

# ***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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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.

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

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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.

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:

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 And Massman is looking at the role of non-ideality, whereas my recollection of Kowalski's contribution (which was withdrawn) was that it was looking at a possibly missing contribution of  $pV$  work in the enthalpy of evaporation (I don't have the link to the Kowalski manuscript at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 In any case, if Kowalski's unpublished (except as a discussion paper) work is referenced at all – and I'm not necessarily sure it should be, I think the physical and logical relationship between the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 Kowalski were considering (irrespective of the methods employed) should be made more explicit.

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:

a) 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

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might consider evaporation in a constant volume system as an intermediate stage for analytical convenience, with subsequent adiabatic expansion to the ambient pressure.

b) 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?

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  $I_B/\chi_v$ ?

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.

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