Andrew Hansen
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Technical Note:

A demonstration of the existence and importance of “hand-to-hand” vapor transport as it relates to the effective vapor diffusion coefficient in low-density snow

Symbols

D	diffusion coefficient
$\boldsymbol{j}$	mass flux
k	thermal conductivity
q	energy flux
u_{sg}	latent heat of sublimation of ice
v_{v}	water vapor diffusion velocity
x	macroscale coordinate
ξ	microscale coordinate
γ_{v}	density of vapor component
θ	absolute temperature
ϕ_{α}	volume fraction of constituent α
	Superscript
eff	effective
*	apparent
	Subscripts
f	fluctuation
i	ice constituent
ha	humid air constituent
p	pore microstructure
v	vapor component within humid air
v-a	water vapor in air
s	snow

Abstract

This technical note addresses the physical significance of “hand-to-hand” vapor transport as it applies to its influence on the effective vapor diffusion coefficient of a layered ice/humid air microstructure in the presence of a temperature gradient. Understanding the mass diffusion process related to this microstructure is a critical feature to understanding how this phenomenon relates to mass transfer and the effective diffusion coefficient in low-density snow.

Two important results from this note are: 1) the hand-to-hand diffusion mechanism is a critical contributor to enhanced diffusion in the layered microstructure compared to vapor diffusion in humid air alone, and 2) the layered microstructure showing enhanced diffusion provides a reasonable estimate of vapor diffusion in low-density snow.

A good deal of the confusion in computing the diffusion coefficient of water vapor in an ice/humid air mixture stems from calculations made using volume averaging techniques for a *Representative Volume Element* (RVE). In that spirit, we also seek to clarify the continuum definition of velocity of water vapor as it relates to volume averaging within an RVE of a layered ice/humid air microstructure.

1. Introduction

Controversy abounds regarding the value of the effective diffusion coefficient for snow—a material property essential for studying macroscale heat and mass transfer in a snowpack. Let $D_{\mathrm{v-a}}$ represent the binary diffusion coefficient of water vapor in air. In the case of snow, the effective diffusion coefficient is influenced by several competing features of mass diffusion that may either enhance or impede mass diffusion compared to vapor diffusion in humid air only. While there is little debate about some factors affecting vapor diffusion, there are notably differing views on the influence of "hand to hand" diffusion as described by Yosida (1955). To be clear, there is no question as to the existence of hand-to-hand diffusion of water vapor in snow. Rather, the debate centers on the relation of this mass transfer mechanism to the effective diffusion coefficient of snow needed for the governing field equations of the macroscale snowpack. Without initially taking a position in this matter, we write the effective diffusion coefficient for snow as $D_{\mathrm{s}}^{\mathrm{eff}}$.

One view of mass transfer in snow is that the effective diffusion coefficient is a linear response of water vapor and ice transport to a thermal driving force. Since the phase transitions that take place at the microscale serve as a temporal storage of vapor, i.e., ice, they should, in principle, reduce the effective transport, and therefore reduce the effective diffusion coefficient. The work of Giddings and LaChapelle (1962), Calonne et al. (2014), and Fourteau et al. (2020) follow this line of reasoning. In brief, they adopt the view

$$D_{\mathrm{s}}^{\mathrm{eff}} < D_{\mathrm{v-a}} \quad .$$

An alternate perspective of mass transfer in snow is that hand-to-hand vapor transport resulting from sublimation and deposition of water vapor is a physical mechanism contributing to an "apparent diffusion coefficient" and, further, this apparent diffusion coefficient is precisely the effective diffusion coefficient, $D_{\mathrm{s}}^{\mathrm{eff}}$, needed in the governing macroscale equations of heat and mass transfer in a continuum formulation. In this context, the ice phase is viewed as a near instantaneous source/sink of water vapor transport, thereby shortening diffusion paths through the humid air and enhancing diffusion rates. The key attribute of this reasoning is that water vapor molecules are indistinguishable from one another. Water vapor condensing on the bottom of an ice grain is identical, in form, to water vapor sublimating off the top of an ice grain. Hence, the apparent diffusion coefficient takes into account phase changes that are not really based on diffusion processes, but consider phase change as contributing to the overall diffusion. Prior research advocating this position may be found in Yosida (1955), Sommerfeld (1982), Colbeck (1993), and Hansen (2019).

The hand-to-hand diffusion mechanism is manifest through an apparent (intrinsic) diffusion velocity that accounts for the instantaneous source/sink phenomenon of ice in vapor transport. The purpose of this technical note is to demonstrate that the effect of this apparent velocity is both real and necessary to model the macroscale continuum level effective diffusion coefficient in ice/humid air mixtures such as snow. The hand-to-hand diffusion mechanism enhances diffusion and generally leads to the result

$$D_{\mathrm{s}}^{\mathrm{eff}} > D_{\mathrm{v-a}} \quad ,$$

at least for low to moderate density snow.

We address the competing views articulated above by studying mass transfer in a layered ice/humid air microstructure in the presence of a temperature gradient as shown in Figure 1. The layered microstructure is an ideal test case of the two approaches in that an analytical solution exists—*a solution based only on one-dimensional heat and mass transfer principles with a long history of supporting development.* The analytical solution leads to a clear interpretation of the existence and importance of hand-to hand diffusion, leading to an enhanced diffusion coefficient of the continuum mixture—a critical feature of understanding diffusion of water vapor in snow.

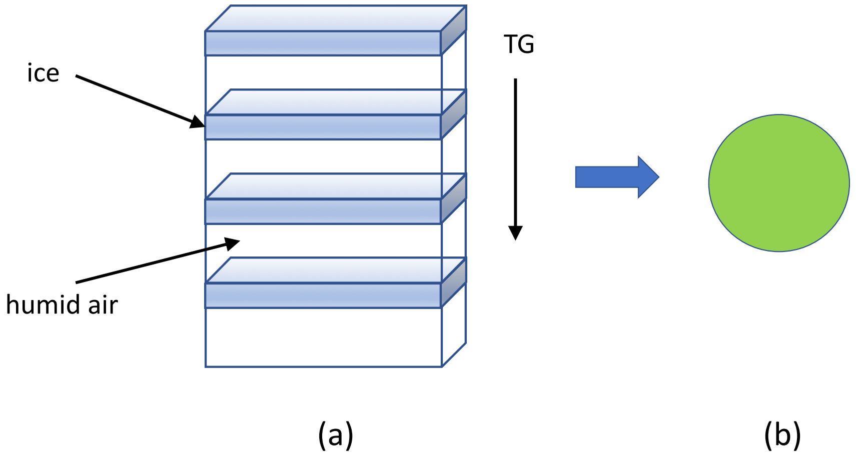

Figure 1. (a) Layered microstructure of ice and humid air in the presence of a vertical temperature gradient. (b) The homogenized continuum point possessing macroscale continuum properties representative of the ice/humid air mixture.

2. Preliminaries

In order to bring clarity to the diffusion process in an ice/humid air mixture, we first lay out a continuum definition of the mass flux. Consider an arbitrary part $\boldsymbol{P}$ of a continuum body $\boldsymbol{B}$ showing a mass flux vector, $\boldsymbol{j}$, emanating from a differential surface, dS, with an associated outward normal vector of $\boldsymbol{n}$, Figure 2. Physically, the inner product $\boldsymbol{j} \cdot \boldsymbol{n}$ represents the mass per unit area per unit of time that is passing through the surface, dS.

The mass flux, ***j***, is computed as the product of the density times the velocity of a continuum point as it crosses the surface, *dS.* When the continuum is viewed as a mixture of ice and humid air undergoing diffusion, the density of interest in the mass flux is the density of water vapor in humid air. There is no question as to the value of this parameter. A much more vexing aspect of the mass flux is an understanding of the velocity of the humid air from ***a macroscale continuum perspective***. We will refer to this continuum velocity as the *apparent velocity* of the water vapor. A lack of a clear interpretation of the apparent velocity of water vapor is the source of some 60 years of confusion surrounding the effective vapor diffusion coefficient in snow.

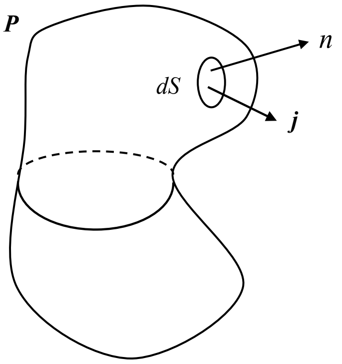

Figure 2. Arbitrary part ***P*** of a continuum body showing mass flux and associated unit normal acting on a differential surface, *dS.*

We often refer to snow in the present note as a means of properly framing the mass transfer problem of interest in the layered ice/humid air microstructure. To begin, let us address some physical and mathematical features associated with a microscale analysis of an RVE. In the case of a layered microstructure, the RVE may be simplified to a single repeating unit cell consisting of one layer of ice and one layer of humid air.

The first point of interest is clarity related to the scale of the microscale and macroscale problems. In the context of snow, a typical macroscale for an alpine snowpack is on the order of tens of centimeters to meters of snow depth. In contrast, if one is interested in studying an RVE for heat and mass transfer that is representative of a continuum point for the snowpack, the scale of the RVE is on the order of millimeters. For example, Calonne et al. (2011) studied thermal conductivity using numerical analysis of snow samples with lineal dimensions of the RVE ranging from 2.5-5.5 mm. The connection between the microscale of the RVE and the macroscale of an alpine snowpack represents a classic multiscale analysis.

For discussion purposes, consider a snowpack of depth 1 meter and suppose we have a macroscale temperature gradient of $40\ \mathrm{K\,m^{-1}}$. A very cold alpine evening might make this a reasonable situation. Choosing an RVE with a lineal dimension of 4 mm in the direction of the temperature gradient, a $40\ \mathrm{K\,m^{-1}}$ temperature gradient is simulated with a temperature differential across the RVE of $0.16\,\mathrm{K}$. This small temperature differential across an RVE is important as, in the development that follows, we will assume that the following variables within the RVE are constant:

i)	$D_{\mathrm{v-a}}$	the binary diffusion coefficient of water vapor in humid air
ii)	γ_{v}	the saturated vapor density of humid air
iii)	$\left(\frac{d\gamma_{\mathrm{v}}}{d\theta}\right)$	the derivative of the saturated density of humid air with respect to temperature
iv)	u_{sg}	the latent heat of sublimation

At $-2^{\circ}\mathrm{C}$, the greatest difference in the above parameters for a temperature change of $-0.16^{\circ}\mathrm{C}$ is approximately 1.3%. Appendix A provides specific formulae for computing the above parameters.

Next, we turn our attention to volume averaging concepts for an RVE and the relation between the volume average of a microscale quantity and its associated macroscale quantity. Of particular interest are volume average relations for the temperature gradient and the energy flux. Here, we follow the excellent discussion provided by Özdemir et al. (2008).

Consider the RVE (unit cell) for the ice/humid air microstructure shown in Figure 3. We identify the boundary of the unit cell by Γ. The four corner locations are identified numerically from 1-4. Following Özdemir, the microscale temperature field may be decomposed into a spatially linear macroscopic field and a fluctuation field $\theta_{\mathrm{f}}(\boldsymbol{\xi})$ as

$$\theta(\boldsymbol{\xi}) = \theta^{1} + \boldsymbol{\nabla}\theta \cdot (\boldsymbol{\xi} - \boldsymbol{\xi}^{1}) + \theta_{\mathrm{f}}(\boldsymbol{\xi}) \quad , \tag{1}$$

where the superscript “1” denotes the lower-left corner of the RVE. The local temperature field is distinguished from the macroscale temperature field by explicitly writing the spatial dependence, $\boldsymbol{\xi}$. The volume averaged microscale temperature gradient may be expressed as

$$\frac{1}{V}\int_{V} \boldsymbol{\nabla}_{\xi}\, \theta(\boldsymbol{\xi})\, dV = \boldsymbol{\nabla}\theta + \frac{1}{V}\int_{\Gamma} \theta_{\mathrm{f}}(\boldsymbol{\xi})\, \boldsymbol{n}\, d\Gamma \quad , \tag{2}$$

where the divergence theorem has been used to transform the volume integral of the fluctuation temperature field into a surface integral. By enforcing the condition

$$\frac{1}{V}\int_{\Gamma} \theta_{\mathrm{f}}(\boldsymbol{\xi})\, \boldsymbol{n}\, d\Gamma = 0 \quad , \tag{3}$$

we arrive at the condition that the volume averaged microscale temperature gradient is equal to the macroscale temperature gradient as

$$\boldsymbol{\nabla}\theta = \frac{1}{V}\int_{V} \boldsymbol{\nabla}_{\xi}\, \theta(\boldsymbol{\xi}) dV \quad . \tag{4}$$

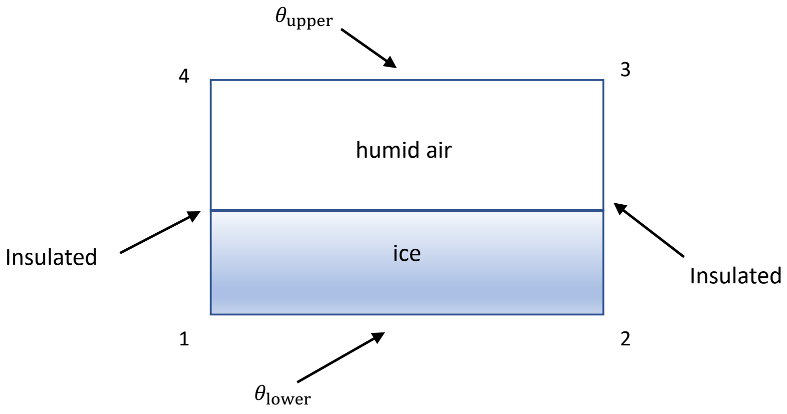

Figure 3. Unit cell for ice/humid air microstructure showing boundary conditions for a coupled thermal and mass balance microscale analysis.

Özdemir et al. (2008) point out that the constraint of Eq. (3) may be achieved with different sets of boundary conditions. One such set that we will use has insulated boundaries on the left and right walls and different but uniform temperatures along the top and bottom surfaces. This choice effectively reduces the heat and mass transfer problem to a one-dimensional analysis for the layered microstructure. We remark that these boundary conditions, generalized to 3-D, are the same as those utilized by Riche and Schneebeli (2013) in their thermal analysis of RVE's of snow samples.

Özdemir et al. (2008) also show the form of the volume averaging relation for the temperature gradient also applies to the energy flux between the microscale and macroscale, leading to

$$q = \frac{1}{V}\int_V q(\boldsymbol{\xi})\, dV \quad . \tag{5}$$

In any discussion of an RVE for snow, or the layered microstructure, we assume the volume averaging conditions of Eqs. (4 & 5) hold true.

Finally, in the interest of physical insight, it is useful to quantify values of several parameters related to mass diffusion in humid air. Key values and the equations used to compute these parameters may be found in Appendix A.

3. One-dimensional heat and mass transfer in a layered ice/humid air microstructure: An analytical solution

Consider the ice/humid air microstructure of Figure 1 subjected to a negative temperature gradient. We assume:

i. Infinitely fast surface kinetics for deposition and sublimation of water vapor
ii. The humid air is saturated
iii. Convection is neglected

Our objective is to homogenize the microstructure shown in Figure 1(a) into a single continuum, Figure1(b), with the proper macroscale heat and mass transfer properties. The results presented below were originally developed by de Quervain (1963) in an effort to gain insight into constructive metamorphism of snow. Although the microstructure is very simple in form, it provides amazing insight into the heat and mass transfer in ice/humid air mixtures in general and, remarkably, provides energy flux results that are strikingly similar to those found in very low-density snow.

The reader familiar with this topic may wish to skip straight to the results for the continuum energy flux found in Eq. (11). Otherwise, we provide a formal development in the interest of completeness.

The governing equations for this 1-D heat and mass transfer problem are straight forward and limited in number. First, the volume fractions for the ice and humid air are space filling, leading to the relation

$$\phi_{\mathrm{ha}} + \phi_{\mathrm{i}} = 1\,. \tag{6}$$

Fourier's law for heat conduction in the ice phase is given by

$$q_{\mathrm{i}} = -k_{\mathrm{i}} \left(\frac{\partial \theta}{\partial \xi}\right)_{\mathrm{i}} \quad . \tag{7}$$

Note that the constituent temperature gradients, $\left(\frac{\partial \theta}{\partial \xi}\right)_{\alpha}$, are spatially constant within each constituent.

The energy flux for the humid air phase includes both conduction in the humid air and energy transport through diffusion. Following the classic text on *Transport Phenomena* (Bird et al., 1960), we can write the humid air energy flux as (Hansen and Foslien, 2015)

$$q_{\mathrm{ha}} = -\left(k_{\mathrm{ha}} + u_{\mathrm{sg}} D_{\mathrm{v-a}} \left(\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta}\right)\right)\left(\frac{\partial \theta}{\partial \xi}\right)_{\mathrm{ha}} \quad . \tag{8}$$

The macroscale temperature gradient is related to the constituent temperature gradients as

$$\frac{\partial \theta}{\partial x} = \phi_{\mathrm{i}} \left(\frac{\partial \theta}{\partial \xi}\right)_{\mathrm{i}} + \phi_{\mathrm{ha}} \left(\frac{\partial \theta}{\partial \xi}\right)_{\mathrm{ha}} \quad . \tag{9}$$

Finally, the energy flux in each constituent is identical and, as a consequence, the energy flux of the continuum mixture is also the same, leading to the relations

$$q = q_{\mathrm{i}} = q_{\mathrm{ha}} \quad . \tag{10}$$

Equations (6-10) may be combined algebraically to show the energy flux of the homogenized continuum is

$$q = -\left(\frac{k_{\mathrm{i}}\left(k_{\mathrm{ha}} + D_{\mathrm{v-a}}\ u_{\mathrm{sg}}\frac{d\gamma_{\mathrm{v}}}{d\theta}\right)}{\phi_{\mathrm{i}}\left(k_{\mathrm{ha}} + u_{\mathrm{sg}}D_{\mathrm{v-a}}\left(\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta}\right)\right) + \phi_{\mathrm{ha}}k_{\mathrm{i}}}\right)\frac{\partial\theta}{\partial x} \qquad (11)$$

We emphasize that the above equation for the energy flux is an analytical result relying on first principles of one-dimensional heat and mass transfer in a layered ice and saturated humid air microstructure. ***Importantly, Eq. (11) is developed without the need to introduce or discuss the influence of an apparent diffusion velocity.***

The energy flux of the ice/humid air continuum mixture given by Eq. (11) may be simplified significantly for ice volume fractions less than approximately 0.8. To begin, for the temperatures of interest, one may show k_{ha} and $(u_{\mathrm{sg}}D_{\mathrm{v-a}}\frac{d\gamma_{\mathrm{v}}}{d\theta})$ are of the same order of magnitude—see, for example, the numerical values found in Appendix A. Now rearrange Eq. (11) by dividing numerator and denominator by k_i, leading to:

$$q = -\left(\frac{\left(k_{\mathrm{ha}} + D_{\mathrm{v-a}}\ u_{\mathrm{sg}}\frac{d\gamma_{\mathrm{v}}}{d\theta}\right)}{\phi_{\mathrm{i}}\left[\frac{k_{\mathrm{ha}} + u_{\mathrm{sg}}D_{\mathrm{v-a}}\left(\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta}\right)}{k_{\mathrm{i}}}\right] + \phi_{\mathrm{ha}}}\right)\frac{\partial\theta}{\partial x} \ . \qquad (12)$$

The value of the thermal conductivity of ice is on the order of 100 times that of the thermal conductivity of humid air. Therefore, neglecting the terms in square brackets in the above equation leads to

$$q = -\left(\left(\frac{k_{\mathrm{ha}}}{\phi_{\mathrm{ha}}}\right) + \left(\frac{D_{\mathrm{v-a}}}{\phi_{\mathrm{ha}}}\right)u_{\mathrm{sg}}\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta}\right)\frac{\partial\theta}{\partial x} \ . \qquad (13)$$

The energy flux for the continuum mixture may be written as

$$q = -\left(k^{\mathrm{eff}} + D^{\mathrm{eff}}\,u_{\mathrm{sg}}\frac{d\gamma_{v}}{d\theta}\right)\frac{\partial\theta}{\partial x} \ . \qquad (14)$$

where k^{eff} and D^{eff} represent the effective themal conductivity and the effective diffusion coefficient of the mixture.

Comparing Eqs. (13) and (14) leads to the relations

$$k^{\mathrm{eff}} = \left(\frac{k_{\mathrm{ha}}}{\phi_{\mathrm{ha}}}\right) , \qquad (15)$$

and

$$\boxed{D^{\mathrm{eff}} = \left(\frac{D_{\mathrm{v-a}}}{\phi_{\mathrm{ha}}}\right)}. \tag{16}$$

Eqs. (15) and (16) generate a desirable trait in that the thermal conductivity and the diffusion coefficient decouple from one another. However, the additional coupling terms neglected in the order of magnitude analysis are important for extremely high ice volume fractions as they serve to keep the solution bounded and, further, generate self-consistent results for the known energy flux in the limiting case of solid ice. For instance, Figure 4 shows the normalized exact energy flux $\left(q/\frac{\partial\theta}{\partial x}\right)$ of Eq. (11) for the layered microstructure compared to the normalized approximate energy flux shown by Eq. (13). For ice volume fractions less than approximately 0.8, the results are nearly identical—an important feature when we turn our attention to heat and mass transfer at low ice volume fractions.

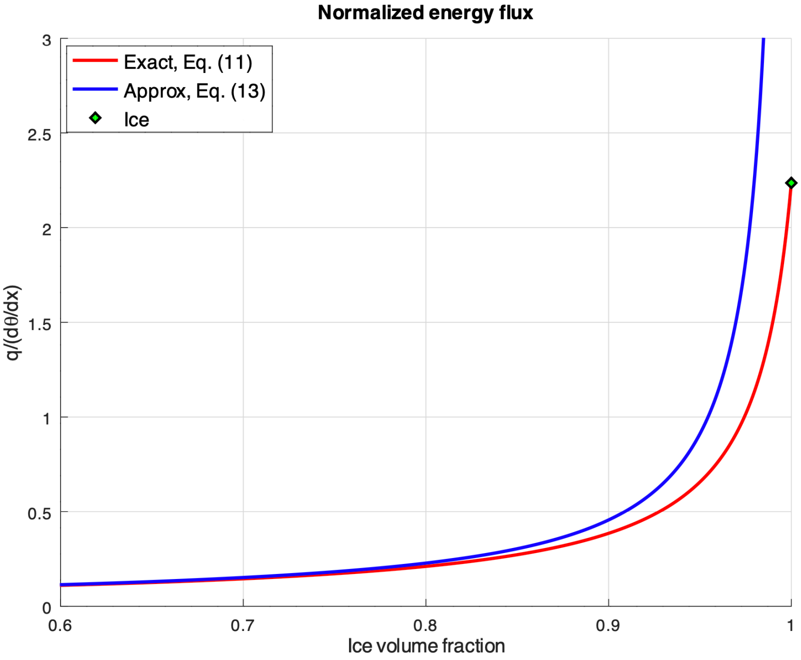

Figure 4. A comparison of the normalized energy flux of the layered microstructure using Eqs. (11 & 13), respectively. Note that the exact energy flux converges to known energy flux for the case of solid ice.

Equation (16) is a critical analytical result showing the effective diffusion coefficient for the layered ice/humid air mixture is enhanced at all ice volume fractions. We emphasize that this result is obtained purely through a 1-D heat and mass transfer analysis. The result is a consequence of requiring the energy flux in the ice, humid air, and mixture to be equal for a steady state solution, Figure 5.

4. Interpreting the water vapor diffusion velocity in an ice/humid air layered microstructure

Given the analytical result of Eq. (16) showing an enhanced diffusion coefficient for the layered ice/humid air mixture, a central question to be resolved is *"what is the appropriate interpretation of the water vapor diffusion velocity that leads to this analytical result?"* The answer is a defining step toward addressing the physical significance of hand-to-hand diffusion in computing an effective diffusion coefficient for snow.

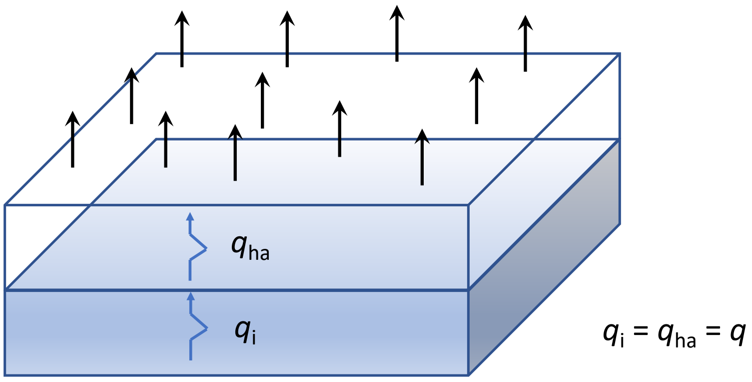

Figure 5. Unit cell showing the energy flux through the ice and humid air are equal and, further, equal to the energy flux of the mixture.

We begin by writing the mass flux for saturated humid air in the presence of a temperature gradients as

$$j_{\mathrm{v}} = \gamma_{\mathrm{v}} v_{\mathrm{v}} = -D_{\mathrm{v-a}} \left(\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta}\right) \frac{\partial\theta}{\partial x} \quad , \tag{17}$$

where $D_{\mathrm{v-a}}$ is the binary diffusion coefficient of water vapor in air.

For a layered ice/humid air mixture, the mass flux of water vapor in the humid air constituent may be written as

$$j_{\mathrm{v}} = \gamma_{\mathrm{v}}\, v_{\mathrm{v}} = -D_{\mathrm{v-a}} \left(\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta}\right) \left(\frac{\partial\theta}{\partial\xi}\right)_{\mathrm{ha}} \quad , \tag{18}$$

where we note the central feature differentiating the above from the mass flux of Eq. (17) for humid air alone is that the temperature gradient in the humid air is elevated for the ice/humid air mixture.

Next, consider the effective vapor diffusion coefficient for a layered ice/humid air mixture denoted by D^{eff}. We introduce the normalized value of the effective diffusion coefficient with respect to the binary diffusion coefficient of water vapor in air as $(D^{\mathrm{eff}} \,/\, D_{\mathrm{v-a}})$. Note that, in the limit as the ice phase goes to zero, this quantity tends to one, i.e.,

$$\lim_{\phi_{\mathrm{i}} \to 0} \left(\frac{D^{\mathrm{eff}}}{D_{\mathrm{v-a}}} \right) = 1 \quad . \tag{19}$$

As the ice volume fraction increases from zero, there are 3 potential factors that may either enhance or reduce the normalized effective diffusion coefficient. Two of these factors are not in dispute and may be stated as:

1. The presence of the ice phase limits where vapor diffusion can occur. Hence, the volume of ice where diffusion cannot occur will lower the volume average of mass transport, thereby impeding macroscale diffusion.

2. Elevated temperature gradients in the humid air phase of the ice/humid air microstructure enhance diffusion. The temperature gradient effect is manifest in the transition from the microscale humid air temperature gradient to the macroscale temperature gradient for the mixture.

There is a third factor that has the potential to influence the effective diffusion coefficient of the layered ice/humid air mixture. Specifically, the fundamental question to address is:

3. *What is the appropriate macroscale diffusion velocity for the vapor component during diffusion?*

We consider two possibilities for the effective macroscale diffusion velocity as articulated by the following positions outlined previously and summarized here as:

A. The ice phase acts as a temporal storage of water vapor. Hence, the ice should, in principle, reduce the effective transport, and similarly, reduce the volume averaged macroscale diffusion velocity of water vapor.

B. The ice phase should be viewed as a near instantaneous source and sink of water vapor transport, thereby creating an elevated apparent diffusion velocity through hand-to-hand diffusion mechanism that effectively enhances mass transfer.

Position A:

Position A may be characterized in a physically straight forward manner by stating the diffusion velocity of water vapor in the ice constituent is zero. The motion of water vapor is then attributed entirely to the local (microscale) diffusion velocity of the humid air—at first blush, an admittedly natural perspective. Hence, we restate Eq. (18) as

$$j_{\mathrm{v}} = \gamma_{\mathrm{v}}\, v_{\mathrm{v}} = -\, D_{\mathrm{v-a}} \left(\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta} \right) \left(\frac{\partial \theta}{\partial \xi} \right)_{\mathrm{ha}} \quad . \tag{20}$$

Next, we address the influence of the elevated temperature gradients in the humid air phase compared to the macroscale temperature gradient. Following the RVE boundary conditions set forth by Özdemir (2008), the macroscale constituent temperature gradients and the temperature gradient of the continuum mixture are related as

$$\frac{\partial\theta}{\partial x} = \phi_{\mathrm{ha}}\left(\frac{\partial\theta}{\partial\xi}\right)_{\mathrm{ha}} + \phi_{\mathrm{i}}\left(\frac{\partial\theta}{\partial\xi}\right)_{\mathrm{i}} \quad . \tag{21}$$

A straight forward algebraic exercise reveals an exact solution for the humid air temperature gradient is given by

$$\left(\frac{\partial\theta}{\partial\xi}\right)_{\mathrm{ha}} = \left(\frac{1}{\phi_{\mathrm{i}}\left[\frac{k_{\mathrm{ha}} + u_{\mathrm{sg}} D_{\mathrm{v-a}}\left(\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta}\right)}{k_{\mathrm{i}}}\right] + \phi_{\mathrm{ha}}}\right)\frac{\partial\theta}{\partial x} \quad . \tag{22}$$

Because the thermal conductivity of ice is approximately 100 times larger than that of humid air, we invoke the same approximation as done in Section 3 and neglect the term in square brackets in Eq. (22), leading to

$$\left(\frac{\partial\theta}{\partial\xi}\right)_{\mathrm{ha}} = \left(\frac{1}{\phi_{\mathrm{ha}}}\right)\frac{\partial\theta}{\partial x} \quad . \tag{23}$$

The approximate form of the humid air temperature gradient defined by Eq. (23) produces near exact results for ice volume fractions below 0.7. Noting this fact as well as the similar approximations of the energy flux shown in Figure 4, we restrict our subsequent discussions to ice volume fractions below 0.7.

Equation (23) allows us to write the mass flux of the humid air constituent within the layered microstructure defined by Eq. (20) as

$$j_{\mathrm{v}} = \gamma_{\mathrm{v}}\, v_{\mathrm{v}} = -\frac{D_{\mathrm{v-a}}}{\phi_{\mathrm{ha}}}\left(\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta}\right)\frac{\partial\theta}{\partial x} \quad . \tag{24}$$

Finally, to obtain the mass flux for the continuum mixture, the relation for the humid air defined above must be volume averaged for the entire unit cell leading to

$$\begin{aligned} j = \phi_{\mathrm{ha}}\,\gamma_{\mathrm{v}}\, v_{\mathrm{v}} &= -D_{\mathrm{v-a}}\left(\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta}\right)\frac{\partial\theta}{\partial x} \\ &= -D^{\mathrm{eff}}\left(\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta}\right)\frac{\partial\theta}{\partial x} \quad , \end{aligned} \tag{25}$$

where the ice phase is recognized as a volume where diffusion does not occur.

The mass flux of Eq. (25) produces an undisputed dilemma in that

$$D^{\mathrm{eff}} = D_{\mathrm{v-a}} \quad . \tag{26}$$

In particular, the effective diffusion coefficient predicted by Eq. (26) does not agree with the analytical solution given in Eq. (16).

The inconsistency of the predicted diffusion coefficient with the analytical solution is enough to invalidate the diffusion perspective advocated in Position A. Moreover, from pure physical intuition, it is troubling that, as the ice volume fraction increases, the effective diffusion coefficient for the macroscale ice/humid air mixture is constant—surely the ice phase impacts diffusion of water vapor!

Position B: Hand to hand diffusion results in an apparent diffusion velocity: v_{v}^{*}

To develop the mass transfer for this approach, the ice is treated as an instantaneous source/sink of water vapor transport. Water vapor undergoing deposition on one side of an ice layer occurs as water vapor is simultaneous sublimating off the opposite side of the ice. Since water molecules are indistinguishable from either side, the net effect is that the ice acts as a diffusing medium with an infinite diffusion velocity for water vapor. The difference from Position A could not be more striking—in one case we assume the vapor velocity in the ice is zero while in the latter case, we assume the vapor velocity through the ice is infinite!

Now consider particle dynamics for rectilinear motion with two velocities, say v_1 and v_2 occurring over two different non-dimensional distances, ϕ_1 and ϕ_2, Figure 6

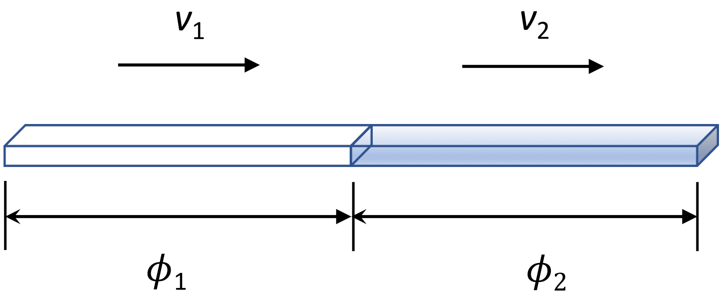

Figure 6. Rectilinear motion for a particle with different velocities covering two different dimensionless distances.

One can readily show the average velocity denoted by v^* may be expressed as

$$v^* = \frac{v_1 \; v_2}{v_1 \, \phi_2 + v_2 \phi_1} \quad , \tag{27}$$

or

$$v^{*} = \frac{v_1}{\left(\frac{v_1}{v_2}\right)\phi_2 + \phi_1} \quad . \tag{28}$$

Now let subscript 1 denote water vapor $(1 = \mathrm{v})$ and subscript 2 denote ice (2 = i) and, further, let $v_2 = v_{\mathrm{i}} \rightarrow \infty$. We arrive at the result:

$$v_{\mathrm{v}}^{*} = \frac{v_{\mathrm{v}}}{\phi_{\mathrm{ha}}} \quad . \tag{29}$$

The above represents an apparent diffusion velocity for water vapor in the layered ice/humid air microstructure under the hypothesis of ice acting as a source/sink for water vapor transport. Physically, the ice phase is acting to speed water vapor along through the mixture. Or, if one prefers, the ice phase acts to shorten the path needed to travel by water vapor. For instance, for a humid air volume fraction of 0.5, the apparent vapor diffusion velocity is twice the actual diffusion velocity because water vapor must only travel half as far because of the source/sink behavior of ice.

As a metaphor to the above, suppose you intend to walk a package from point A across town to a point B an hour away. If instead, you are given a car ride half-way there and you walk the remainder, an observer at B sees your *apparent walking velocity* for the entire trip as twice your actual walking velocity. The car ride is, in essence, the equivalent of the ice phase in water vapor transport.

Now begin the analysis of water vapor diffusion in the layered ice/humid air microstructure by utilizing the apparent diffusion velocity in the humid air and writing the volume averaged mass flux through the continuous medium as

$$j = \phi_{\mathrm{ha}}\, \gamma_{\mathrm{v}}\, v_{\mathrm{v}}^{*}, \tag{30}$$

where v_{v}^{*} is the apparent humid air diffusion velocity. The leading volume fraction in the above equation is a consequence of the ice phase occupying volume where diffusion does not occur.

Recognizing that $v_{\mathrm{v}}^{*} = v_{\mathrm{v}}/\phi_{\mathrm{ha}}$ leads to

$$j = \gamma_{\mathrm{v}}\, v_{\mathrm{v}} = -\, D_{\mathrm{v-a}} \left(\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta}\right) \left(\frac{\partial\theta}{\partial\xi}\right)_{\mathrm{ha}} \quad . \tag{31}$$

Finally, introduce the macroscale temperature gradient to arrive at

$$j = \gamma_{\mathrm{v}}\, v_{\mathrm{v}} = -\left(\frac{D_{\mathrm{v-a}}}{\phi_{\mathrm{ha}}}\right) \left(\frac{d\,\gamma_{v}}{d\,\theta}\right) \frac{\partial\theta}{\partial x} \quad . \tag{32}$$

In the case of the ice/humid air mixture, the mass flux may be expressed in terms of the effective diffusion coefficient as

$$j = -\, D^{\mathrm{eff}} \left(\frac{d\,\gamma_{v}}{d\,\theta}\right) \frac{\partial\theta}{\partial x} \quad . \tag{33}$$

Comparing equations (32) and (33) leads directly to Eq. (16), the known diffusion enhancement result predicted strictly from 1-D heat and mass transfer principles:

$$\boxed{D^{\mathrm{eff}} = \left(\frac{D_{\mathrm{ha}}}{\phi_{\mathrm{ha}}}\right)} \quad . \tag{34}$$

The analytical solution for the effective diffusion coefficient given in Eq. (16) is entirely compatible with the apparent diffusion velocity concept used in conjunction with volume averaging, yielding Eq. (34).

An additional harmony in the solution of Position B exists by examining the mass flux crossing the boundaries of the unit cell, Figure 5. The mass flux across the upper and lower boundaries of the unit cell is given by

$$j = -D_{\mathrm{v-a}}\left(\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta}\right)\left(\frac{\partial\theta}{\partial\xi}\right)_{\mathrm{ha}} \quad . \tag{35}$$

Expressing the above in terms of the macroscale temperature gradient gives

$$j = \gamma_{\mathrm{v}}\, v_{\mathrm{v}} = -\left(\frac{D_{\mathrm{v-a}}}{\phi_{\mathrm{ha}}}\right)\left(\frac{d\,\gamma_v}{d\,\theta}\right)\frac{\partial\theta}{\partial x} \quad , \tag{36}$$

Hence, the volume averaged mass flux (Eq. 32), the analytical solution for the mass flux obtained from first principles of heat and mass transfer (Eq. 13), and the known surface flux across the boundaries of the RVE (Eq. 36) are all in perfect agreement. The results of Eq. (36) appear as far back as de Quervain (1963).

In contrast, in Position A, the volume averaged mass flux does not agree with either the analytical solution for mass flux or the known surface flux across the boundaries of the RVE. This untenable outcome is attributed to neglecting the influence of ice on the apparent diffusion velocity of water vapor. It defies logic to acknowledge hand to hand diffusion as an important mass transfer mechanism and then neglect this mechanism in the accompanying mathematical development of mass transfer at the macroscale.

The conclusion, then, is that hand-to-hand diffusion is a critical component of mass transfer enhancing the effective diffusion coefficient through an elevated vapor velocity we have coined the apparent (intrinsic) velocity. This apparent velocity is quite real and is the result of shortened distance a water vapor molecule must travel through the humid air. Once the water vapor transport reaches the ice and undergoes deposition, it is effectively immediately transferred through the ice and begins sublimation. Of course, it is not the same water molecule—no matter—the resulting diffusion effect as applied to mass transfer is a real physical mechanism caused by hand-to-hand diffusion of water vapor.

In retrospect, the existence and importance of hand-to-hand diffusion to macroscale mass transfer should come as no surprise. Mass flux across a surface of a continuum mixture of humid air and ice involves topology such as an ice phase occupying a volume within a continuum point where diffusion will not occur. However, mass flux is also dependent on diffusion velocity and the apparent diffusion velocity in the ice/humid air microstructure is elevated by the ice as the ice acts to speed along water vapor transport in the continuous mixture. ***Moreover, it cannot be overstated that the analytical solution of Eq. (16) requires no such interpretation of apparent diffusion velocity and represents an independent calculation of macroscale mass diffusion in the layered microstructure.***

The layered microstructure shows enhanced water vapor diffusion at all ice volume fractions compared to diffusion in humid air alone (see Eq. 16). Moreover, the hand-to-hand vapor transport mechanism is an important mechanism contributing to this enhanced diffusion. A natural question is what, if any, insight does this result provide for mass diffusion in snow. A complete discussion of mass diffusion in snow is beyond the scope of this technical note. However, it is possible to infer some expected properties of water vapor diffusion for low-density snow.

5. Some insights into water vapor diffusion in low-density snow

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Note: I am willing to add this content if The Cryosphere wishes to consider the full text as submission for publication. Otherwise, I will defer and present this work for full consideration by a journal at a later date.

6. Discussion

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Appendix A

Formulae for Key Parameters

The binary diffusion coefficient of water vapor in air may be represented as (Incropera and DeWitt, 1985)

$$D_{\mathrm{v-a}} = 0.26\,(10)^{-4}\left(\frac{\theta}{298}\right)^{1.5}\ \mathrm{m}^2\ \mathrm{s}^{-1} \quad , \qquad \text{(A.1)}$$

where θ is the absolute temperature.

The saturated vapor density is given by Dorsey (1968, pg 598) as

$$\gamma_{\mathrm{v}} = (10)^{\left\{\frac{C_1}{\theta}+\frac{c_2 \ln(\theta)}{\ln(10)}+c_3\,\theta+c_4\theta^2+c_5\right\}}\, c_6/R_{\mathrm{v}}/\theta \quad , \qquad \text{(A.2)}$$

where

$c_1 = -2445.56$

$c_2 = 8.2312$

$c_3 = -1.667\,(10)^{-2}$

$c_4 = 1.205\,(10)^{-5}$

$c_5 = -6.7572$

$c_6 = 133.32$

$\mathrm{R_v} = 461.5\ \mathrm{J\ kg}^{-1}\ \mathrm{K}^{-1}$ Cengal, Y.A.: Thermodynamics: An Engineering Approach

Differentiating the saturated vapor density with respect to temperature leads to

$$\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta} = \gamma_{\mathrm{v}} \ln(10)\left(-\frac{c_1}{\theta^2}+\frac{c_2}{\theta\ln(10)}+c_3+2\,c_4\,\theta\right)-\frac{\gamma_{\mathrm{v}}}{\theta} \quad . \qquad \text{(A.3)}$$

The latent heat of sublimation is given by

$$u_{\mathrm{sg}} = 2626.1\,(10)^3 + 1317.6\,\theta - 3715.8\,\theta^2 \quad . \qquad \text{(A.4)}$$

The thermal conductivity of ice is taken from Fukusako (1990) as

$$k_{\mathrm{i}} = 1.16\,[\,1.91 - 8.66(10)^{-3}(\theta - 273.15) + 2.97(10)^{-5}\,(\theta - 273.15)^{2}\,] \,. \qquad \text{(A.5)}$$

The thermal conductivity of air is obtained from interpolated data provided by Incoprera and Dewitt (1985).

Diffusion in an ice/humid air mixture is most active at high temperatures and strong temperature gradients. Therefore, consider humid air with a temperature of 271.15 K (-2°C) and a relatively strong temperature gradient of 40 K m^{-1}. Some parameters of interest include:

$\gamma_{\mathrm{v}} = 4.419\ (10)^{-3}\ \mathrm{kg\ m^{-3}}$	Vapor density of humid air
$\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta} = 3.53(10)^{-4}\ \mathrm{kg\ m^{-3}\ K^{-1}}$	Derivative of vapor density with respect to temperature
$D_{\mathrm{v-a}} = 2.257\ (10)^{-5}\ \mathrm{m^2\ s^{-1}}$	Binary diffusion coefficient of water vapor in air
$j = 3.188\ (10)^{-7}\ \mathrm{kg\ m^{-2}\ s^{-1}}$	Mass flux of humid air
$k_{\mathrm{ha}} = 0.024\ \mathrm{W\ m^{-1}\ K^{-1}}$	Thermal conductivity of air (Incropera and DeWitt, 1985)
$k_{\mathrm{i}} = 2.236\ \mathrm{W\ m^{-1}\ K^{-1}}$	Thermal conductivity of ice (Fukusako, 1990)
$u_{\mathrm{sg}} = 2710(10)^{3}\ \mathrm{J\ kg^{-1}}$	Latent heat of sublimation of ice
$u_{\mathrm{sg}} D_{\mathrm{v-a}} \left(\frac{d\,\gamma_{\mathrm{v}}}{d\,\theta}\right) =$ $0.0216\ \mathrm{W\ m^{-1}\ K^{-1}}$	It is useful to compare the magnitude of this term to k_{ha} as a measure of the influence of heat transfer due to diffusion in the humid air constituent.
$v_{\mathrm{v}} = 7.214\ (10)^{-5}\ \mathrm{m\ s^{-1}}$	Humid air diffusion velocity

The values provided above serve to ground one's physical intuition while also allowing for comparisons with known published values where possible.

Appendix B

Thermal conductivity discussion

While water vapor transport in snow is shrouded in controversy, there is little debate on the thermal conductivity properties of snow. Calonne et al. (2011) presented experimental data for thermal conductivity over a wide range of densities as shown in Figure B.1. In addition, they developed an empirical best fit of numerical thermal conductivity values they generated from finite element analyses of snow samples characterized through x-ray tomography.

Riche and Schneebeli (2013) also performed numerical thermal conductivity calculations for snow samples obtained from x-ray tomography. Their study focused on snow samples exhibiting characteristics of depth hoar, producing ice grains that were more columnar in nature, aligned with the temperature gradient. As expected, the thermal conductivities, aligned with the temperature gradient, for the depth hoar samples show higher values than snow samples of Calonne containing more rounded ice grains. They also performed a regression analyses and generated a curve fit of thermal conductivity.

Fourteau et al. (2020b) performed a third set of numerical thermal conductivity calculations for snow samples obtained from x-ray tomography. They included heat transfer due to diffusion and used the term effective thermal conductivity (a personal observation is that terminology of the word effective continues to be a struggle—I do not have a great solution). They also performed a regression analyses and generated a curve fit of thermal conductivity. The empirical relation generated for 263 K is given by (the subscript con+d is used to emphasize that both conduction and heat transfer due to mass diffusion are included).

$$k_{\mathrm{con+d}}^{\mathrm{eff}} = 1.985\,\phi_{\mathrm{i}}^{2} + 0.073\,\phi_{\mathrm{i}} + 0.0336 \quad . \qquad \text{(B.1)}$$

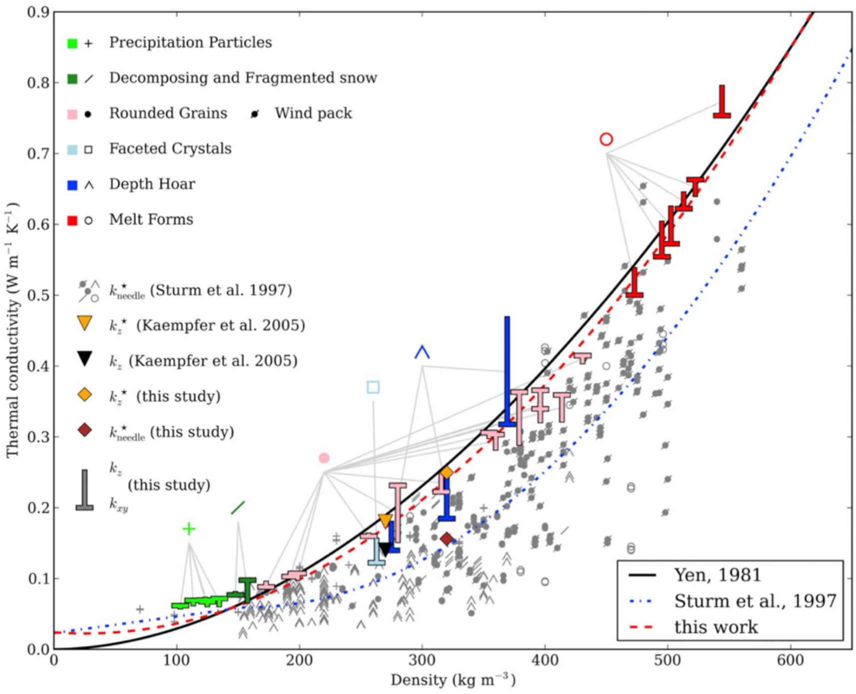

Figure B.1. Experimental and numerical modeling of thermal conductivity for snow (Calonne et al., 2011).

Finally, we draw attention to Foslien's (1994) theoretical model (see Hansen and Foslien, 2015) for both thermal conductivity and the effective diffusion coefficient. Motivated by physical arguments and observations from quantitative stereology, Foslien's model is developed from first principles applied to simplified microstructures combined with valuable information from stereology and some key insights into heat transfer mechanisms.

The theoretical equation for thermal conductivity including heat transfer due to diffusion assumes the simplified form valid for low to moderate densities as

$$k_{\text{con+d}}^{\text{eff}} = \phi_{\text{i}}(\phi_{\text{ha}}\, k_{\text{ha}} + \phi_{\text{i}}\, k_{\text{i}}) + k_{\text{ha}} + u_{\text{sg}}\, D_{\text{v-a}}(1 + \phi_{\text{i}}\phi_{\text{ha}}) \quad . \qquad \text{(B.2)}$$

An exact expression for $k_{\text{con+d}}^{\text{eff}}$, valid for all densities, may be found in Hansen and Foslien (2015).

Figure B.2 shows the regression curves for thermal conductivity of snow developed by Riche and Schneebeli (2013), Calonne et al. (2011), and Fourteau et al. (2020b), along with the theoretical model of Foslien (1994). The curves are rather remarkable in that Foslien's model, developed nearly 25 years earlier than the present work, tracks the three regression curves extremely well. In the comparison with Fourteau, the two curves are nearly indistinguishable for ice volume fractions up to 0.25. Additionally, we note that the exact formulation of Foslien is self-consistent, meaning the curve predicts the known thermal conductivity of ice for an ice volume fraction of one.

The correlation of Foslien's model with the finite element predictions provides important credibility to the analytical energy flux model of Foslien (1994). It also provides valuable clues related to the effective diffusion coefficient for low-density snow—a topic for future publication.

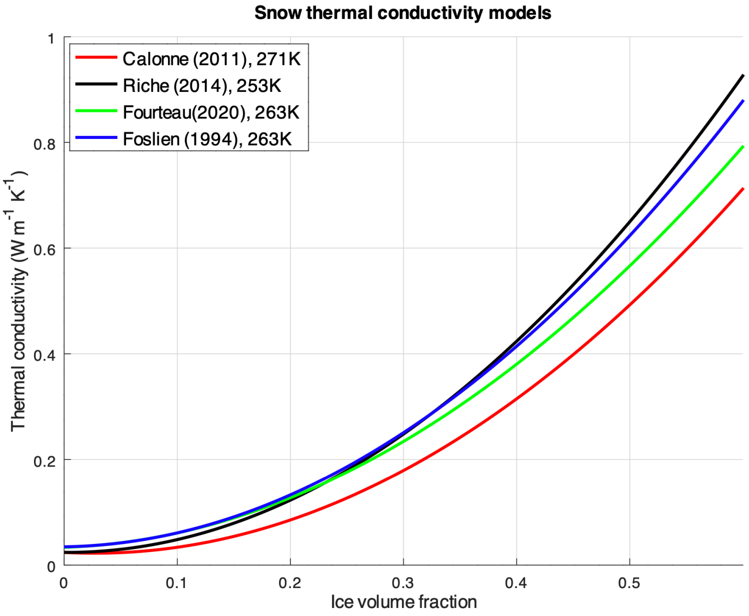

Figure B.2. Regression fits of thermal conductivity obtained from numerical RVE analyses: i) Calonne (2011), ii) Riche and Schneebeli (2013), and Fourteau (2020b). Also shown is the theoretical model of thermal conductivity of Foslien (1994), Eq. (42).

Figure B.3 shows the temperature dependence of the thermal conductivity as predicted by Foslien's (1994) model. Consistent with results shown in Figure 9 of Fourteau (2020b), the curves in Figure B.3 show a flattening of thermal conductivity with increasing temperature. The similarities between Fourteau et al (202b) and Foslien's 1994 model shown below are striking. The curves generated by Foslien's model are all analytical in nature and generated from a single equation (Eq. B.2) with no adjustable parameters, demonstrating the veracity of Foslien's theory.

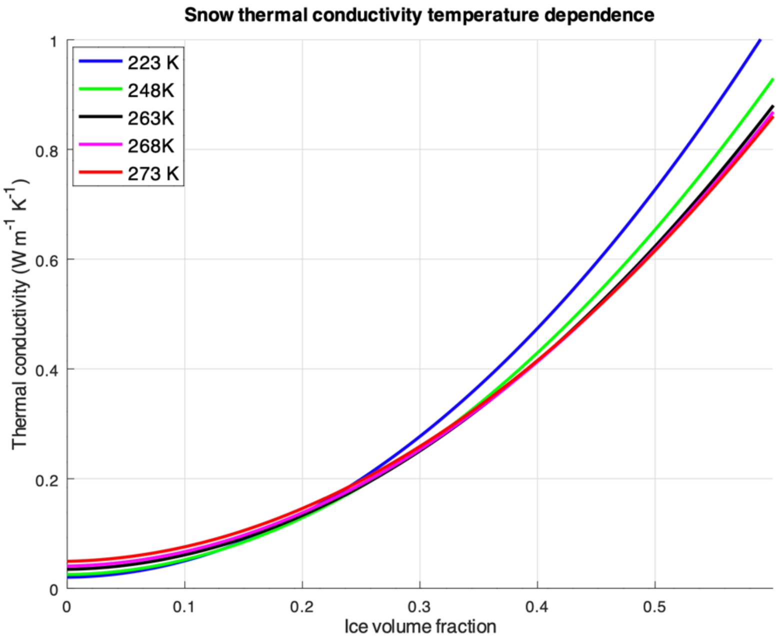

Figure B.3 Temperature dependence of the effective thermal conductivity of Foslien (1994).

As a final worthy comparison, I would suggest the authors compare results for the contributions of vapor transport to thermal conductivity from Figure 8 of Hansen and Foslien (2015) with the low and high density, fast kinetics results shown in Figure 5 of Fourteau (2020b). Given Foslien's analytical results were developed in 1994 and contain no adjustable coefficients, the accuracy of the vapor contribution to the energy flux is, again, truly remarkable.