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Heat Conduction in a Porous Medium

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The thermodynamical theory of mixtures is applied to the process of heat conduction associated with the flow of fluids through isotropic, rigid, porous medi?. A simplified model for conduction is proposed and the restrictions imposed by the second law of thermodynamics are analyzed. Using this model, the heat flux is given by $h = -K \operatorname{grad} 0$, where $K = k_0 [\alpha_0(||\mathbf{q}||)\mathbf{1} + \beta_1(||\mathbf{q}||)\mathbf{q} \otimes \mathbf{q}]$ is a tensor valued function of the percolation velocity q. The experimental data available permits the determination of the functions α_0 and β_1 over a limited range of velocities.

A teoria termodinâmica de misturas é aplicada ao processo da condução de calor associado ao escoamento de fluídos através de meios porosos, isotrópicos e rígidos. Um modelo simplificado para a condução é proposto e as restrições impostas pela segunda lei da termodinâmica são analisadas. Partindo desse modelo, resulta que o fluxo de calor é dado por h = -K grad 0, onde $K = k_0 [\alpha_0(||q||) \mathbf{1} + \beta_1(||q||) \mathbf{q} \otimes \mathbf{q}]$ é uma função tensorial da velocidade de percolação q. Os dados experimentais disponíveis permitem a determinação das funções a, e β_1 , em uma faixa limitada de velocidades.

1. Introduction

The basic conservation laws, which describe the theory of fluxes in mixtures, were established by Truesdell' in relation to continuum mechanics and, later, generalized by Kelly², Eringen and Ingram^{3,4}, Green and Naghdi^{5,6,7,8}, Bowen⁹, Bowen and Wiese¹⁰ and by Gurtin^{••}.

This theory can be readily applied to the study of flows, through porous media, as has been shown by Crochet and Naghdi¹², who investigated the restrictions imposed by the second law of thermodynamics upon a certain class of non linear constitutive equations. Their results are perfectly capable of explaining the majority of mechanical phenomena observed in porous media, including, as special cases, Darcy's law and all of its generalizations. However, their treatment of heat conduction is not complete and the linearized equation employed is too special and not able to explain the difference in conductivity, in directions

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normal to and parallel to the velocity of the fluid, which has been explained experimentally.

In this work, we follow the above mentioned authors very closely and apply similar methods to the study of the interaction of the fluid flow with the mechanism of heat conduction in a rigid, isotropic, porous medium. In particular, we examine the restrictions imposed by the second law upon the constitutive class proposed, and obtain the reduced dissipation inequality which is needed to restrict the coefficients of a simple model for heat conduction. The main result are represented by equations (5-21) and equation (6-10) with the acompanying restrictions (5-11) and (5-13).

2. Basic Laws

To formulate the basic field equations, we consider the flow of a fluid, with mass density ρ_f flowing with velocity \mathbf{v}_1 through a porous medium of porosity ε and velocity \mathbf{v}_2 . The medium is made of particles with mass density ρ_s . In addition,

$$\rho_1 = \varepsilon \rho_f, \quad P_2 = (1 - \varepsilon) \rho_s, \quad \rho = \rho_1 + P_2, \quad \rho w = \rho_1 v_1 + p_2 v_2, \quad (2-1)$$

where ρ is the global density of the mixture and w is the velocity of the center of mass.

Given a scalar field, f, we define the material time derivative, \dot{f} , by the expression

$$\mathbf{f} = \frac{\partial f}{\partial t} + (\operatorname{grad} f) \cdot \mathbf{w}. \tag{2-2}$$

With the help of these definitions, the basic conservation laws are mass balance for each constituent,

$$\frac{\partial \rho_i}{\partial t} + \operatorname{div} \left(\rho_i \, \mathbf{v}_i \right) = 0, \tag{2-3}$$

momentum balance for each constituent,

$$\rho_i \left[\frac{\partial \mathbf{v}_i}{\partial t} + (\text{grad } \mathbf{v}_i) \mathbf{v}_i \right] = \text{div } \mathbf{T}_i + \rho_i \mathbf{l}_i + \rho_i \mathbf{b}_i, \qquad (2-4)$$

energy balance for the mixture,

$$\rho e = -\operatorname{div} \mathbf{h} + \operatorname{tr} \left\{ \sum_{i=1}^{2} T_{i}^{\mathrm{T}} \operatorname{grad} \mathbf{v}_{i} \right\} - \sum_{i=1}^{2} \rho_{i} \mathbf{l}_{i} \cdot (\mathbf{v}_{i} - \mathbf{w}) + \rho r, \quad (2-5)$$

growth of entropy for the mixture,

$$ps \ge - \operatorname{div}(\mathbf{h}/\theta) + r/\theta.$$
 (2-6)

In these relations, i = 1 applies to the fluid and i = 2 to the solid mesh.

In Eq. (2-4), \mathbf{T}_i is the stress tensor for each phase and \mathbf{l}_i the diffusive force, representing the total force exerted by one phase upon the other, per unit mass of phase *i*. The body forces, or external actions, act through the field forces \mathbf{b}_i .

The expression for the energy balance, given by equation (2-5), expresses the growth of internal energy e of the mixture due to: heat conduction represented by the heat flux h; the irreversible working due to the surface and diffusive forces; the heat r supplied from the environment.

Equation (2-6) represents the second law of thermodynamics and is called the Gibbs-Duhem inequality.

Compatibility of equations (2-4), with the expression for the momentum balance of the mixture, implies a balance of diffusive forces:

$$\rho_1 \mathbf{l}_1 + \rho_2 \mathbf{l}_2 = 0. \tag{2-7}$$

Then, letting

$$\mathbf{m} = \rho_1 \, \mathbf{l}_1 \tag{2-8}$$

and substituting this in equations (2-4) and (2-5), and eliminating *pr* in equation (2-6), using equation (2-5), the following equivalent forms, for expressions (2-4), (2-5) and (2-6), are obtained:

$$\rho_1 \left[\frac{\partial \mathbf{v}_1}{\partial t} + (\text{grad } \mathbf{v}_1) \mathbf{v}_1 \right] = \text{div } \mathbf{T}_1 + \mathbf{m} + \rho_1 \mathbf{b}_1, \qquad (2-9)$$

$$\rho_2 \left[\frac{\partial \mathbf{v}_2}{\partial t} + (\text{grad } \mathbf{v}_2) \mathbf{v}_2 \right] = \text{div } \mathbf{T}_2 - \mathbf{m} + \rho_2 \mathbf{b}_2, \qquad (2-10)$$

$$\dot{\rho e} = -\operatorname{div} h + \operatorname{tr} \{ T_1^T \operatorname{grad} \mathbf{v}_1 + T_2^T \operatorname{grad} \mathbf{v}_1 \} - - \mathbf{m} \cdot (\mathbf{v}_1 - \mathbf{v}_1) + \rho r, \qquad (2-11)$$

$$\rho(\dot{\psi} + s\dot{\theta}) - \operatorname{tr} \{\mathbf{T}_{1}^{\mathsf{T}} \operatorname{grad} \mathbf{v}_{1} + \mathbf{T}_{2}^{\mathsf{T}} \operatorname{grad} \mathbf{v}_{2}\} + \mathbf{m} \cdot (\mathbf{v}_{1} - \mathbf{v}_{2}) + \frac{1}{\vartheta} \mathbf{h} \cdot \operatorname{grad} \vartheta \leq 0. \quad (2-12)$$

The last relation is the reduced dissipation inequality, where ψ is the Helmholtz free energy,

$$\psi \equiv e - 0 \,\mathrm{s} \,. \tag{2-13}$$

This inequality plays a central role in modern thermodynamics of continua, since it limits the possible forms for the constitutive equations.

Different representations of Eqs. (2-1) to (2-13) are presented in all references cited at the introduction. Bowen and Wiese¹⁰ give an excellent survey and comparison of the various forms proposed.

For the study of heat conduction it will be convenient to restrict attention to rigid porous media. In this case, the velocity v_2 can be set equal to zero the choice of a suitable frame of reference. Also, the porosity E is independent of time. Equations (2-3) and (2-9) to (2-12), consequently, assume a simplified form:

$$\operatorname{E} \frac{\partial \rho_{\mathrm{f}}}{dt} + \operatorname{div} \left(\rho_{\mathrm{f}} \, \mathrm{q} \right) = 0, \qquad (2-14)$$

$$\rho_{\rm f}\left\{\frac{\partial \mathbf{q}}{\partial t} + \left[\operatorname{grad}\left(\mathbf{q}/\varepsilon\right)\right]\mathbf{q}\right\} = \operatorname{div}\mathbf{T}_1 + \mathbf{m} + \varepsilon\,\rho_{\rm f}\,\mathbf{b}_1,\qquad(2-15)$$

div
$$\mathbf{T}_2 - \mathbf{m} + \rho_2 \mathbf{b}_2 = \mathbf{0},$$
 (2-16)

$$\rho \dot{e} = -\operatorname{div} \mathbf{h} + \operatorname{tr} \left\{ \mathbf{T}_{1}^{\mathrm{T}} \operatorname{grad} \left(\mathbf{q} / \varepsilon \right) \right\} - \frac{1}{\varepsilon} \mathbf{m} \cdot \mathbf{q} + \rho r, \qquad (2-17)$$

$$\rho(\dot{\psi} + s\dot{\theta}) - \operatorname{tr}\left\{\mathbf{T}_{1}^{\mathrm{T}}\operatorname{grad}\left(\mathbf{q}/\varepsilon\right)\right\} + \frac{1}{\varepsilon}\mathbf{m}\cdot\mathbf{q} + \frac{1}{\theta}\mathbf{h}\cdot\operatorname{grad}\theta \leq 0, \quad (2-18)$$

where q, the percolation velocity, is defined by

$$q = \varepsilon \mathbf{v}_1 . \tag{2-19}$$

3. Formulation of Constitutive Equations

To study those aspects of heat conduction not involving problems of compressibility or heat transfer between phases, we shall assume the system to be described by a single temperature θ and, additionally, that the constitutive equations are independent of the density of the fluid.

We now make the assumption that, for all processes, the free energy, the entropy, the diffusive force, the stress on the fluid and the heat flux are determineá by the temperature, the percolation velocity and the temperature gradient:

$$\psi = \psi(\theta, \mathbf{q}, \mathbf{g}), \quad s = s(\theta, \mathbf{q}, \mathbf{g}), \quad \mathbf{m} = \mathbf{m}(\theta, \mathbf{q}, \mathbf{g}),$$

$$\mathbf{T}_1 = \mathbf{T}_1 \quad (\theta, \mathbf{q}, \mathbf{g}), \quad \mathbf{h} = \mathbf{h} \quad (\theta, \mathbf{q}, \mathbf{g}),$$
(3-1)

where \mathbf{g} is the temperature gradient vector

$$\mathbf{g} = \operatorname{grad} \theta \,. \tag{3-2}$$

Crochet and Naghdi¹² include, in the constitutive equations, the deformation gradients and the material time derivatives of the deformation gradients for both phases. For rigid media, the deformation gradient of the solid mesh can be set equal to 1 and consequently it need not appear explicitly in equations (3-1). If the material flowing through the porous medium is indeed a fluid in the sense of Noll¹³, dependence on these variables must reduce to a dependence upon the symmetric part of the velocity gradient. Such dependence apparently has never been experimentally detected.

Gurtinⁱ assumes a constitutive **class** similar to Eqs. (3-1). He includes dependence on partial densities ρ_i and on their gradients. To be consistent with his assumptions, the gradient of porosity should be included. We believe this to be an important variable in the case of non-homogeneous media, but we neglect such a dependence in this work. In fact, attention will be exclusively confined to media of constant porosity.

Defining the pressure p by the relations

$$\varepsilon p = -\frac{1}{3} \operatorname{tr} \mathbf{T}_{1}, \qquad (3-3)$$

then we can write

$$\operatorname{tr} \{\mathbf{T}_1 \text{ grad } \mathbf{v}_1\} = \operatorname{tr} \{(\mathbf{T}_1 + \varepsilon p \mathbf{1}) (\operatorname{grad } \mathbf{v}_1)\}, \quad (3-4)$$

since for incompressible fluids, in a constant porosity medium, Eq. (2-3) implies div $v_1 = 0$.

Taking the time derivative of ψ and substituting it into the dissipation inequality, (2-18), gives:

$$\rho \left(\frac{\partial \psi}{\partial \theta} + s\right) \dot{\theta} - \operatorname{tr} \left\{ (\mathbf{T}_{1}^{\mathrm{T}} + \varepsilon p \, \mathbf{1}) \, (\operatorname{grad} \, \mathbf{v}_{1}) \right\} + \rho \, \frac{\partial \psi}{\partial \mathbf{q}} \cdot \dot{\mathbf{q}} + \rho \, \frac{\partial \psi}{\partial \mathbf{q}} \cdot \dot{\mathbf{g}} + \frac{1}{\varepsilon} \, \mathbf{m} \cdot \mathbf{q} + \frac{1}{\theta} \, \mathbf{h} \cdot \mathbf{g} \le 0. \quad (3-5)$$

Gurtin¹¹ has demonstrated a lemma for the independence of $\dot{\theta}$, grad \mathbf{v}_1 , \mathbf{q} , and g on the values of the state variables. This theorem states that, for a given point in the flow field and for all values of θ_o , \mathbf{q}_o , \mathbf{g}_o , there exists processes for which, at $\mathbf{x} = \mathbf{x}_o$ and $\mathbf{t} = t_o$,

$$\theta(x_o, t_o) = \theta_o, \quad \mathbf{q}(x_o, t_o) = \mathbf{q}_o, \quad \mathbf{g}(x_o, t_o) = \mathbf{g}_o, \quad (3-6)$$

with arbitrarily chosen values for the derivatives $\hat{\theta}$, grad \mathbf{v}_1 , q, and g. From this fact, it follows immediately that the inequality (3-5) is satisfied in all these processes if, and only if, the coefficients of those variables are all zero. Consequently,

$$s = -\frac{\partial \psi}{\partial \theta}, \ \psi = \psi(\theta), \ s = s(\theta), \ \mathbf{T}_1 = -\varepsilon p \ \mathbf{1},$$
 (3-7)

and in all processes the inequality

$$\delta(\mathbf{q}, \mathbf{g}) \equiv -\frac{1}{\varepsilon} \mathbf{m} \cdot \mathbf{q} - \frac{1}{\theta} \mathbf{h} \cdot \mathbf{g} \ge 0$$
(3-8)

must be satisfied.

The free energy and the entropy assume their equilibrium value irrespectively of the values of velocity and temperature gradient. This fact might be interpreted as a local equilibrium hypothesis. Also, the stress field always reduces to a hydrostatic pressure field. This result is a consequence of the simple form postulated for the second law which neglects the entropy flux due to mixing. In more general theories, the stress may be non-isotropic.

The simplified form of the reduced dissipation inequality includes, as special cases when q = 0, the Fourier inequality and, when g = 0,

$$\delta(\mathbf{q}, 0) = \mathbf{m} \cdot \mathbf{q} \ge 0. \tag{3-9}$$

If the diffusive force m is indeed a function of the temperature gradient, then inequality (3-9) does not necessarily hold. On the other hand, inequality (3-8) must be true for all processes in rigid and homogeneous porous media for which the constitutive equations (3-1) are a model.

4. Isotropy and Frame Indifference '

The restrictions on the functions m and h imposed by the second law, Eq. (3-8), are not the only ones that need be considered. Material symmetries and material frame indifference play also extremely important roles. The **conjugation** of symmetry properties with frame indifference implies that for all orthogonal tensors Q which belong to the symmetry group of the porous **media**¹³, the following conditions hold:

$$\mathbf{m}(\theta, \mathbf{Q}\mathbf{q}, \mathbf{Q}\mathbf{g}) = \mathbf{Q} \mathbf{m}(\theta, \mathbf{q}, \mathbf{g}), \\ \mathbf{h}(\theta, \mathbf{Q}\mathbf{q}, \mathbf{Q}\mathbf{g}) = \mathbf{Q} \mathbf{h}(\theta, \mathbf{q}, \mathbf{g}).$$
(4-1)

For isotropic materials, Eqs. (4-1) must be satisfied for all orthogonal tensors. Functions of this type, called isotropic functions, have been intensively studied. Recently, Wang^{14,15} and Smith¹⁶ arrived at a general representation theorem for them. In our special case, i.e., for vector valued isotropic functions of two vectors, this theorem reads:

$$\mathbf{m}(\theta, \mathbf{q}, \mathbf{g}) = Z_q(\theta, \|\mathbf{q}\|, \|\mathbf{g}\|, \mathbf{q} \cdot \mathbf{g}) \mathbf{q} + Z_g(\theta, \|\mathbf{q}\|, \|\mathbf{g}\|, \mathbf{q} \cdot \mathbf{g}) \mathbf{g}, \mathbf{h}(\theta, \mathbf{q}, \mathbf{g}) = \varphi_q(\theta, \|\mathbf{q}\|, \|\mathbf{g}\|, \mathbf{q} \cdot \mathbf{g}) \mathbf{q} + \varphi_g(\theta, \|\mathbf{q}\|, \|\mathbf{g}\|, \mathbf{q} \cdot \mathbf{g}) \mathbf{g},$$
(4-2)

where Z_q , Z_g , φ_q , φ_g are scalar valued functions of the arguments shown. We notice **that**, **although** the materials considered are isotropic, the diffusive force is not parallel to the percolation velocity q, unless $Z_g = 0$ or g = 0. In the same way, the heat flux is not parallel to the temperature gradient, **unless** $\varphi_q = 0$ or q = 0.

The substitution of formulae (4-2) into Eq. (3-8) yields:

$$\delta(\mathbf{q}, \mathbf{g}) = -\frac{1}{\varepsilon} Z_q \|\mathbf{q}\|^2 - \frac{1}{\theta} \varphi_g \|\mathbf{g}\|^2 - \left(\frac{Z_g}{\varepsilon} + \frac{\varphi_q}{\theta}\right) (\mathbf{q} \cdot \mathbf{g}) \ge 0. \quad (4-3)$$

This inequality places important restrictions on the functions Z_q , Z_g , φ_q , φ_q but it is much too general to permit a conclusive analysis.

5. Simple Model for Heat Conduction

The principal aim of this research is to establish the simplest model for heat conduction in a porous media which is compatible with frame indifference and with the dissipation inequality, but still able to explain some, if not all, of the experimental evidence. Of central importance is the fact that the heat flux depends on the relative orientation of the velocity and temperature gradient vectors.

It would be tempting to write, as a first approximation,

$$\mathbf{h} = -\mathbf{K}(\|\mathbf{q}\|)\,\mathbf{g},\tag{5-1}$$

where K is a tensor valued function of the absolute value of q. In fact, this appears to be the normal $practice^{17,18,19}$. It will be shown that, for isotropic materials, in the very special case where such a tensor function exists, it cannot be a function of the absolute value of the percolation velocity only.

To arrive at a simple model for heat copduction, we notice by considering the representation theorem, Eqs. (4-2), that dependence of heat flux on the relative orientation of the two vectors q and g must arise from the dependence on the scalar product (q · g). Such dependence was considered by Lagarde²⁰ who wrongly concluded that the dissipation inequality ruled it out. The simple model to be analysed in detail assumes that the diffusive force is not altered by the temperature gradient, and that φ_q and φ_g in Eq. (4-2) are linear in the scalar product (q · g), and independent of $\|\mathbf{g}\|$:

$$\mathbf{m} = -R\Omega(\theta, \|\mathbf{q}\|) \mathbf{q}, \mathbf{h} = -k_o \{ [\alpha_o(\theta, \|\mathbf{q}\|) + \alpha_1(\theta, \|\mathbf{q}\|) (\mathbf{q} \cdot \mathbf{g})] \mathbf{g} \\ + [\beta_o(\theta, \|\mathbf{q}\|) + \beta_1(\theta, \|\mathbf{q}\|) (\mathbf{q} \cdot \mathbf{g})] \mathbf{q} \}.$$
(5-2)

The temperature θ occurs in these functions as a parameter which is irrelevant to the arguments that follow. It can, therefore, be omitted in the variable list, while still allowing explicit dependence on the temperature of the functions in Eqs. (5-2). In the expression for the diffusive force m, R is the resistivity of the porous media and its inverse is the permeability. If Ω is equal to unity, this expression reduces to Darcy's law. In the formula for the heat flux h, k_o is the thermal conductivity of the mixture at stagnation. In fact, we have:

$$\frac{\partial \mathbf{m}}{\partial \mathbf{q}}\Big|_{\mathbf{q}=\mathbf{0}}=-R\mathbf{1},$$

$$\frac{\partial \mathbf{h}}{\partial \mathbf{g}}\Big|_{\substack{\mathbf{q}=\mathbf{0}\\\mathbf{g}=\mathbf{0}}} = -k_0 \mathbf{1}.$$
 (5-3)

Consequently,

$$\Omega(0) = 1, \quad \alpha_0(0) = 1.$$
 (5-4)

Upon substitution of Eqs. (5-2) into the dissipation inequality (4-3), we obtain:

$$\delta(\mathbf{q}, \mathbf{g}) = \frac{1}{\varepsilon} R \Omega(\|\mathbf{q}\|) \|\mathbf{q}\|^2 + \frac{1}{\theta} k_0 \alpha_0(\|\mathbf{q}\|) \|\mathbf{g}\|^2 + \frac{k_0}{\theta} \alpha_1(\|\mathbf{q}\|) (\mathbf{q} \cdot \mathbf{g}) \|\mathbf{g}\|^2 + \frac{k_0}{\theta} \beta_0(\|\mathbf{q}\|) (\mathbf{q} \cdot \mathbf{g}) + \frac{k_0}{\theta} \beta_1(\|\mathbf{q}\|) (\mathbf{q} \cdot \mathbf{g})^2 \ge 0.$$
(5-5)

This inequality must be satisfied for all values of q and g. Thus, letting q = 0 and, subsequently, g = 0, it is a simple matter to show the well known results

$$R \ge 0, \quad \Omega(\|\mathbf{q}\|) \ge 0, \quad k_0 \ge 0. \tag{5-6}$$

Note that for a fixed value of q, Eq. (5-5) is of the general form

$$a + b(\mathbf{q} \cdot \mathbf{e}_g) \|\mathbf{g}\| + [c + d(\mathbf{q} \cdot \mathbf{e}_g)^2] \|\mathbf{g}\|^2 + f(\mathbf{q} \cdot \mathbf{e}_g) \|\mathbf{g}\|^3 \ge 0,$$
(5-7)

where a, b, c and f are functions of $\|\mathbf{q}\|$ only, and \mathbf{e}_q is the unit vector in the direction of the temperature gradient. If f is negative, then let e, be such that $\mathbf{q} \cdot \mathbf{e}$, is positive. For sufficiently large values of $\|\mathbf{g}\|$, the cubic term would dominate the expression and the dissipation would be negative.

Conversely, were f positive, the same reasoning could be applied with the choice of e, such that $q \cdot e$, is negative. Consequently, f must be zero and this implies that

$$\alpha_1(\|\mathbf{q}\|) = 0. \tag{5-8}$$

With this result, inequality (5-5) assumes the form:

$$\delta(\mathbf{q}, \mathbf{g}) = \frac{1}{\varepsilon} R \, \Omega(\|\mathbf{q}\|) \, \|\mathbf{q}\|^2 + \frac{k_0}{\theta} \, \alpha_0(\|\mathbf{q}\|) \, \|\mathbf{g}\|^2 + \frac{k_0}{\theta} \, \beta_0(\|\mathbf{q}\|) \, \|\mathbf{q}\| \, \|\mathbf{g}\| \, (\mathbf{e}_{\mathbf{q}} \cdot \mathbf{e}_{\mathbf{g}}) + \frac{k_0}{g} \, \beta_1(\|\mathbf{q}\|) \, \|\mathbf{q}\|^2 \, \|\mathbf{g}\|^2 (\mathbf{e}_{\mathbf{q}} \cdot \mathbf{e}_{\mathbf{g}})^2 \ge 0.$$
(5-9)

If we the percolation velocity and the temperature gradient be orthogonal, there results:

$$\frac{1}{\varepsilon} R\Omega(\|\mathbf{q}\|) \|\mathbf{q}\|^2 + \frac{1}{\theta} k_0 \alpha_0(\|\mathbf{q}\|) \|\mathbf{g}\|^2 \ge 0.$$
(5-10)

From this expression, we conclude that

$$\alpha_0(\|q\|) \ge 0, \tag{5-11}$$

which is compatible with the previously established value for α_0 at the origin.

Introducing $\mathbf{e}, \cdot \mathbf{e}, = 1$ and $\mathbf{e}, \cdot \mathbf{e}, = -1$ into Eq. (5-9) and adding the two resulting inequalities:

$$\frac{1}{\varepsilon} R\Omega(\|\mathbf{q}\|) \|\mathbf{q}\|^2 + \frac{k_0}{\theta} [\alpha_0(\|\mathbf{q}\|) + \beta_1(\|\mathbf{q}\|) \|\mathbf{q}\|^2] \|\mathbf{g}\|^2 \ge 0, \quad (5-12)$$

implying that

$$\alpha_0(\|\mathbf{q}\|) + \beta_1(\|\mathbf{q}\|) \|\mathbf{q}\|^2 \ge 0.$$
 (5-13)

This inequality cannot be reduced further unless some other hypotheses are made about the functions α_0 and β_1 . For instance, if α_0 and β_1 are constants, then they are necessarily non-negative. However, this hypothesis will not be made.

We can write inequality (5-9) in the form:

$$\delta = a + b \|\mathbf{g}\|^2 + c \|\mathbf{g}\| \ge 0, \tag{5-14}$$

where

$$a \equiv \frac{R}{\varepsilon} \Omega(\|\mathbf{q}\|) \|\mathbf{q}\|^2 \ge 0,$$

$$b \equiv \frac{k_0}{\theta} \left[\alpha_0(\|\mathbf{q}\|) + \beta_1(\|\mathbf{q}\|^2) \|\mathbf{q}\|^2 (\mathbf{e}_{\mathbf{q}} \cdot \mathbf{e}_{\mathbf{g}})^2 \right] \ge 0,$$

$$c \equiv \frac{k_0}{\theta} \beta_0(\|\mathbf{q}\|) \|\mathbf{q}\| (\mathbf{e}_{\mathbf{q}} \cdot \mathbf{e}_{\mathbf{g}}).$$

We shall now establish the conditions under which the dissipation has a minimum and when this minimum is positive, i.e.

$$\frac{\partial \delta}{\partial \|\mathbf{g}\|} = 2b \|\mathbf{g}\| + c, \quad \frac{\partial^2 \delta}{\partial (\|\mathbf{g}\|)^2} = 2b \ge 0. \tag{5-15}$$

Since b is non-negative, then, if δ has an extremum, it is necessarily a minimum and will occur at $\|\mathbf{g}\| = -(c/2b)$, if $c \leq 0$ and $b \neq 0$

Then,

$$\delta_{\min} = a - \frac{c^2}{4b} \ge 0 \tag{5-16}$$

and

$$\beta_0^2(\|\mathbf{q}\|) (\mathbf{e}_{\mathbf{q}} \cdot \mathbf{e}_{\mathbf{g}})^2 \le \frac{4\theta R}{\varepsilon k_0} \Omega(\|\mathbf{q}\|) [\alpha_0(\|\mathbf{q}\|) + \beta_1(\|\mathbf{q}\|) \|\mathbf{q}\|^2 (\mathbf{e}_{\mathbf{q}} \cdot \mathbf{e}_{\mathbf{g}})^2].$$
(5-17)

The last equation holds if and only if

$$0 \leq \beta_0^2(\|\mathbf{q}\|) \leq \frac{4\theta R \Omega(\|\mathbf{q}\|)}{\varepsilon k_0} [\alpha_0(\|\mathbf{q}\|) + \beta_1(\|\mathbf{q}\|) \|\mathbf{q}\|^2].$$
 (5-18)

In particular,

$$|\beta_0(0)| \le (4\theta R/\varepsilon k_0)^{1/2}.$$
 (5-19)

Equations (5-18) and (5-19) are statements that a heat flux *can* exist even when grad $\theta = 0$, but such a flux must be small in the sense that

$$\|\mathbf{h}(\mathbf{q},\mathbf{0})\| \leq \left\{\frac{4\theta R \ \Omega(\|\mathbf{q}\|)}{\varepsilon k_0} \left[\alpha_0(\|\mathbf{q}\|) + \beta_1(\|\mathbf{q}\|) \|\mathbf{q}\|^2\right]\right\}^{\frac{1}{2}} \|\mathbf{q}\|.$$
(5-20)

The linear form of this result, that is, a statement equivalent to Eq. (5-19), was derived by Crochet and Naghdi¹². If this effect *can* be neglected, i.e., if β_0 can be set equal to zero, then Eq. (5-2) reduces to h = -Kg, where

$$\mathbf{K} = k_0 [\alpha_0(\|\mathbf{q}\|) \ \mathbf{1} + \beta_1(\|\mathbf{q}\|) \ \mathbf{q} \otimes \mathbf{q}].$$
 (5-21)

The tensor-valued function K is symmetric, with eigenvalues λ_i :

$$\lambda_{1} = k_{0} \left[\alpha_{0}(\|\mathbf{q}\|) + \beta_{1}(\|\mathbf{q}\|) \|\mathbf{q}\|^{2} \right], \qquad (5-22)$$

$$\lambda_{2} = \lambda_{3} = k_{0} \alpha_{0}(\|\mathbf{q}\|).$$

The characteristic spaces of K_i consist of a line in the direction of q and a plane normal to q.

Note that with this simple model.

$$h(-q, g) = h(q, g), h(q, -g) = -h(q, g).$$
 (5-23)

Equations (5-21) and (5-23) can be easily tested. The experimental evidence available at the moment is inconclusive with respect to the result (5-23). If future investigations disprove this result, then terms in higher powers of $(\mathbf{q} \cdot \mathbf{g})$ must be added to Eq. (5-2).

Equation (5-21) can be written in the following equivalent form:

$$\mathbf{K} = k_0 \left[\alpha_0(\|\mathbf{q}\|) \ 1 + \beta_1(\|\mathbf{q}\|) \ \|\mathbf{q}\|^2 \ \mathbf{e}_{\mathbf{q}} \otimes \mathbf{e}_{\mathbf{q}} \right], \tag{5-24}$$

where e, is the unit vector in the direction of the percolation velocity. This formula is more convenient for comparison with experimental data.

Under suitable hypotheses, this analysis can be made applicable to mass transfer in the fluid phase. In that case, Eq. (5-21) would read

$$\mathbf{j} = - \mathbf{D} \text{ grad } \mathbf{C},$$
$$\mathbf{D} = D_0 \left[\gamma_0(\|\mathbf{q}\|) \mathbf{1} + \gamma_1(\|\mathbf{q}\|) \|\mathbf{q}\|^2 \mathbf{e}_{\mathbf{q}} \otimes \mathbf{e}_{\mathbf{q}} \right], \tag{5-25}$$

where j is the mass flux of a component dissolved in the fluid with concentration C.

6. Analysis of Experimental Data

Experimental results relating to heat conduction in porous media refer to the following situations: conduction with stagnant fluid, **con**duction in the direction normal to the fluid velocity, and conduction in a **direction** parallel to the fluid **velocity**. It is shown in what follows that **these** observations qualitatively **agree** with the theoretical conclusions of last item, **and** are also **sufficient** for the determination of the parameters in the tensor function K of Eq. (5-24).

For the stagnant fluid, the equation assumes the form:

$$\mathbf{h} = k_0 \, \mathbf{g}, \tag{6-1}$$

where k_0 depends on the porous media-fluid system. Theoretical or partially theoretical results, and experimental values as well, resulted in various expressions^{21,22,23,24} which allow an estimate of k_0 with appreciable accuracy. The expression proposed by Kunii and Smith²¹ is

$$\frac{k_0}{k_f} = \varepsilon + \frac{0.9 \left(1 - \varepsilon\right)}{\phi + \frac{2}{3} \left(k_f / k_s\right)},\tag{6-2}$$

where k_f and k_s are, respectively, the thermal conductivity of the fluid and of the **solid**, making **up** the porous material; ϕ is a function of the porosity and of the ratio k_f/k_s . For thermal wnduction normal to the percolation velocity, equation (5-24) reduces to:

$$\mathbf{h} = k_0 \ \alpha_0(\|\mathbf{q}\|)\mathbf{g}, \quad \alpha_0(0) = 1.$$
(6-4)

Experimental results obtained by various investigators^{18,19,25} lead to the conclusion that

$$\alpha_0(\|\mathbf{q}\|) = 1 + c_1 \frac{k_f}{k_0} \text{ Re Pr.}$$
 (6-5)

The Reynolds and Prandtl numbers, involving the physical **properties** of the **fluid**, are **defined** by:

$$\operatorname{Re} = \frac{d_p \ \rho_f \ \|\mathbf{q}\|}{\mu}, \qquad (6-6)$$

$$\Pr = \frac{c_p \ \mu}{k_f}, \tag{6-7}$$

where d_p is a characteristic dimension of the solid particles. In Eq. (6-5), the coefficient c_1 depends upon geometric factors of the porous media and apparently also upon thermal conductivity. According to the experimental measurements c_1 varies from 0.1 to 0.3.

For parallel conduction, Eq. (5-24) assumes the form:

$$\mathbf{h} = k_0 \left[\alpha_0(\|\mathbf{q}\|) + \beta_1(\|\mathbf{q}\|) \|\mathbf{q}\|^2 \right] \mathbf{g}.$$
 (6-8)

Experimental data for this situation are extremely scarce. They all refer to very low velocities and are restricted to the case in which the heat flux opposes the velocity. With the help of the data taken by Kunii and collaborators^{26,27}, and with the help of equation (6-5) it is possible to obtain

$$\beta_1(||\mathbf{q}||) ||\mathbf{q}||^2 = c_2 \frac{k_f}{k_0} \text{ Re Pr},$$
 (6-9)

where the coefficient c_2 is of the order of 0.6 for the very few systems investigated.

In accordance with the experimental evidence, we arrive at the following form for Eq. (5-24):

$$\mathbf{k} = k_0 \left[1 + c_1 \, \frac{k_{\rm f}}{k_0} \, \operatorname{Re} \, \Pr\left(1 + \frac{c_2}{c_1} \, \mathbf{e}_{\rm q} \otimes \mathbf{e}_{\rm q} \right) \right] \tag{6-10}$$

It is interesting to note that data taken on diffusion in porous mat e r i a l assume a form analogous to Eq. (6-9). This fact substantiates our comments at the end of last section.

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