. This revision also eliminates Kowalski's concern about the flow of the manuscript being interrupted by the interjection of "Note ..." about the enhancement factor f (page 4, lines 12-16 of the original manuscript).*

For an ideal gas the final pressure is $p_{v,sat}$ (Pa), but for a non-ideal gas the saturated vapor pressure is $f p_{v,sat}$ (Hyland and Wexler 1983; Goff 1949), where $f = f(T_K, p_a)$ is termed the enhancement factor and $1 < f < 1.006$ near STP (Hyland and Wexler 1983; Nelson and Sauer 2004). Consequently, the final pressure of the water vapor will exceed $p_{v,sat}$ by a small amount. On the other hand, the final pressure of the dry air, $p_{d,final}$ (Pa), will be slightly less than p_d because the final gas volume of the system will be slightly greater than the initial volume due to the decrease in the volume of liquid with the evaporative loss of N_v mols of liquid. In the present scenario this difference between the final and initial pressures is small: $\approx 0.001 p_d$. Because both f and this relative pressure difference are so small and they tend to compensate for one another, it is reasonable to ignore both effects and approximate the final total pressure, p_a (Pa), as simply as $p_a = p_d + p_{v,sat}$; meaning that the present purposes evaporation occurring within an isolated system can be considered as an archetypical constant pressure process. Nonetheless, it is also worth emphasizing that, in fact, evaporation in the present isolated system (as well as within the atmospheric surface layer) is neither a constant volume, nor a constant pressure, process. Rather it is a combination or hybrid of the two

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processes.

GP 2b) Section 2 is explicitly looking at the effects of non-ideality, but line 31 on p. 3 states that $p_a = p_d + p_{v,sat}$, implying that Dalton's law of partial pressures is exact for this system. Doesn't the existence of non-zero B_a (2nd virial coeff. for moist air) imply that the final pressure will be greater or less than the sum of the individual pressures?

RESPONSE 2b) *The reviewer is correct. Non-ideality does imply that the final pressure is different than for an ideal case, for which Dalton's law implies $p_a = p_d + p_{v,sat}$. The revisions – see my RESPONSE 2a) above – now address this issue plus another issue related to the final pressure of the dry air. I think my revisions should cover Dr. Petty's concern.*

GP 3) I would have liked to see more slightly more context for equation (5) at the bottom of p. 4. For those who don't normally work with the virial coefficients, what does the equation of state look like when B_a , B_d , and B_v are included, and how does (5) arise from that equation and from the definition of I_B/χ_v ? **RESPONSE 3)** *I have revised the manuscript to accommodate GP's request. The text now reads: **In general I_B is expressed in terms of the second and third virial coefficients (Hyland and Wexler 1983; Wagner and Pruß 2002), which are defined by the virial equation of state (Hyland and Wexler 1983; Sattar 2000) as follows:***

$$\frac{p_i v_i}{RT_K} = 1 + \frac{B_i}{v_i} + \frac{C_i}{v_i^2} + \dots \quad (6)$$

where the subscript 'i' refers to water vapor ($i = v$), dry air ($i = d$), or moist air ($i = a$); B_i ($m^3 \text{ mol}^{-1}$) is the second virial coefficient, C_i ($m^6 \text{ mol}^{-2}$) is the third virial coefficient, and in general B_i and C_i are both functions of temperature, T_K ; p_i is the gas pressure (Pa) and v_i is the molar volume ($m^3 \text{ mol}^{-1}$) of the gas. For this study it is sufficient to consider only the second virial coefficients. For

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dry air and water vapor, $B_i = B_i(T_K)$ is determined by empirical curve fitting of observed data. For this study $B_v(T_K)$ is taken from Equation (6) of Harvey and Lemon (2004) and $B_d(T_K)$ is taken from Equation (10) of Hyland and Wexler (1983). Because moist air is a mixture of dry air and water vapor the second virial coefficient for moist air takes the form $B_a = \chi_v^2 B_v + 2\chi_v\chi_d B_{vd} + \chi_d^2 B_d$ (Sattar 2000), where B_{vd} ($\text{m}^3 \text{mol}^{-1}$) is the cross virial coefficient for moist air. For the present study $B_{vd}(T_K)$ is taken from Equation (15) of Hyland and Wexler (1983). Once the equation of state has been specified, the general expression for I_B can be derived (e.g., Sattar 2000), yielding ...

But note, I have not elaborated on the methods used for employing the virial equation of state to produce I_B or equivalently $I_B/\chi_v =$ Equation (7) of the revised text. I just simply refer to Sattar (2000), who only briefly sketches what is needed for this step. This is a non-trivial step and needs some understanding of the kinetic theory of gases and the electrostatic interaction potential (e.g., Lennard-Jones potential) between water molecules and other water molecules and between water molecules and dry air molecules, which I think is well beyond the intent of the present study. But knowing that H_2O is a polar molecule and that O_2 and N_2 are non-polar is sufficient to recognize that the major component of B_a is B_v , followed by B_{vd} and that B_d is essentially negligible.

GP 4) line 12, p. 5: Under what conditions might evaporation occurring on the Earth's surface be poorly approximated as isobaric? I can't think of any, except perhaps in the interior of a leaf with very high stomatal resistance, and I'm not even completely persuaded in that case.

RESPONSE 4) *I agree that it is more logical to assume that evaporation into the atmosphere occurs at constant pressure than at constant volume. But as I pointed out in the revision discussed under 2a) above evaporation occurs by a process that is neither constant pressure nor constant volume, but is really a mixture of the two*

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pathways. In which case, it is important to consider both pathways since the results will bound the true enthalpy of vaporization and the specific heat estimates derived in this study. More importantly though it should not be surprising that these two pathways yield nearly identical results, except maybe under extremely hot and moist conditions (figures 2 and 3). Nonetheless, I added a sentence to the paragraph that follows Equation (7) of the revised text to suggest that evaporation into the atmosphere is better approximated by a constant pressure pathway than a constant volume pathway. These two sentences now read:

The final step is to specify whether the enthalpic change occurs at constant pressure or at constant volume. Although assuming a constant pressure pathway for modeling evaporation into the atmosphere is likely to be more appropriate than assuming a constant volume pathway, both pathways need to be considered here because any evaporation occurring on the earth's surface is going to lie somewhere between these two (bounding) pathways.

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