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Discussions

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

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Response to Comments from Andrew Kowalski dated 19 June 2019

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

ASK (a) This manuscript examines two thermodynamic issues that the author intends to improve the surface energy balance at the margins. I applaud Dr. Massman's dedication to this unresolved and important dilemma in micrometeorology. The two

issues addressed are, first the relevance of the virial (versus ideal) gas law, and second the definition of the pressure-work term $p\Delta v$ as regards the role of the water vapour flux on sensible heat exchange. The former, I believe, represents a substantial contribution to the state of knowledge, if a slight adjustment to thermodynamic accounting, and certainly deserves publication.
RESPONSE (a) *Thank you for your positive response to the first portion of the paper.*

ASK (b) The latter is framed in a way that is based on two previous publications, both of which I believe to be erroneous, and so should be deleted. Consequently, my recommendation is for major revision in order to publish the most valuable aspect of this manuscript, namely the impact of non-ideality on the Surface Energy Balance.
RESPONSE (b) *As far as the second half of the paper is concerned. I do not agree that it should be deleted solely on basis of whether the papers I cited were flawed or erroneous. My result in this section can stand on its own merits without reference to Paw U et al. (2000) or Kowalski (2018), which would certainly argue for keeping it regardless of whether other papers have made mistakes or not. I admit that it is possible to reframe the paper, but the paper would lose context.*

RESPONSE (c) *These two papers motivated my thinking and interest in this subject and in writing this paper and not to cite them is to avoid giving credit where credit is due. I personally am less interested in errors made than I am in trying to understand the issues and the nature of the physical processes processes they are invoking. In this regard, I have been discussing Appendix C of Paw U et al.'s paper with Paw U off-and-on for much of the last decade and more intensely in the past couple years. I thought Appendix C raised an interesting question that I wanted better to understand. But what provided the final impetus to research this subject was Kowalski (2018) and the comments it generated from Paw U, Petty, and Meester. So I felt that a paper that delved a little deeper into the role of thermodynamics might be of benefit to the community. And I certainly benefited by the effort of researching and writing it.*

Specific comments

ASK - Page 2, line 2: I see no benefit to framing the introduction based on these two references, and suggest a restructuring of the introduction along different lines. The Kowalski citation is to a manuscript that the referees discredited and the author withdrew. It is incorrect, and so Hydrology and Earth System Sciences did not publish it. Furthermore Dr. Massman seems to have realised its irrelevance, since his last reference to this manuscript (at page 2, line 23) indicates an intention to present further analysis and discussion, which later did not follow. I recommend not citing such grey literature that failed to pass the peer-review process.

RESPONSE *I cited HESS-Discussions for Kowalski (2018), not HESS. I also note that the paper does have a doi and is archived on and retrievable from the journal website. As I explained in my **Response (c)** above I do not agree that the paper is without merit. But I did reword the sentence on page 2, lines 24-25 that the author identifies as being on page 2, line 23.*

ASK - The Paw U paper is cited only regarding its appendix C, which I believe is patently incorrect (see below). I also recommend not citing this paper, for reasons provided below.

RESPONSE *I agree that there is an obvious contradiction in Paw U et al., but I disagree that it obviates the reason for citing it. I provide further discussions on the point below as well.*

ASK - Page 2, line 23: The author makes inconsistent use of the first person plural/singular (I/we) at different places in the manuscript (compare with line 26 of the same page). It would be best to homogenize this, perhaps taking into account that this is a single author manuscript.

RESPONSE *I agree. The text has been changed to "I" throughout (if the "we" wasn't just eliminated instead).*

ASK - Page 4, line 4: The assumption of no change in temperature for the liquid has not been adequately justified. Given that there are million times more moles of liquid (N_l) than vapour (N_v), the appropriateness of neglecting (in equation 2) a term with the form $N_l\ (h_{l,final} - h_{l,inital})$ is hardly obvious. Please make more explicit the justification of this assumption.

RESPONSE *The reviewer is correct. I did not properly account for the change in temperature of the system associated with evaporative cooling. I have corrected this error and revised the main text and the appendix accordingly. The revised text now points out that the change in the enthalpy of the system has two components. One associated with the change of phase during evaporation and one associated with the resulting temperature change. For the purposes of this study it is sufficient to focus solely on the first term – the enthalpy of vaporization – in order to estimate the effects of non-ideality of dry air and water vapor on the surface energy balance.*

ASK - Page 4, lines 12-16: The note put forth in this paragraph seems to be an unnecessary digression, whose elimination would improve the flow of the manuscript.

RESPONSE *I agree the eliminating this paragraph would improve the flow of the paper. But there are many papers that are either devoted to this enhancement factor or actually use it for algorithm development. Maybe it is obvious to others that the enhancement factor, f, results from non-ideality of gases, but it was not to me until I started looking into this subject more closely. I would prefer to keep this paragraph.*

ASK - Page 5, line 26: Perhaps you could support the assertion that $C_p = dL_v/dT$ is a definition, either with a citation or an explanation.

RESPONSE *My assertion that $C_p = dL_v/dT$ (by definition) is in error. In fact, after a few seconds of thought it is obvious that it is a mistake. The revisions correct this misstatement and provide a derivation of the corrected ΔC_p term. Equation (6) and Figure 3 have also been revised accordingly. But numerically the error is very slight.*

ASK - Page 6, line 23: Equation 8 comes from equation C2 of the Paw U paper, which I believe is in error. Those authors put forth relationship to describe "the density of air change solely from the perturbation in water vapour", yielding a negative proportionality between perturbations in the specific volume and those in the water vapour density ($\alpha' \propto -\rho_v'$). Note that the context of this relationship is the Webb et al. (1980) paper, which assumes constant pressure. Excluding temperature effects (the other WPL correction), the effect of isobaric and isothermal evaporation is to humidify the air. According to the ideal gas law (equation 4 of Webb et al. (1980)), under such conditions the total number of molecules per unit volume remains constant, such that – for a fixed Eulerian volume – dry air molecules disappear at the same rate that water vapour molecules appear due to humidification. Since water vapour has less mass than does dry air, the effect of such humidification is a reduction in air density, and hence an increase in the specific volume, demonstrating that the proportionality between perturbations in the specific volume and those in the water vapour density is in fact positive. Therefore, I believe that equation C2 of the Paw U paper is patently incorrect. Since the entirety of Section 3 based on this, I recommend its elimination.

RESPONSE *I agree that Paw U et al.'s statement that $\alpha' \propto -\rho_v'$ violates physical reality. This can be shown relatively simply. By definition $\alpha = 1/\rho_a$, from which is immediately follows that $\alpha' = -\rho_a'/\overline{\rho}_a^2$. Next using the displacement assumption, $\rho_v' + \rho_a' = 0$, it also follows that $\rho_v' = -\rho_a'$. Therefore, $\alpha' = \rho_v'/\overline{\rho}_a^2$ or $\alpha' \propto \rho_v'$, which is now in concordance with the ASK's analysis. For my restatement of Paw U et al.'s* *derivation of T_e' and H_e' (their Appendix C) I simply maintained the correct sign and focused on what Paw U et al. would have derived if they had not made a sign error. As I said in an earlier response I am less concerned about specific errors than I am in trying to understand the physics of the idea that the authors are trying to express.*

ASK - Page 6, line 24: This part of the paper (if not eliminated) would be more clear if T_e' were defined more explicitly, as “the temperature perturbation equivalent to the energy needed for expansion" as in the Paw U paper.

RESPONSE *I concur. The manuscript has been changed.*