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LETTERS TO THE EDITORS

Discussion of "Approche expérimentale et théorique de la conductivité thermique des milieux poreux humides"

In three recent papers, published in this journal, Moyne, Degiovanni, and co-workers [1–3] have newly attacked the long standing problem of the thermal conductivity of moist porous media. They present interesting and thought-provoking new theoretical and experimental results. In a review paper [4], also published in this journal, I presented my views on this problem, based on the theory of Philip and de Vries [5, 6].

The purpose of this letter is threefold:

(1) to rectify some misinterpretations regarding the so-called method of de Vries;

(2) to present a realistic comparison of the findings of Moyne *et al.* with my own views;

(3) to point out a possible error in the treatment of the influence of a gradient of total pressure, given in ref. [3].

The nomenclature of ref. [4] will be used below, together with that of the papers discussed.

In ref. [1] Moyne and co-workers introduced a new factor, f_{exp}, defined by the equation

$$k = \lambda_0 + f_{\mathrm{exp}} \lambda_{\mathrm{dif}}. \qquad (1)$$

Here k is an apparent conductivity, found experimentally, λ_0 is approximately equal to λ' in ref. [4], and λ_{dif} is similar to λ_{vs}. The difference between these quantities arises from the fact that in defining λ_{vs} the air is considered to be stagnant, whereas for λ_{dif} it is assumed that the centre of gravity of the water–vapour/air mixture is at rest. λ_{vs} is the same quantity as λ^*_{dif}, given by equation (51) in ref. [2].

The factor f_{exp} serves to analyse the experimental results presented in ref. [1] and the results obtained by numerical simulation in ref. [2]. It is misleadingly called "le facteur 'experimental' de de Vries" (Section 4.4 in ref. [1]), because I have never suggested or carried out an analysis of the kind proposed in Section 4.4. It should therefore be understood that the so-called "analyse de de Vries, de caractère séduisant" was not invented by me, but by Moyne and co-workers themselves. All remarks made in refs. [1, 2] about this analysis/method should be seen in this light.

In ref. [2] the authors presented a theoretical analysis based on the formalism of volume averages developed by Whitaker and others. Introducing some further assumptions, they derived coupled differential equations for average temperature and average moisture content. For isotropic media or for a one-dimensional system the theoretical apparent conductivity, k, is written as

$$k = \lambda + f \lambda_{\mathrm{dif}}. \qquad (2)$$

Here λ is called the 'true' conductivity and f the resistance factor for diffusion, caused by the presence of the solid and liquid phases. Two examples are given: one for a simple one-dimensional case, the other for a two-dimensional artificial medium. In the first case it can be easily checked that $f = \varepsilon_{\mathrm{g}}(\nabla T)_{\mathrm{g}}/\nabla T$, or $f = a\zeta$ in the notation of ref. [4]. It will be argued below that the same expression may hold for the second case.

I now come to a comparison with my results. Equation (A11) of ref. [4] is rewritten as follows (see equation (18) of ref. [6]):

$$\mathbf{q}_{\mathrm{h}} = -(\lambda^+ - L\rho_1 D_{T\mathrm{v}})\nabla T + L\mathbf{q}_{\mathrm{v}}. \qquad (3)$$

The convective term with $\mathbf{q}_{\mathrm{m}}$ has been omitted, because it is neglected in the paper under discussion. $\lambda^+ - L\rho_1 D_{T\mathrm{v}}$ can be interpreted as a 'true' conductivity, similar to, but not necessarily identical with, λ in equation (2). One has

$$\lambda^+ - L\rho_1 D_{T\mathrm{v}} = \lambda^+ - f\lambda_{\mathrm{vs}} = \lambda^+ - hf(a)\zeta\lambda_{\mathrm{vs}}. \qquad (4)$$

For the case of 'wet walls' the relative humidity $h = 1$. $f(a)$ is a 'geometrical' factor that expresses the influence of the liquid and solid phases on vapour transport, including the transport through liquid islands, as suggested in ref. [5]. Because of the latter effect $f(a) > a$.

For the one-dimensional example in ref. [2] it will be clear that $f(a) = a$. It should be noted that there must be a mechanism to transfer the liquid condensing at the cold side of a pore back to the opposite warm side.

For the second example the situation is less clear. The authors assume that the liquid is immobile; hence, evaporation and condensation ought to be compensating at each gas–liquid interface. This will not be so for some of the interfaces. Also some tortuosity is involved for the vapour transport, especially at low values of saturation (S). Nevertheless the numerical simulation indicates that $f(a) = a$ is a good first approximation.

In early work [7–9] I developed a physical–mathematical model for calculating λ^+ of moist granular media from their composition. The procedure used is that mentioned in Section 4.5 of ref. [2]. The value of ζ follows also from this model (see equation (17) of ref. [5]).

I used this model to analyse the second example. For this purpose I replaced the solid square cross section of Fig. 3 by a circular one with the same ε_{s}. The calculated λ^+ for $S = 1$ is 0.82 W m^{-1} K^{-1}, the same as given in Figs. 6 and 7 for k. Calculated values for $S = 0.1$, cases b and e, are close to those of Fig. 7. However, for $S = 0$ the calculated λ^+ is 0.34 W m^{-1} K^{-1}, thus considerably higher than that following from Fig. 7. I can offer no explanation for this discrepancy.

The calculated values of $a\zeta$ for $S = 0.1$, cases b and e, differ by less than 10% from those given in Fig. 9 for f.

Hence the above comparison leads to the tentative conclusion that for 'wet walls' $k = \lambda^+$ and $f = a\zeta$. The 'true' conductivity of equation (2) can tentatively be identified with $\lambda^+ - f\lambda_{\mathrm{vs}}$ of equation (4). It remains to be seen whether this also holds for a more realistic three-dimensional case.

In ref. [3] Degiovanni and Moyne treat in detail transport in the gas phase, including the influence of a gradient of total pressure (P). I believe that here an omission is made in finding the diffusive mass flux density, q_{vdif}. For non-uniform temperature and pressure fields the full expression for the diffusive mass flux density of component 1 in a binary gas mixture with respect to its centre of gravity is

$$\mathbf{q}_1 = -\rho_{\mathrm{g}} D\left[\nabla\omega_1 + \frac{\alpha\omega_1\omega_2}{T}\nabla T + \frac{M_2 - M_1}{M_1 M_2}(M_2\omega_1 + M_1\omega_2)\frac{\nabla P}{P}\right]. \qquad (5)$$

The second term within brackets represents thermal diffusion; it is generally negligible in the situations dealt with here. Incorporation of the third term in equation (6) of ref.

[3] leads to

$$\mathbf{q}_{\mathrm{vdif}} = -\frac{P}{RT} Df \frac{M_a M_v}{M_g}\left[\nabla \frac{p_{vs}}{P} + \frac{M_a - M_v}{M_a M_v}(M_a \omega_{vs} + M_v \omega_a)\frac{\nabla P}{P}\right]. \quad (6)$$

Here the second term within brackets has the opposite sign of $p_{vs}\nabla(1/P)$ and is of the same order of magnitude. This term is missing in ref. [3]. For $P = 1$ atm the expression in brackets is zero for $p_{vs}/P = 0.54$, corresponding with a temperature of 83.6°C. It is positive for lower values of p_{vs}/P.

If the authors agree with my point of view, the analysis of the pressure influence in ref. [3] should be revised.

Note added in proof—Dr Moyne has pointed out to me that in the pressure term of equation (5) a factor $\omega_1\omega_2$ is missing. This reduces the corresponding term in equation (6) by a factor of 4 or more. Hence, this term will be negligible in comparison with $p_{vs}\nabla P^{-1}$ in most cases.

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Reply to 'Discussion of "Approche expérimentale et théorique de la conductivité thermique des milieux poreux humides"'

IN REPLY to the discussion of our articles [1–3] by Prof. de Vries, we want to bring the foregoing comments following the order of his remarks.

1. *Method of de Vries or not*

De Vries' analysis in his pioneering work in 1958 [4] suggested a tentative formulation to express the apparent thermal conductivity of a wet porous medium (which is k in our notation) in the form (see equations (10) and (16) in ref. [4] or equations (5) and (9) in ref. [5] with the definition of the thermal vapour diffusivity D_{Tv})

$$k = \lambda' + f_{\mathrm{de\,Vries}}\,\zeta\lambda_{\mathrm{dif}} \quad (1)$$

where λ' is 'the thermal conductivity of the porous medium in the hypothetical case where no moisture movement occurs', 'excluding vapour movement'; $f_{\mathrm{de\,Vries}}$ is a factor which appears due to the section reduction for effective transfer (including the hypothetical transport through isolated islands); ζ is the ratio between the intrinsic gas phase average temperature gradient and the volume-averaged temperature gradient; and λ_{dif} is the apparent thermal conductivity of the pores due to the contribution of the vapour diffusion.

In our article [1], we proposed to use this tentative formulation in order to analyse our own experimental results by determining a so-called 'de Vries' experimental factor' $f_{\exp}$ by writing

$$f_{\exp} = f_{\mathrm{de\,Vries}}\,\zeta \quad (2)$$

and by identifying λ' with the thermal conductivity λ_0 measured at low temperature ($T \leqslant 20$°C) where the evaporation–condensation effects seem to be experimentally negligible. Thus

$$k = \lambda_0 + f_{\exp}\lambda_{\mathrm{dif}}. \quad (3)$$

We called this factor 'de Vries' experimental factor' because we determined it experimentally following the conjecture of de Vries (in this view, the second line of Section 4.4 of ref. [1] should have read "la conjecture de de Vries conduit à" rather than "de Vries propose de").

Nevertheless we are pleased to accept the authorship of this method which gives a simple and efficient methodology to reach the apparent thermal conductivity k of a moist porous medium as a function of temperature and moisture content.

2. *Comparison between de Vries' work and our work*

With the notation of ref. [2], we express the vapour mass flux through the porous medium by analogy with Fick's law in the form

$$(\mathbf{n}_v)_i = -\rho_g \mathscr{D} f_{ij} \frac{\partial \langle \omega_v \rangle^g}{\partial x_j}. \quad (4)$$

where f_{ij} is the resistance factor to gaseous diffusion through the porous medium. The physical significance of the tensor f_{ij} is made clear by noting that f_{ij} is the tensor unity in the case of an homogeneous gas phase.

In his discussion de Vries argues that, neglecting the transport through liquid islands, we have in the 'wet walls' case

$$f = \varepsilon_g \zeta \quad (5)$$

which is the form that he proposed (without derivation) in his own papers [4, 6].

In fact we can derive this result beginning with equation (46) in ref. [2], noting that in the 'wet walls' case $\xi_g \equiv 0$ and applying the averaging theorem (knowing that $\langle \chi^g \rangle = 0$). Therefore, we have

$$f_{ij} = \varepsilon_g\left(\delta_{ij} + \left\langle \frac{\partial \chi_j^g}{\partial x_i} \right\rangle^g\right). \quad (6)$$