Review: Macroscopic water vapor diffusion is not enhanced in snow

General comments

This paper addresses the long standing controversy on effective water vapor diffusion in snow. The paper is a welcome contribution to the topic, and include numerical simulations showing that the effective diffusion is not enhanced. Although the paper is missing a rigourous mathematical derivation of the statements on the definition of the effective vapor diffusion coefficient, its bounds and upscaling approach, it makes up for it by the valuable assessment of the dependency of the effective water vapor transport in snow on the accommodation coefficient α. The authors go at great length into the history and details of the problem and the different angles previous studies took, and along the way narrow down how the effective diffusion coefficient should be defined. The paper describes a rich number of simulations to solve the coupled static heat and mass flux equations with Robin boundary conditions: introducing the Hertz-Knudsen-Langmuir equation and is the first of its kind within the snow microstructure community. This equation is primarily dependent on the accommodation/sticking/condensation/sublimation/... coefficient. This equation is introducing a natural way to continuously move from an inert media with no crystal growth, to locally enhanced diffusion driven by local sinks ans sources throughout the media. This setup enables to compute the effective diffusion coefficient defined by total volume averaged mass flux divided by macroscopic water vapor concentration gradient.

Overall the paper is well written, including a clear motivation, strong methods, and reasonable conclusions, and I congratulate the authors with this work. In principle it can be published with minor revisions, since all the computations and simulations are, to an acceptable degree physically sound, and the results will prove valuable to the snow physics community.

The comments that follow are in general a matter of taste and representation. That said, I think the paper deserves a more classical setup (introduction, theoretical background, methods, results...). Especially a clear description that starts with a formal definition of the involved equations. An unambiguous mathematical upscaling method (volumetric averaging) is desired and would help the reader to be convinced by the conclusions of the paper. Given the fact that effective diffusion at the microscale is difficult to measure experimentally, such a study that includes simulations that resolve the water vapor concentration at the microscale deserves a central approach. In my opinion this paper should be primarily centered around the simulations and the influence of finite kinetics to the overall water vapor transport and secondary on how it relates to previous (experimental) studies. The latter can be discussed at length in the discussion section. The title could also reflect the importance of the influence of finite kinetics to the effective diffusion coefficient. In general I would encourage the authors to refocus the manuscript in the formerly described manner.
Comments that refer to restructuring of the whole manuscript are optional, others are considered to be essential (bold-faced).

General comments:

1 The chosen upscaling method of 'volumetric averaging' over 'cross-section averaging' (l.120 -l.132) is based on the argument that microscopic scale variations are not accessible by area averaging. To my understanding this is an issue related to the Representative Element Volume (REV). Snow microstructures are measured with μCT, large enough such that the volume is representative and homogeneous

in a volumetric manner. If cross-sections are used this might not be satisfied anymore as rightly addressed by Pinzer et al. [2012] and volumetric averaging can be chosen. It is therefore not the intrinsically preferred method, but one that is dictated by the specific microstructure.

2 The chosen upscaling method is important especially if we couple the effective diffusion to the macroscopic mass and heat transport Calonne et al. [2014]. This study should explicitly relate its results to this study, and how these equations should be adapted.

3 The accommodation coefficient, including its name, should be introduced in the introduction including experimental observations such as Libbrecht [2005], Harrington et al. [2019] and possibly other studies. The choice of values for the simulations should be linked and/or motivated by deficiencies of these studies.

4 Although symbols in equations are generally well described and it is clear from the context what they mean, it might be helpful to the reader to introduce systematic notation to distinguish between upscaled quantities and local quantities, e.g.

$$F = \frac{1}{V} \int_V f \, dx^3, \tag{1}$$

in other words, how are F and C related to their microscopic quantities?

5 In case of volume averaging, gradients of microscopic fluxes are influenced by sources and sinks at internal ice-air iterfaces Whitaker [1998], Krol and Löwe [2018], i.e.

$$\langle \boldsymbol{\nabla} f \rangle = \boldsymbol{\nabla} \langle f \rangle + \int_\Gamma f d\boldsymbol{n}. \tag{2}$$

In case of the idealized spheres the second term vanishes because of symmetry, but for your snow samples it might not be the case, and should be shown, either by estimating the order of magnitude of the gradient of your sources and sinks, or by analysis of the simulations that this term is rightfully neglected. Here it matters how the macroscopic quantities are related to their microscopic counterparts. Note that in your simulations you average over both phases, vapor and ice, but you neglect the sinks and sources. I believe with these microstructures it is probably alright, but it should be estimated/shown that you can do so.

Specific comments

l.10 Naming of the coefficient α. This coefficient is often related to the phase-change it represents i.e. deposition, sublimation, or sticking parameter.

l.11 There is no evidence or discussion in the paper that suggests that convection is one of the candidates responsible for the experimentally observed mass deficiency.

l.46 Suggestion to shorten this paragraph and move to the discussion. The notion of hand-to-hand diffusion should be discarded on the fact this is simply no physical transport of water molecules.

l.120-132 Please be very specific about your methods of upscaling. See general comments 1, 2, and 5.

l.133 Here I would expect a mathematical definition, including upscaling methods, see comment 5.

l.137 Semantic comment: What does 'ideally' mean in this context? Maybe include that intrinsic, in this context, means that D_{eff} is independent of the external temperature gradient. When D_{eff} is dependent on the external gradient, one could say that the response of the material is non-linear. Does this break the definition of the effective diffusion coefficient, meaning the coefficient that quantifies the vapor flux as a linear response to an applied concentration gradient?

l.150 In this paragraph I suspect at least an expression for the the macroscopic vapor flux as suggested by the title.

l.165 and l.308 . How infinite can αv_{kin} be? v_{kin} is finite $\sim 10^2$, and $0 < \alpha < 1$. In principle it should be compared to the actual interface velocity v_n in the Robin b.c. as stated in Kaempfer and Plapp [2009]. A discussion on α and its values would be appreciated Libbrecht [2005], Saito [1996], Legagneux and Dominé [2005].

l.263 This paragraph includes an important realization, how does it relate to the expression for the macroscopic heat transport provided by Calonne et al. [2014]. This could be treated in the discussion.

l.282 Some more details on the technicalities of the simulation should be provided, are T and c computed simultaneously? or is c computed given T? How is it parallelized, and how long does it take? What are the meshing requirements, how many points etc.

l.367 For the non-linear kinetics results it might be useful to state the surface averaged simulated α and its variance.

l.367 How sensitive is your result to the value σ_0? Since it might differ for different crystallographic surfaces.

Fig.4 I suggest to split this plot into two figures. One for linear simulations $D_{\text{eff}}^{\text{norm}}$ vs α and the other for non-linear dynamics $D_{\text{eff}}^{\text{norm}}$ vs ∇T including colorbar for surface averaged α. This suggestion is given to observe the type of transition between purely tortuous diffusion and phase transition enhanced diffusion. The data on the non-linear dynamics seems to rapidly depart from the tortuous diffusion case: is there a reason for this? We would expect also here a smoother transition between the two limiting cases, such as in Fig.6. The results for small temperature gradients puzzle me. A discussion on the results in this regime might be helpful.

l.402 Moreover? Is there a reason not to compute the non-linear cases? In my opinion it is interesting and worth it to quantify the different non-linear responses of the 6 different snow types.

Fig.7 and Table 1 The Figure and Table have approximately the same information. Consider plotting again $D_{\text{eff}}^{\text{norm}}$ vs α and colorbar on density. Alternative, plot $D_{\text{eff}}^{\text{norm}}/\phi$ and discuss the remaining influence of SSA. If SSA is presented in either a table or a plot, then a note in the discussion on its influence is desirable.

l.440 A list of the general causes to why vapor flux was considered to be enhanced in the past is expected in the discussion.

l.440 A reasonable explanation for why convection could be the cause of the experimentally observed mass deficit could go here.

l.448 'Disagree', is an understatement. You show with numerical simulation that this concept is ill-defined. Suggestion: We show with numerical simulations that increased vapor flux by the hand-to-hand mechanism is not present.

l.458 Avoid 'intuitive'. Suggestion: consistent with actual water vapor transport.

Appendix B, l.492 incorrect use of 'inferior', use 'less than'.

Technical corrections Overall technical comments,

l.59 The use of pore phase, throughout the manuscript is incorrect. Please use pore space, or vapor/gas phase. Also air phase is not commonly used.

Overall The use of colons is not consistent, e.g. before equations introduced by 'given by' it is not very common to use them. Use of colons is generally restricted to lists or 'may' be used between independent clauses when the second sentence explains, illustrates, paraphrases, or expands on the first sentence. Equations are part of sentences and therefore colons should not appear more often before an equation than in other parts of your text.

l.296 Outer brackets in the exponent should be larger, (use \left(and \right) commands).

l.304 Condensation is reserved for the gas-liquid phase-transition, use deposition (or desublimation) also at other places throughout the manuscript.

l.336 Goes → go.

l.437 ? citation missing.

l.454 Similar → Equivalent.

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