Review of HESS Manuscript #2019-153

Title: Impacts of non-ideality and the thermodynamic pressure work term p∆v on the Surface Energy Balance

Author:Massman

Review by A. S. Kowalski

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∆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. 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.

Specific comments

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.

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.

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.

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.

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.

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.

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.

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.