Review on Comment on: Macroscopic water vapor diffusion is not enhanced in snow

Dear Editor,

This *comment paper* discusses how the work of Fourteau et al. is supposedly incorrect. Since I have reviewed and approved this particular paper, I owe it to the writer of the comment and the writers of paper to at least take a look at the major issues that the writer of the *comment* brings to the table. In conclusion that is brought forward by my review below I found the critics to be unfounded. In the following the I use *comment* to address the comment paper.

As is clear from the discussion section both sides claim the other one is wrong with varying degrees of proof, and leap on a tangent expressing their own views on the matter. This stands at the origin, as the historical discussion already suggests, of an exponentially growing amount of discouraging work of fact checking. My time dedicated to the matter is purely based on the respect both authors deserve.

Firs of all, this is my *opinion*, take it or leave it: Please try to be civil. Any subjective adjectives and expressions of feelings should have no place here, especially in a public place of scientific debate: keep the mud-throwing for an obscure party at a soon to be forgotten conference. Whether you are aware of it or not, this makes for a very unpleasant working environment, and it should not come at a surprise that sincere scientists who do not like conflict, but love a good scientific debate are likely to flee the scene.

To the grid of of vapor diffusion. I will comment only on the critics raised by the *comment* on the paper, and not on content that is tangent to the paper. If a new paper on vapor flux is submitted, I will consider reviewing it by that point.

Please note that in order to conclude on this matter it might be wise to seek a third reviewer that has no previous ties (writer, editor, reviewer of, professional relation) to either Fourteau et al. or Hansen.

I will first comment on the first half of the abstract and then comment on the issues raised by the *comment*'s' author in the main body of the text.

abstract

The abstract in red, my comments in black.

The central thesis of the authors paper is that macroscopic water vapor diffusion is not enhanced in snow compared to diffusion through humid air alone. Further, mass diffusion occurs entirely as the result of water vapor diffusion in the humid air at the microscale and the ice phase has no effect other than occupying volume where diffusion cannot occur.

Technically this is not true. The paper deals with the ice phase appropriately. The ice phase acts as sinks and sources to balance the diffusion present in the humid air. This is enforced by the Robin boundary condition (Eq. 3)

The foundation of their conclusion relies on the premise that the synchronous sublimation and deposition of water vapor across ice grains, known as hand-to-hand water vapor transport, does not lead to enhanced mass diffusion.

Synchronous sublimation and deposition of water vapor across ice grains is not "known" as hand-to-hand vapor transport. Some authors have used the term to explain mass transfer found in experiments that suggest faster transport than diffusion of water vapor alone. There are other candidates, such as convection, wind pumping and experimentally flawed definitions that could explain the matter too. The authors of the accused paper do not make any assumptions on transport mechanisms. They 'just' perform a numerical experiment that show that when transport is purely diffusion limited, it does not speed up mass transport of water vapor.

We use a layered microstructure to rigorously show that diffusion is enhanced at all ice volume fractions compared to diffusion through humid air alone, and further, the hand-to-hand model of diffusion correctly predicts this diffusion enhancement.

This sentence is technically incorrect, since there is no water vapor diffusion in the ice volume fractions, simply because it is a difference phase and now molecules are moving. The second part of the sentence relates to a prediction of a diffusion enhancement. I haven't found an experiment to date that actually shows that the predicted model based on enhanced transport in the layered microstructure is actually correct.

The authors attempt to dismiss the concept of enhanced mass transfer resulting from hand-to-hand water vapor transport by arguing that there is a counterflux of water vapor in the form of downward motion of ice.

This is not what the authors do, the base their conclusion on observations of their numerical simulations based on well defined set of equations and boundary conditions.

While the ice phase appears to be propagating downward, all continuum material points of water (either vapor or ice) are moving upward (counter to the temperature gradient) with a monotonically increasing (nonnegative) motion.

Monotonically increasing motion? What is the cause of the increase of motion? Within the context of this discussion, the flux of vapor is assumed to be uniform over the control volume.

Specifically, material points of water in vapor form are diffusing upward through the humid air while material points of water in the form of ice are at zero velocity while locked in the ice phase. Material points of water never exhibit downward motion, despite the ice phase appearance of downward motion. Since the motion of all material points of water is monotonically increasing for all time, there is no counter flux of mass due to downward motion of the ice and such apparent motion is a mirage in the context of mass transfer.

Again, what is monotonically increased motion? What is mend by mirage? The authors have argued at some point, that if you do not include the ice phase in the control volume one speaks about an apparent flux (Hansen). And as a consequence there are other 'apparent' fluxes that you must calculate that to get the correct answer. This has been adequately explained by the rebuttal of the authors of the paper.

The rest of the abstract addresses content which is how vapor diffusion should be defined in the eyes of the author. I will not go into this at this point.

General comments:

As I understand from the comment and the discussion, the author criticized that the paper on mainly two points. The first being that they have used the volume averaging technique wrongly and secondly about the decomposition of the heat flux into a conduction and vapor diffusion part. I will discuss these two points further below.

The first point

In the discussion he takes the reviewers Fig. 1 as an example that highlights the hart of the problem. He states that by taking an arbitrary control volume that includes the ice phase and is not moving with the ice sublimation/deposition interface velocity the paper neglects the temporal nature of the problem. I will argue why this is not the case.

Volume averaging can always be applied, but the outcome is either a local or macroscopic measure depending on whether the integrated volume represents a the macroscopic microstructure, i.e. a statistical representative volume. By introducing a toy-model such as a layered microstructure a unit-cell (with periodicity in its geometry) will suffice, since having many copies of them will not change the outcome. But there are rules for unit-cells that are often violated by the author of the *comment.* Not including the zero contribution in the ice phase will not lead to a zero contribution to the average, but will lead to a wrong normalization factor in the denominator $\mathcal{V} = \mathcal{V}_i + \mathcal{V}_{h-a}$:

$$F = \overline{f} = \frac{1}{\mathcal{V}} \int_{\mathcal{V}} f \, dv \tag{1}$$

Although the temperature gradient is enhanced by approximately $1/\phi$ with ϕ the porosity, at most as shown later, it is averaged out when correctly including a zero contribution of the ice phase.

All authors agree that the *local* diffusion in the humid air is enhanced because the local temperature gradient, which is forcing the diffusion, is enhanced, but they differ in how to compute its macroscopic average.

The author of the comment suggest that the paper fails to move to a co-moving frame, the natural frame of the problem. I don't share this opinion, since there are no actual material points moving. It is rather a question of sampling enough of the microstructure such that you get a reliable macroscopic flux. If a static frame is chosen to be a unit cell of the layered microstructure (including the ice phase!) there is never a change in density within this cell, hence no need to apply Taylors averaging theorem. By volume averaging the unit cell it is naturally sampling all fluxes through all possible surfaces at all time stages of the cell, since each slice,(all together building up the total volume of the unit cell), is representing any slice at a certain time. In other words: take one cross-section in either ice or humid air and evaluate its flux at all times until the ice matrix has moved a unit-length of the unit cell, is exactly the same as volume averaging the unit cell. Therefore there is no need to move into the a *co-moving* unit frame. Note that if you are in a moving frame, you could take the boundaries also through the ice phase instead of the lying on the interface and by the same argument given by the author of the *comment* in the rebuttal of Reviewer 1, it mass flux is equal to the mass balance given at the moving interface, regardless of the thickness of the humid air phase. This will lead to the conclusion that the enhancement is independent of porosity . . . which is a dubious outcome regardless. This also means that there is mass transport through an impermeable ice layer in the midst of a snow pack, by means of diffusion.

There is also no disagreement on the mass conservation between the flux in the humid air and deposition/sublimation rates. These are correctly identified in the paper [Fourteau et al.] Eq. (2).

Therefore I don't see any legitimate points of criticism in the volumetric averaging approach used by Fourteau et al..

The second point

When we describe mass flux of vapor diffusion it only makes sense to start from the local vapor flux and upscale to the macroscopic description with an appropriate method. Since we assume (ground truth) saturated conditions $\gamma_v(x) = \gamma_{\mathrm{v,sat}}(\theta(x))$, it becomes mathematically the same problem as the heat equation, meaning: once we have established the temperature field at all locations we also know the vapor field and its diffusive fluxes. However, starting from the solution of those equations and assigning its contributions to conductive fluxes, vapor fluxes and latent heat fluxes is not straightforward. As argued by the rebuttal to this *comment*, previously proven by the reviewer of Hansen and Foslien, and identified in the Appendix B of Fourteau et al., the decomposition into conductive and effective diffusion as suggested by Hansen and Foslien serves as definition of the effective diffusion constant and has yet to be (dis)proven to be equivalent to the volume averaging approach. However it is not upon the authors of Fourteau et al. to disprove this, it is up to the author of Hansen and Foslien to prove that it is equivalent, since volume averaging is a legitimate method of calculating effective transport properties of porous media Whitaker, Torquato.

Since we have established that volume averaging, as done by Fourteau et al. is done correctly, the only part that one can criticize in their paper is that they haven't included the latent heat when solving the heat equation to obtain $\theta(\mathbf{x})$. The authors [Fourteau et al.] have argued that this would lead to a decrease in the temperature gradients in the pore-space and can therefore not lead to any enhanced fluxes (Section 5, first paragraph). The question is therefore essentially this: is this true or not? They more or less show that in their Appendix C, but it is not that straight forward to me.

In the following I will proof to myself that this is true. Note that this is a tangent line of thoughts too. Therefore feel free to ignore it.

In case of the laminar microstructure it is easy to solve the heat equation. What we are after is to evaluate to what extent the temperature gradient in humid air is enhanced and to what extent it depends on latent heat flux in the ice phase (the phase transitions).

To start from ground truths, with macroscopic temperature gradient G, expressed in volume averaged temperature gradients in the humid air (h-a) with porosity ϕ, and ice with volumetric density $1-\phi$

$$G = \frac{\Delta\theta}{\Delta x} = \phi\left(\frac{d\theta}{dx}\right)_{\mathrm{h-a}} + (1-\phi)\left(\frac{d\theta}{dx}\right)_{\mathrm{i}} \tag{2}$$

Given the local boundary condition (for solving the heat equation $\nabla^2\theta = 0$) at the depositing interface

$$k_i\left(\frac{d\theta}{dx}\right)_i - k_{\mathrm{h-a}}\left(\frac{d\theta}{dx}\right)_{\mathrm{h-a}} = L_{\mathrm{sg}}w_n, \tag{3}$$

with all gradients > 0. Here the latent heat is given by Lsg and the velocity of the depositing interface $w_n > 0$ and conductivity of ice k_{i} and humid air $k_{\mathrm{h-a}}$. For the sublimating side all terms are multiplied by -1 because the normal vector changes sign (see Eq.9 in Calonne et al.).

For fixed gradient G over the unit cell (however you want to define it, given the periodicity requirement) we can express the G in terms of the local temperature gradient and latent heat contributions, using the previously stated boundary condition:

$$\begin{aligned} G = & \quad \phi\left(\tfrac{d\theta}{dx}\right)_{\mathrm{h-a}} + (1-\phi)\left[\tfrac{k_{\mathrm{h-a}}}{k_{\mathrm{i}}}\left(\tfrac{d\theta}{dx}\right)_{\mathrm{h-a}}\right] + (1-\phi)\tfrac{L_{\mathrm{sg}}w_n}{k_{\mathrm{i}}} & (4) \\ = & \quad \left(\tfrac{d\theta}{dx}\right)_{\mathrm{h-a}}\left[\phi + (1-\phi)\tfrac{k_{\mathrm{h-a}}}{k_{\mathrm{i}}}\right] + (1-\phi)\tfrac{L_{\mathrm{sg}}w_n}{k_{\mathrm{i}}} & (5) \end{aligned}$$

Therefore the we can write

$$\left(\frac{d\theta}{dx}\right)_{\mathrm{h-a}} = \left(G - (1-\phi)\frac{L_{\mathrm{sg}} w_n}{k_{\mathrm{i}}}\right) / \left[\phi + (1-\phi)\frac{k_{\mathrm{h-a}}}{k_{\mathrm{i}}}\right] < G/\phi \tag{6}$$

Note that all terms in the right-hand-side of the equation are constants. From this we can conclude that the latent heat contribution can only reduce the local gradient in humid air. By setting the latent heat to zero (the contribution in this case is less than 10^{-3} compared to the temperature gradient which is usually in the order of 10^1) and acknowledging the $\frac{k_{\mathrm{h-a}}}{k_{\mathrm{i}}} \approx 10^{-2}$, the local gradient $\left(\frac{d\theta}{dx}\right)_{\mathrm{h-a}} < G/\theta$. When we use this upper bound to calculate the effective diffusion constant by volume averaging the vapor flux we obtain

$$\begin{aligned} F \equiv & \quad D_{\mathrm{eff}} \tfrac{d\gamma_v}{d\theta} G & (7) \\ = & \quad \tfrac{D_{\mathrm{v-a}}}{\mathcal{V}} \int_{\mathcal{V}} \tfrac{d\gamma_v}{d\theta} \tfrac{d\theta}{dx}\, dv & (8) \\ = & \quad \tfrac{D_{\mathrm{v-a}}\phi}{\phi+(1-\phi)} \tfrac{d\gamma_v}{d\theta} \left(\tfrac{d\theta}{dx}\right)_{\mathrm{h-a}} & (9) \\ < & \quad D_{\mathrm{v-a}} \tfrac{d\gamma_v}{d\theta} G & (10) \end{aligned}$$

Therefore we can conclude that $D_{\mathrm{eff}} < D_{\mathrm{d-a}}$ and concludes the matter.

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