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The problem of gray body radiant energy transport in porous media is analyzed using the volume averaging method. For a rigid solid-stagnant gas system the analysis yields an energy transport equation of the form

$$\langle\rho\rangle C_p \frac{\partial\langle T\rangle}{\partial t} = \nabla\cdot\{\mathbf{K}_{\text{eff}}\cdot\nabla\langle T\rangle\} + \sigma\langle T\rangle^3\mathbf{B}:\nabla\nabla\langle T\rangle + \sigma\langle T\rangle^3\boldsymbol{\lambda}\cdot\nabla\langle T\rangle + \sigma\langle T\rangle^2\mathbf{C}:\nabla\langle T\rangle\nabla\langle T\rangle$$

where $\sigma\langle T\rangle^3\mathbf{B}$ represents the radiant energy conductivity tensor, and the last term represents a nonlinear contribution to the "conductive" portion of the radiant energy transport. The vector $\boldsymbol{\lambda}$ is entirely associated with the anisotropic structure of the porous medium, and arguments are presented which suggest that $\boldsymbol{\lambda}$ is proportional to the gradient of the void fraction. Because of this, $\boldsymbol{\lambda}\cdot\nabla\langle T\rangle$ becomes large near the bounding surface of a porous medium or packed bed and gives rise to a nonlinear temperature profile. The form of the transport equation near a bounding surface is discussed, and the effects of conduction and radiation on wall heat transfer coefficients are noted. The theory indicates that $\mathbf{B}$, $\boldsymbol{\lambda}$, and $\mathbf{C}$ depend on the emissivity, the geometrical structure of the porous media, and the physical properties of the two phases.

1. Introduction

Radiant energy transport in gas-solid systems is generally important at elevated temperatures such as those encountered in fluid bed catalytic cracking operations (Batterill, 1975; Szekely and Fisher, 1969) or monolith catalytic reactors (Finlayson, 1978; Degan and Wei, 1978); however, under certain circumstances radiation can be important at low temperatures. This situation is illustrated by high void fraction systems, such as fiber glass insulation, in which the majority of the energy is transported through the gas phase. For such systems the ratio of radiant energy transport to conductive transport can be estimated as

$$\text{radiant energy transport/conductive transport} = 4\epsilon\sigma T^3\ell_\gamma/k_\gamma \quad (1\text{-}1)$$

Here k_γ is the gas phase thermal conductivity and ℓ_γ is a characteristic length for the gas phase. At 25 °C this ratio is unity when the gas is air and $\epsilon\ell_\gamma = 0.36$ cm. In many heat transfer processes of practical importance the potential influence of radiant energy transport is subordinated by high rates of transfer in both the solid and gas phases; nevertheless, the subject deserves a precise analysis. Previous studies have examined special cases (Szekely and Fisher, 1969; Hill and Wilhelm, 1959; Held, 1953) and have been unable to obtain a general governing differential equation from the original integral-differential equation (Held, 1953, 1954). However, the volume averaging method (Slattery, 1967; Anderson and Jackson, 1967; Whitaker, 1967) can provide just such an equation which should prove useful in the analysis of combined energy transport processes.

In the following paragraphs we will consider the problem of radiant energy transport in a system consisting of a rigid, solid matrix imbedded with a stagnant gas. The analysis will follow the line of attack given in a previous study of transport processes in porous media (Whitaker, 1977a).

2. Foundations

We consider the system illustrated in Figure 1 in which the solid is identified as the σ phase and the gas as the γ phase. We will assume that the gas is transparent to radiation, and that the solid is an opaque, gray body. In both the gas and solid phases we assume that energy transport is described by

$$\rho c_p\left(\frac{\partial T}{\partial t}\right) = -\nabla\cdot(\mathbf{q} + \mathbf{q}^R) \quad (2\text{-}1)$$

where $\mathbf{q}^R$ denotes the radiant energy heat flux vector. Since the gas phase is transparent to radiation we require

$$\nabla\cdot\mathbf{q}^R{}_\gamma = 0 \quad (2\text{-}2)$$

The effect of convective transport in the gas phase is easily included (Whitaker, 1977a); however, our intent here is to focus attention on the radiant energy transport process; thus we wish to keep the system as simple as possible.

In order to analyze the type of system shown in Figure 1, we need to form the volume average of the transport equations for the solid and gas phases. To accomplish this, we associate with every point in space an averaging volume V such as that shown in Figure 1. We define the *spatial average* of some function ψ as

$$\langle\psi\rangle = \frac{1}{V}\int_V \psi\, dV \quad (2\text{-}3)$$

It is useful to think of $\langle\psi\rangle$ as a spatially smoothed function defined at the centroid of the averaging volume. The matter of the size of the averaging volume is discussed elsewhere (Whitaker, 1969). For quantities associated only with a single phase, there are two other averages that are useful. The first of these is the *phase average* which is given (for example) by

$$\langle\rho_\gamma\rangle = \frac{1}{V}\int_V \rho_\gamma\, dV = \frac{1}{V}\int_{V_\gamma}\rho_\gamma\, dV \quad (2\text{-}4)$$

and the second is the *intrinsic phase average* which is defined by

$$\langle\rho_\gamma\rangle^\gamma = \frac{1}{V_\gamma}\int_V \rho_\gamma\, dV = \frac{1}{V_\gamma}\int_{V_\gamma}\rho_\gamma\, dV \quad (2\text{-}5)$$

Here we note that the final form for these averages follows from the fact that the gas-phase density ρ_γ is zero in the

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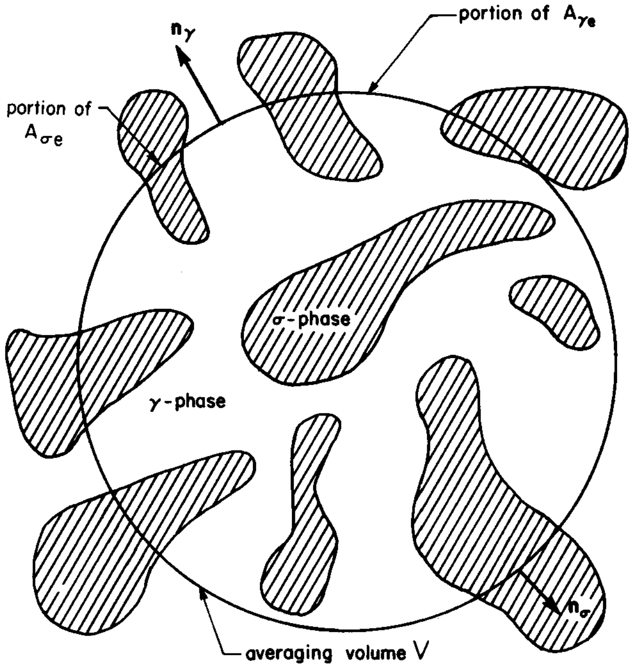

Figure 1. A rigid porous medium.

solid phase. The phase average and intrinsic phase average are related by

$$\langle \rho_\gamma \rangle = \epsilon_\gamma \langle \rho_\gamma \rangle^\gamma \tag{2-6}$$

where ϵ_γ is the volume fraction of the γ phase

$$\epsilon_\gamma = V_\gamma / V \tag{2-7}$$

For a gas-solid system we generally refer to ϵ_γ as simply the void fraction.

The key mathematical tool to be used in the construction of the volume averaged transport equations is the spatial averaging theorem (Slattery, 1967; Anderson and Jackson, 1967; Whitaker, 1967; Bachurat, 1972; Drew, 1971; Gray and Lee, 1977) which can be expressed as

$$\langle \nabla T_\sigma \rangle = \nabla \langle T_\sigma \rangle + \frac{1}{V} \int_{A_{\sigma\gamma}} T_\sigma \mathbf{n}_{\sigma\gamma} \, dA \tag{2-8}$$

Here T_σ represents the temperature at a point in the solid phase, $A_{\sigma\gamma}$ is the interfacial area contained within the averaging volume, and $\mathbf{n}_{\sigma\gamma}$ is the unit normal vector pointing from the σ phase into the γ phase.

We begin our analysis with the appropriate form of eq 2-1 for the solid phase

$$\rho_\sigma (c_p)_\sigma \left(\frac{\partial T_\sigma}{\partial t} \right) = -\nabla \cdot (\mathbf{q}_\sigma + \mathbf{q}_\sigma^R) \tag{2-9}$$

and note that $\mathbf{q}_\sigma^R$ will be zero everywhere in the solid phase except at the σ-γ interface.

Assuming that the density and heat capacity are essentially constant within the averaging volume, we form the volume average of eq 2-9 and use eq 2-8 to obtain

$$\rho_\sigma (c_p)_\sigma \frac{\partial \langle T_\sigma \rangle}{\partial t} = -\nabla \cdot \langle \mathbf{q}_\sigma + \mathbf{q}_\sigma^R \rangle - \frac{1}{V} \int_{A_{\sigma\gamma}} (\mathbf{q}_\sigma + \mathbf{q}_\sigma^R) \cdot \mathbf{n}_{\sigma\gamma} \, dA \tag{2-10}$$

By using the divergence theorem in conjunction with eq 2-8 one can show that

$$\nabla \cdot \langle \mathbf{q}_\sigma^R \rangle = \frac{1}{V} \int_{A_{\sigma e}} \mathbf{q}_\sigma^R \cdot \mathbf{n}_\sigma \, dA \tag{2-11}$$

where $A_{\sigma e}$ represents the area of entrances and exits of the σ phase contained in the averaging volume. A portion of $A_{\sigma e}$ is shown in Figure 1 along with the unit normal $\mathbf{n}_\sigma$. Since the solid is opaque, $\mathbf{q}_\sigma^R$ is zero over the surface $A_{\sigma e}$ and we obtain

$$\nabla \cdot \langle \mathbf{q}_\sigma^R \rangle = 0 \tag{2-12}$$

Use of this result in eq 2-10 allows us to write the solid phase thermal energy equation as

$$\rho_\sigma (c_p)_\sigma \frac{\partial \langle T_\sigma \rangle}{\partial t} = -\nabla \cdot \langle \mathbf{q}_\sigma \rangle - \frac{1}{V} \int_{A_{\sigma\gamma}} (\mathbf{q}_\sigma + \mathbf{q}_\sigma^R) \cdot \mathbf{n}_{\sigma\gamma} \, dA \tag{2-13}$$

In attacking the volume average heat flux, we assume a neglibible variation of k_σ within the averaging volume and use eq 2-8 to obtain

$$\langle \mathbf{q}_\sigma \rangle = -\langle k_\sigma \nabla T_\sigma \rangle = -k_\sigma \left[\nabla \langle T_\sigma \rangle + \frac{1}{V} \int_{A_{\sigma\gamma}} T_\sigma \mathbf{n}_{\sigma\gamma} \, dA \right] \tag{2-14}$$

It is important to derive an equation for the *intrinsic phase average* temperature rather than the *phase average* temperature; thus we make use of

$$\langle T_\sigma \rangle^\sigma = \epsilon_\sigma \langle T_\sigma \rangle \tag{2-15}$$

in eq 2-13 and 2-14 to obtain

$$\epsilon_\sigma \rho_\sigma (c_p)_\sigma \frac{\partial \langle T_\sigma \rangle^\sigma}{\partial t} = \nabla \cdot \left\{ k_\sigma \left[\nabla (\epsilon_\sigma \langle T_\sigma \rangle^\sigma) + \frac{1}{V} \int_{A_{\sigma\gamma}} T_\sigma \mathbf{n}_{\sigma\gamma} \, dA \right] \right\} - \frac{1}{V} \int_{A_{\sigma\gamma}} (\mathbf{q}_\sigma + \mathbf{q}_\sigma^R) \cdot \mathbf{n}_{\sigma\gamma} \, dA \tag{2-16}$$

We can repeat this analysis for the gas phase, keeping in mind that $\nabla \cdot \mathbf{q}_\gamma^R = 0$ everywhere, in order to obtain

$$\epsilon_\gamma \rho_\gamma (c_p)_\gamma \frac{\partial \langle T_\gamma \rangle^\gamma}{\partial t} = \nabla \cdot \left\{ k_\gamma \left[\nabla (\epsilon_\gamma \langle T_\gamma \rangle^\gamma) + \frac{1}{V} \int_{A_{\gamma\sigma}} T_\gamma \mathbf{n}_{\gamma\sigma} \, dA \right] \right\} - \frac{1}{V} \int_{A_{\gamma\sigma}} \mathbf{q}_\gamma \cdot \mathbf{n}_{\gamma\sigma} \, dA \tag{2-17}$$

In eq 2-16 and 2-17 we are confronted with three problems: (1) representation of the area integrals of the temperature, (2) representation of the interphase fluxes $\mathbf{q}_\sigma$ and $\mathbf{q}_\gamma$, and (3) analysis of the radiant energy flux. The first two problems are relatively straightforward and will be discussed in section 4. Here we move directly to the radiant energy flux problem.

3. Radiant Energy Exchange

We have already noted that the gas is assumed to be transparent to radiation; thus we are concerned only with the radiant energy exchange between elements of the solid matrix shown in Figure 1. There is an array of surfaces that we need to identify in order to analyze the radiant energy transfer process. These are listed as follows.

A_1 is the σ-γ interfacial area contained within the averaging volume. This surface has been previously designated as $A_{\sigma\gamma}$.

A_2 is the σ-γ interfacial area "seen" by points on A_1. Much of A_2 will coincide with A_1, but portions of A_2 will obviously lie outside the averaging volume.

A_{j+1} is the interfacial area "seen" by points on A_j. Much of A_{j+1} will coincide with A_j, but portions of A_{j+1} will obviously lie outside the volume occupied by A_j.

A_N is the interfacial area "seen" by points on A_{N-1}. The area A_N contains all the solid-gas interfacial area in the

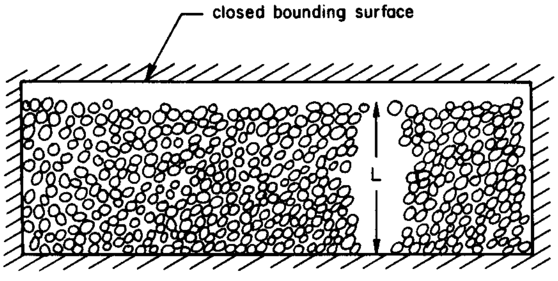

Figure 2. A bounded porous medium.

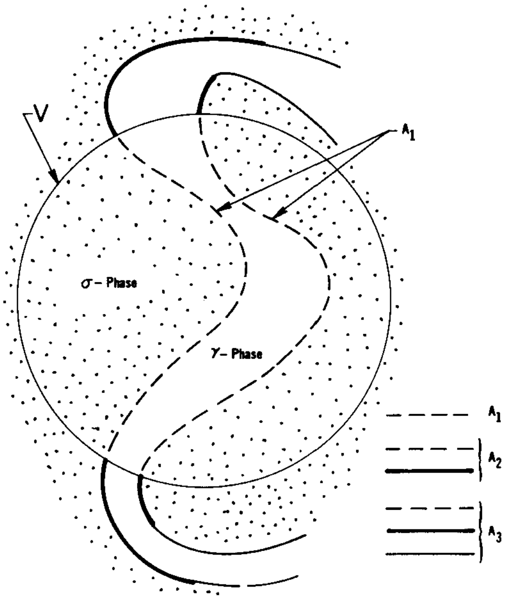

Figure 3. Radiant energy exchange areas.

porous media, in addition to the bounding surface illustrated in Figure 2.

In Figure 3, the areas A_1, A_2, and some, but not all, of A_3 are illustrated for a highly idealized porous medium and averaging volume. There it is clear that the area A_2 contains all of A_1 in addition to some area which is not contained in the averaging volume.

We will restrict our analysis to gray body radiation so that the total hemispherical emissivity ϵ, absorptivity α and reflectivity ρ are related by

$$\alpha = \epsilon; \qquad \rho = 1 - \epsilon \tag{3-1}$$

The total hemispherical emitted flux for a black body is designated by $q_b^{(e)}$ and the energy transported among the three surfaces illustrated in Figure 4 is given by

$$(\text{energy emitted from } dA_1 \text{ and incident on } dA_2) = \epsilon q_{b1}^{(e)}\Omega_{12}\, dA_1\, dA_2 \tag{3-2}$$

$$(\text{energy emitted and reflected from } dA_2 \text{ which is incident on } dA_1) = [\epsilon q_{b2}^{(e)} + q_2^{(r)}]\Omega_{21}\, dA_2\, dA_1 \tag{3-3}$$

$$(\text{energy emitted and reflected from } A_3 \text{ which is incident on } dA_2) = \int_{A_3} [q_{b3}^{(e)} + q_3^{(r)}]\Omega_{32}\, dA_3\, dA_2 \tag{3-4}$$

Here $q_j^{(r)}$ is used to represent the reflected radiation from the jth surface, and the geometrical factor Ω_{ji} is given by (Whitaker, 1977b)

$$\Omega_{ji} = \cos\theta_{ji}\cos\theta_{ij}/\pi r_{ji}^2 \tag{3-5}$$

The generalized version of eq 3-4 can be expressed as

$$(\text{energy emitted and reflected from } A_j \text{ which is incident on } dA_i) = \int_{A_j} [\epsilon q_{bj}^{(e)} + q_j^{(r)}]\Omega_{ji}\, dA_j\, dA_i \tag{3-6}$$

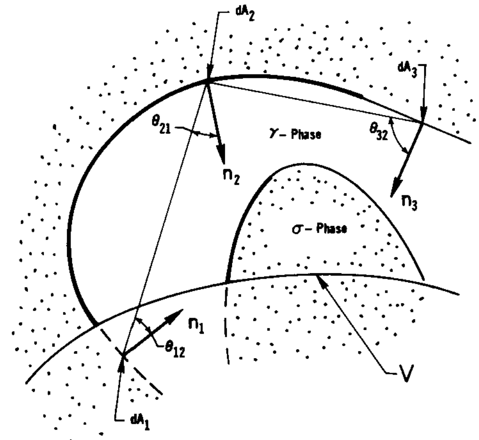

Figure 4. Radiant energy exchange.

where $i = j - 1$.

The net radiant energy flux at a point on the surface A_1 is given by

$$\mathbf{q}_\sigma^{R}\cdot\mathbf{n}_{\sigma\gamma} = \epsilon\int_{A_2} q_{b1}^{(e)}\Omega_{12}\, dA_2 - \epsilon\int_{A_2}[\epsilon q_{b2}^{(e)} + q_2^{(r)}]\Omega_{21}\, dA_2 \tag{3-7}$$

where the absorptivity has been replaced by the emissivity according to eq 3-1. The reflected energy in eq 3-7 is obtained from eq 3-4 and represented as

$$q_2^{(r)} = (1 - \epsilon)\int_{A_3}[\epsilon q_{b3}^{(e)} + q_3^{(r)}]\Omega_{32}\, dA_3 \tag{3-8}$$

and when this relation is substituted into eq 3-7 we obtain

$$\mathbf{q}_\sigma^{R}\cdot\mathbf{n}_{\sigma\gamma} = \epsilon\int_{A_2} q_{b1}^{(e)}\Omega_{12}\, dA_2 - \epsilon\left\{\int_{A_2}\epsilon q_{b2}^{(e)}\Omega_{21}\, dA_2 + \int_{A_2}\int_{A_3}(1-\epsilon)[\epsilon q_{b3}^{(e)} + q_3^{(r)}]\Omega_{32}\, dA_3\Omega_{21}\, dA_2\right\} \tag{3-9}$$

The general representation of eq 3-8 is

$$q_i^{(r)} = (1-\epsilon)\int_{A_j}[q_{bj}^{(e)} + q_j^{(r)}]\Omega_{ji}\, dA_j \tag{3-10}$$

and repeated use of this relation leads to

$$\begin{aligned}\mathbf{q}_\sigma^{R}\cdot\mathbf{n}_{\sigma\gamma} = {} & \epsilon\int_{A_2} q_{b1}^{(e)}\Omega_{12}\, dA_2 - \epsilon^2\int_{A_2} q_{b2}^{(e)}\Omega_{21}\, dA_2 - \\ & \epsilon^2(1-\epsilon)\int_{A_2}\int_{A_3} q_{b3}^{(e)}\Omega_{32}\, dA_3\Omega_{21}\, dA_2 - \\ & \epsilon^2(1-\epsilon)^2\int_{A_2}\int_{A_3}\int_{A_4} q_{b4}^{(e)}\Omega_{43}\, dA_4\Omega_{32}\, dA_3\Omega_{21}\, dA_2 \ldots - \\ & \epsilon^2(1-\epsilon)^{N-2}\int_{A_2}\int_{A_3}\ldots\int_{A_N} q_{bN}^{(e)}\Omega_{NM} dA_N \ldots \Omega_{21} dA_2 - \\ & \epsilon(1-\epsilon)^{N-2}\int_{A_2}\int_{A_3}\ldots\int_{A_N} q_N^{(r)}\Omega_{NM}\, dA_N \ldots \Omega_{21}\, dA_2\end{aligned} \tag{3-11}$$

where $M = N - 1$. In order to proceed with the analysis, we are restricted to systems such that the last term in eq 3-11 can be neglected. This simply means that we are dealing with systems for which N is large enough so that $\epsilon(1-\epsilon)^{N-2} \lll 1$. This situation is characteristic of porous media and is not a severe limitation in the theoretical development.

We can simplify the form of eq 3-11 by using the sum and product signs leading to

$$\mathbf{q}_\sigma^{R}\cdot\mathbf{n}_{\sigma\gamma} = \epsilon\int_{A_2} q_{b1}^{(e)}\Omega_{12}\, dA_2 - \sum_{j=2}^{j=N}\prod_{2}^{j}\epsilon^2(1-\epsilon)^{j-2}\int_{A_2}\ldots\int_{A_j} q_{bj}^{(e)}\Omega_{ji}\, dA_j \ldots \Omega_{21}\, dA_2 \tag{3-12}$$

In order to obtain a suitable representation for the integrals in eq 3-12 we need to express the temperature T_σ in terms of the intrinsic phase average temperature $\langle T_\sigma\rangle^\sigma$ and gradients of $\langle T_\sigma\rangle^\sigma$. We begin by noting that $\langle T_\sigma\rangle^\sigma$ is a continuous function everywhere in the region under consideration and thus can be expressed as

$$\langle T_\sigma\rangle^\sigma|_r = \langle T_\sigma\rangle^\sigma + \boldsymbol{r}\cdot\nabla\langle T_\sigma\rangle^\sigma + \frac{1}{2}\boldsymbol{rr}:\nabla\nabla\langle T_\sigma\rangle^\sigma + \ldots \tag{3-13}$$

Here we use $\langle T_\sigma\rangle^\sigma$ to represent the intrinsic phase average temperature at the centroid of the averaging volume and $\boldsymbol{r}$ is the position vector relative to the centroid. The gradients of $\langle T_\sigma\rangle^\sigma$ in eq 3-13 are evaluated at the centroid in keeping with the nature of a Taylor series expansion. Higher order terms could be included in eq 3-13; however, it seems reasonable at this time to restrict the analysis to situations for which eq 3-13 is an adequate representation of the σ-phase temperature field.

At this point it will be useful to introduce Gray's representation (1975) which takes the form

$$T_\sigma = \langle T_\sigma\rangle^\sigma + \tilde{T}_\sigma \qquad \text{(in the } \sigma \text{ phase)} \tag{3-14a}$$

$$T_\sigma = \tilde{T}_\sigma = 0 \qquad \text{(in the } \gamma \text{ phase)} \tag{3-14b}$$

Combining this with eq 3-13 allows us to write

$$T_\sigma|_r = \langle T_\sigma\rangle^\sigma + \tilde{T}_\sigma|_r + \boldsymbol{r}\cdot\nabla\langle T_\sigma\rangle^\sigma + \frac{1}{2}\boldsymbol{rr}:\nabla\nabla\langle T_\sigma\rangle^\sigma \tag{3-15}$$

where $\boldsymbol{r}$ locates a point in the σ phase or on the σ–γ interface.

Thinking back to the notation used in eq 3-12 encourages us to alter the nomenclature at this point and express eq 3-15 as

$$T_j = \langle T_\sigma\rangle^\sigma + \tilde{T}_j + \boldsymbol{r}_j\cdot\nabla\langle T_\sigma\rangle^\sigma + \frac{1}{2}\boldsymbol{r}_j\boldsymbol{r}_j:\nabla\nabla\langle T_\sigma\rangle^\sigma \tag{3-16}$$

where $\boldsymbol{r}_j$ locates a point on the jth surface. In addition to the restriction imposed by eq 3-13 we also assume that we can use an approximation of the type

$$(T + \Delta T)^4 = T^4 + 4T^3\Delta T + 6T^2\Delta T^2 \tag{3-17}$$

For values of T on the order of 300 K and values of ΔT on the order of 100 K, this approximation is accurate to better than 6% and its use is consistent with the gray body radiation assumption. Use of eq 3-17 with the representation given by eq 3-16 leads to

$$T_j^4 = (\langle T_\sigma\rangle^\sigma)^4 + 4(\langle T_\sigma\rangle^\sigma)^3\left[\tilde{T}_j + \boldsymbol{r}_j\cdot\nabla\langle T_\sigma\rangle^\sigma + \frac{1}{2}\boldsymbol{r}_j\boldsymbol{r}_j:\nabla\nabla\langle T_\sigma\rangle^\sigma\right] + 6(\langle T_\sigma\rangle^\sigma)^2\left[\tilde{T}_j^2 + (\boldsymbol{r}_j\cdot\nabla\langle T_\sigma\rangle^\sigma)^2 + \left(\frac{1}{2}\boldsymbol{r}_j\boldsymbol{r}_j:\nabla\nabla\langle T_\sigma\rangle^\sigma\right)^2 + 2\tilde{T}_j(\boldsymbol{r}_j\cdot\nabla\langle T_\sigma\rangle^\sigma) + 2(\boldsymbol{r}_j\cdot\nabla\langle T_\sigma\rangle^\sigma)\left(\frac{1}{2}\boldsymbol{r}_j\boldsymbol{r}_j:\nabla\nabla\langle T_\sigma\rangle^\sigma\right) + 2\left(\frac{1}{2}\boldsymbol{r}_j\boldsymbol{r}_j:\nabla\nabla\langle T_\sigma\rangle^\sigma\right)\tilde{T}_j\right] \tag{3-18}$$

It is shown elsewhere (Whitaker, 1977a, section IIIB) that a reasonable representation for $\tilde{T}_\sigma$ is

$$\tilde{T}_\sigma = \boldsymbol{C}_\sigma\cdot\nabla\langle T_\sigma\rangle^\sigma$$

where $\boldsymbol{C}_\sigma$ is determined by the structure of the porous media and the physical properties of the two phases. This equation represents $\tilde{T}_\sigma$ in terms of the gradient of $\langle\tilde{T}_\sigma\rangle^\sigma$ *at some point* $\boldsymbol{r}$ and in order to obtain an expression for T_σ in terms of functions evaluated at the centroid, we make use of a Taylor series expansion to write

$$\tilde{T}_\sigma = \tilde{T}_j = \mathbf{C}_\sigma\cdot(\nabla\langle \mathrm{T}_\sigma\rangle^\sigma + \boldsymbol{r}_j\cdot\nabla\nabla\langle T_\sigma\rangle^\sigma) \tag{3-19}$$

Here the vector $\boldsymbol{C}_\sigma$ is evaluated at the position denoted by $\boldsymbol{r}_j$ while the gradients of the temperature are evaluated at the centroid of the averaging volume.

Substitution of eq 3-19 into eq 3-18 leads to

$$T_j^4 = (\langle T_\sigma\rangle^\sigma)^4 + 4(\langle T_\sigma\rangle^\sigma)^3\left\{(\boldsymbol{C}_\sigma + \boldsymbol{r}_j)\cdot\nabla\langle T_\sigma\rangle^\sigma + \left(\frac{1}{2}\boldsymbol{r}_j\boldsymbol{r}_j + \boldsymbol{C}_\sigma\boldsymbol{r}_j\right):\nabla\nabla\langle T_\sigma\rangle^\sigma\right\} + 6(\langle T_\sigma\rangle^\sigma)^2\left\{(\boldsymbol{C}_\sigma\boldsymbol{C}_\sigma + 2\boldsymbol{C}_\sigma\boldsymbol{r}_j + \boldsymbol{r}_j\boldsymbol{r}_j):\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma + (\boldsymbol{r}_j\boldsymbol{r}_j\boldsymbol{r}_j + \boldsymbol{C}_\sigma\boldsymbol{r}_j\boldsymbol{r}_j + 2\boldsymbol{C}_\sigma\boldsymbol{C}_\sigma\boldsymbol{r}_j + 2\boldsymbol{r}_j\boldsymbol{C}_\sigma\boldsymbol{r}_j)\vdots(\nabla\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma) + \left(\frac{1}{4}\boldsymbol{r}_j\boldsymbol{r}_j\boldsymbol{r}_j\boldsymbol{r}_j + \boldsymbol{C}_\sigma\boldsymbol{r}_j\boldsymbol{r}_j\boldsymbol{r}_j + \boldsymbol{C}_\sigma\boldsymbol{r}_j\boldsymbol{c}_\sigma\boldsymbol{r}_j\right)::(\nabla\nabla\langle T_\sigma\rangle^\sigma\nabla\nabla\langle T_\sigma\rangle^\sigma)\right\} \tag{3-20}$$

Here we should remember that all functions on the right hand side of eq 3-20 are evaluated at the centroid of the averaging volume with the exception of $\boldsymbol{C}_\sigma$ which is evaluated at $\boldsymbol{r}_j$.

We can simplify eq 3-20 by neglecting some of the terms that are multiplied by $(\langle T_\sigma\rangle^\sigma)^2$. An order of magnitude analysis yields

$$\boldsymbol{C}_\sigma\cdot\nabla\langle T_\sigma\rangle^\sigma = \boldsymbol{O}\left[\left(\frac{C_\sigma}{L}\right)\Delta T\right] \tag{3-21a}$$

$$\boldsymbol{r}_j\cdot\nabla\langle T_\sigma\rangle^\sigma = \boldsymbol{O}\left[\left(\frac{r_0}{L}\right)\Delta T\right] \tag{3-21b}$$

$$\frac{1}{2}\boldsymbol{r}_j\boldsymbol{r}_j:\nabla\nabla\langle T_\sigma\rangle^\sigma = \boldsymbol{O}\left[\left(\frac{r_0}{L}\right)^2\Delta T\right] \tag{3-21c}$$

where r_0 is the radius of the averaging volume and ΔT represents the maximum temperature change that occurs in the system. The length L is illustrated in Figure 2. Since the terms in eq 3-20 that are multiplied by $(\langle T_\sigma\rangle^\sigma)^2$ will be of secondary importance, it seems reasonable to drop terms of order $(r_0/L)^4$ and $(r_0/L)^3$ relative to terms of order $(r_0/L)^2$ in the groups of terms multipled by $(\langle T_\sigma\rangle^\sigma)^2$. This allows us to simplify eq 3-20 to

$$T_j^4 = (\langle T_\sigma\rangle^\sigma)^4 + 4(\langle T_\sigma\rangle^\sigma)^3\left\{(\boldsymbol{C}_\sigma + \boldsymbol{r}_j)\cdot\nabla\langle T_\sigma\rangle^\sigma + \left(\frac{1}{2}\boldsymbol{r}_j\boldsymbol{r}_j + C_\sigma\boldsymbol{r}_j\right):\nabla\nabla\langle T_\sigma\rangle^\sigma\right\} + (6\langle T_\sigma\rangle^\sigma)^2\{(\boldsymbol{C}_\sigma\boldsymbol{C}_\sigma + 2\boldsymbol{C}_\sigma\boldsymbol{r}_j + \boldsymbol{r}_j\boldsymbol{r}_j):\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma\} \tag{3-22}$$

Here we have also used $C_\sigma \ll L$, a result that follows from the assumption that $\tilde{T}_\sigma \ll \Delta\langle T_\sigma\rangle^\sigma$. This latter constraint is generally valid when the principle of local thermal equilibrium applies (Whitaker, 1980, section IIIC).

In order to simplify eq 3-22 we define the vector γ_j and the tensors $\mathbf{B}_j$ and $\mathbf{C}_j$ as

$$\lambda_j = 4(\mathbf{C}_\sigma + \boldsymbol{r}_j) \tag{3-23}$$

$$\mathbf{B}_j = 2\boldsymbol{r}_j\boldsymbol{r}_j + 4\boldsymbol{C}_\sigma\boldsymbol{r}_j \tag{3-24}$$

$$\mathbf{C}_j = 6[\boldsymbol{C}_\sigma\boldsymbol{C}_\sigma + 2\boldsymbol{C}_\sigma\boldsymbol{r}_j + \boldsymbol{r}_j\boldsymbol{r}_j] \tag{3-25}$$

so that eq 3-22 takes the form

$$T_j^4 = (\langle T_\sigma\rangle^\sigma)^4 + (\langle T_\sigma\rangle^\sigma)^3\lambda_j\cdot\nabla\langle T_\sigma\rangle^\sigma + (\langle T_\sigma\rangle^\sigma)^3\mathbf{B}_j:\nabla\nabla\langle T_\sigma\rangle^\sigma + (\langle T_\sigma\rangle^\sigma)^2\mathbf{C}_j:\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma \tag{3-26}$$

The black body radiant energy flux can now be written as

$$q_{bj}^{(e)} = \sigma T_j^4 = \sigma(\langle T_\sigma\rangle^\sigma)^4 + \sigma(\langle T_\sigma\rangle^\sigma)^3\mathbf{B}_j{:}\nabla\nabla\langle T_\sigma\rangle^\sigma + \sigma(\langle T_\sigma\rangle^\sigma)^3\boldsymbol{\lambda}_j{\cdot}\nabla\langle T_\sigma\rangle^\sigma + \sigma(\langle T_\sigma\rangle^\sigma)^2\mathbf{C}_j{:}\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma \quad (3\text{-}27)$$

where σ is the Stefan–Boltzmann constant.

We wish to use this result in eq 3-12; however, in order to simplify the resulting expression we define an operator $\mathcal{L}(\psi_j)$ as

$$\mathcal{L}(\psi_j) = \sum_{j=2}^{j=N}\prod_2^j \epsilon^2(1-\epsilon)^{j-2}\int_{A_2}\ldots\int_{A_j}\psi_j\Omega_{ji}\,dA_j\ldots\Omega_{21}\,dA_2 \quad (3\text{-}28)$$

This allows us to express eq 3-12 in the form

$$\boldsymbol{q}_\sigma^{\mathrm{R}}{\cdot}\boldsymbol{n}_{\sigma\gamma} = \epsilon\int_{A_2} q_{b1}^{(e)}\Omega_{12}\,dA_2 - \mathcal{L}(q_{bj}^{(e)}) \quad (3\text{-}29)$$

and use eq 3-27 to obtain

$$\boldsymbol{q}_\sigma^{\mathrm{R}}{\cdot}\boldsymbol{n}_{\sigma\gamma} = \sigma\epsilon\int_{A_2}\{(\langle T_\sigma\rangle^\sigma)^4 + (\langle T_\sigma\rangle^\sigma)^3\mathbf{B}_1{:}\nabla\nabla\langle T_\sigma\rangle^\sigma + (\langle T_\sigma\rangle^\sigma)^3\boldsymbol{\lambda}_1{\cdot}\nabla\langle T_\sigma\rangle^\sigma + (\langle T_\sigma\rangle^\sigma)\mathbf{C}_1{:}\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma\}\Omega_{12}\,dA_2 - \sigma\{(\langle T_\sigma\rangle^\sigma)^4\mathcal{L}(1) + (\langle T_\sigma\rangle^\sigma)^3\mathcal{L}(\mathbf{B}_j){:}\nabla\nabla\langle T_\sigma\rangle^\sigma + (\langle T_\sigma\rangle^\sigma)^3\mathcal{L}(\boldsymbol{\lambda}_j){\cdot}\nabla\langle T_\sigma\rangle^\sigma + (\langle T_\sigma\rangle^\sigma)^2\mathcal{L}(\mathbf{C}_j){:}\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma\} \quad (3\text{-}30)$$

Here we must remember that $\langle T_\sigma\rangle^\sigma$, $\nabla\langle T_\sigma\rangle^\sigma$, etc. are evaluated at the centroid of the averaging volume; thus it is permissible to take these terms outside the area integrals. The radiant energy source term in eq 2-16 can now be expressed as

$$-\frac{1}{V}\int_{A_{\sigma\gamma}}\boldsymbol{q}_\sigma^{\mathrm{R}}{\cdot}\boldsymbol{n}_{\sigma\gamma}\,dA = \sigma(\langle T_\sigma\rangle^\sigma)^4 S + \sigma(\langle T_\sigma\rangle^\sigma)^3\mathbf{B}{:}\nabla\nabla\langle T_\sigma\rangle^\sigma + \sigma(\langle T_\sigma\rangle^\sigma)^3\boldsymbol{\lambda}{\cdot}\nabla\langle T_\sigma\rangle^\sigma + \sigma(\langle T_\sigma\rangle^\sigma)^2\mathbf{C}{:}\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma \quad (3\text{-}31)$$

where S, $\mathbf{B}$, λ, and $\mathbf{C}$ are defined by

$$S = \frac{1}{V}\int_{A_1}\mathcal{L}(1) - \frac{\epsilon}{V}\int_{A_1}\int_{A_2}\Omega_{12}\,dA_2\,dA_1 \quad (3\text{-}32)$$

$$\mathbf{B} = \frac{1}{V}\int_{A_1}\mathcal{L}(\mathbf{B}_j)\,dA_1 - \frac{\epsilon}{V}\int_{A_1}\int_{A_2}\mathbf{B}_1\Omega_{12}\,dA_2\,dA_1 \quad (3\text{-}33)$$

$$\boldsymbol{\lambda} = \frac{1}{V}\int_{A_1}\mathcal{L}(\boldsymbol{\lambda}_j)\,dA_1 - \frac{\epsilon}{V}\int_{A_1}\int_{A_2}\boldsymbol{\lambda}_1\Omega_{12}\,dA_2\,dA_1 \quad (3\text{-}34)$$

$$\mathbf{C} = \frac{1}{V}\int_{A_1}\mathcal{L}(\mathbf{C}_j)dA_1 - \frac{\epsilon}{V}\int_{A_1}\int_{A_2}\mathbf{C}_1\Omega_{12}\,dA_2\,dA_1 \quad (3\text{-}35)$$

Clearly the radiant energy source term must be zero when the temperature is uniform; thus the scalar S is zero and eq 3-31 simplifies to

$$-\frac{1}{V}\int_{A_{\sigma\gamma}}\boldsymbol{q}_\sigma^{\mathrm{R}}{\cdot}\boldsymbol{n}_{\sigma\gamma}\,dA = \sigma(\langle T_\sigma\rangle^\sigma)^3\mathbf{B}{:}\nabla\nabla\langle T_\sigma\rangle^\sigma + \sigma(\langle T_\sigma\rangle^\sigma)^3\boldsymbol{\lambda}{\cdot}\nabla\langle T_\sigma\rangle^\sigma + \sigma(\langle T_\sigma\rangle^\sigma)^2\mathbf{C}{:}\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma \quad (3\text{-}36)$$

Before returning to the total energy transport process outlined in section 2, we need to discuss the tensor $\mathbf{B}$ and the vector λ appearing in eq 3-36. Obviously the term $\sigma(\langle T_\sigma\rangle^\sigma)^3\,\mathbf{B}$ will play the role of a radiant energy conductivity tensor, while the term $\sigma(\langle T_\sigma\rangle^\sigma)^3\,\lambda$ may be a dominant factor in describing radiant energy transport in anisotropic porous media such as the monolith catalytic converter discussed by Young and Finlayson (1976). The term $\sigma(\langle T_\sigma\rangle^\sigma)^2\,\mathbf{C}$ could be thought of as a manifestation of the inherently nonlinear process of radiant energy transfer. By referring to eq 3-23 through 3-25 and eq 3-33 through 3-35 we see that $\mathbf{B}$, λ, and $\mathbf{C}$ are functions of the geometry of the porous media and the emissivity. In addition, we note that these quantities depend on the vector $\mathbf{C}_\sigma$ and therefore can depend on a number of other parameters (Whitaker, 1977a, section IIIB). For an isotropic porous media we require that

$$\boldsymbol{\lambda} = 0; \qquad \mathbf{B} = B\mathbf{U}; \qquad \mathbf{C} = C\mathbf{U} \quad (3\text{-}37)$$

and the source term resembles that which one encounters in the diffusion theory of absorbing–emitting media (Siegel and Howell, 1972; Chapter 19). For an anisotropic porous media the components of $\mathbf{B}$ and $\mathbf{C}$ must be determined experimentally, although certain constraints can be imposed for the special case of a transversely isotropic media allowing $\mathbf{B}$ and $\mathbf{C}$ to be specified in terms of only two distinct components. This is an important simplification which would be applicable, for example, to the typical monolith catalytic converter.

The vector λ for an anisotropic porous media presents something of a problem for there is *no single vector* that uniquely characterizes an anisotropic system. In thinking about an anisotropic porous media we should note that there are structural effects and spatial effects. For example, a porous media constructed of randomly arranged spheres should have no structural anisotropy; however, if the average distance between the spheres is a function of position, the system will be anisotropic because of the nonhomogeneity. In this case, the vector, $\nabla\epsilon_\gamma$ characterizes the anisotropy and we have an example of a spatial effect. As an example of a porous media having both structural and spatial anisotropy, we could think of a porous media constructed of regularly arranged ellipsoids whose orientation is designated by a vector ω. We could think of this vector as being parallel to the major axis and having a magnitude proportional to $(a-b)/a$ where a and b are the major and minor axis. Such a system has an obvious structural anisotropy; however, if the ratio a/b depends on position we have a spatial anisotropy characterized by $\nabla(a/b)$. If, in addition, there is a variation in the void fraction, the anisotropy is characterized by ω, $\nabla(a/b)$, and $\nabla\epsilon_\gamma$. It seems possible that the vector λ may depend on both structural and spatial anisotropic effects; however, there is some analysis available to us that suggests that λ depends on the spatial anisotropy described by $\nabla\epsilon_\gamma$. This analysis is presented in the following paragraphs.

Earlier we noted that the gas was transparent to radiation so that

$$\nabla{\cdot}\boldsymbol{q}_\gamma^{\mathrm{R}} = 0 \quad (3\text{-}38)$$

Volume averaging this result leads to

$$\langle\nabla{\cdot}\boldsymbol{q}_\gamma^{\mathrm{R}}\rangle = \nabla{\cdot}\langle\boldsymbol{q}_\gamma^{\mathrm{R}}\rangle + \frac{1}{V}\int_{A_{\gamma\sigma}}\boldsymbol{q}_\gamma^{\mathrm{R}}{\cdot}\boldsymbol{n}_{\gamma\sigma}\,dA = 0 \quad (3\text{-}39)$$

At the solid–gas interface the radiant energy flux must satisfy the condition

$$\boldsymbol{q}_\sigma^{\mathrm{R}}{\cdot}\boldsymbol{n}_{\sigma\gamma} + \boldsymbol{q}_\gamma^{\mathrm{R}}{\cdot}\boldsymbol{n}_{\gamma\sigma} = 0 \quad (3\text{-}40)$$

(note that the individual balancing of the conductive and radiant energy fluxes occurs only because the gas is assumed to be transparent to radiation) so that eq 3-36 can be used along with eq 3-39 to obtain

$$0 = \nabla{\cdot}\langle\boldsymbol{q}_\gamma^{\mathrm{R}}\rangle + \sigma(\langle T_\sigma\rangle^\sigma)^3\mathbf{B}{:}\nabla\nabla\langle T_\sigma\rangle^\sigma + \sigma(\langle T_\sigma\rangle^\sigma)^3\boldsymbol{\lambda}{\cdot}\nabla\langle T_\sigma\rangle^\sigma + \sigma(\langle T_\sigma\rangle^\sigma)^2\mathbf{C}{:}\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma \quad (3\text{-}41)$$

Use of eq 2-11 for the gas phase leads to

$$\nabla{\cdot}\langle\boldsymbol{q}_\gamma^{\mathrm{R}}\rangle = \frac{1}{V}\int_{A_{\gamma e}}\boldsymbol{q}_\gamma^{\mathrm{R}}{\cdot}\boldsymbol{n}_\gamma\,dA \quad (3\text{-}42)$$

where $A_{\gamma e}$ is the area of entrances and exits for the γ phase contained within the averaging volume. A portion of $A_{\gamma e}$ and the unit normal vector $\boldsymbol{n}_\gamma$ are shown in Figure 1. Use of eq 3-42 in eq 3-41 allows us to write

$$\frac{1}{V}\int_{A_{\gamma e}} \boldsymbol{q}_\gamma^{R}\cdot\boldsymbol{n}_\gamma dA = -\sigma(\langle T_\sigma\rangle^\sigma)^3\mathbf{B}:\nabla\nabla\langle T_\sigma\rangle^\sigma - \sigma(\langle T_\sigma\rangle^\sigma)^3\boldsymbol{\lambda}\cdot\nabla\langle T_\sigma\rangle^\sigma - \sigma(\langle T_\sigma\rangle^\sigma)^2\mathbf{C}:\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma \quad (3\text{-}43)$$

We now make use of a representation of the form given by eq 3-14 to write

$$\boldsymbol{q}_\gamma^{R} = \langle \boldsymbol{q}_\gamma^{R}\rangle^\gamma + \tilde{\boldsymbol{q}}_\gamma^{R} \qquad \text{(in the } \gamma \text{ phase)} \quad (3\text{-}44a)$$

$$\boldsymbol{q}_\gamma^{R} = \tilde{\boldsymbol{q}}_\gamma^{R} = 0 \qquad \text{(in the } \sigma \text{ phase)} \quad (3\text{-}44b)$$

This representation allows us to express eq 3-43 as

$$\langle \boldsymbol{q}_\gamma^{R}\rangle^\gamma\cdot\left\{\frac{1}{V}\int_{A_{\gamma e}}\mathbf{n}_\gamma\, dA\right\} + \frac{1}{V}\int_{A_{\gamma e}}\tilde{\boldsymbol{q}}^{R}\cdot\boldsymbol{n}_\gamma\, dA = -\sigma(\langle T_\sigma\rangle^\sigma)^3\mathbf{B}:\nabla\nabla\langle T_\sigma\rangle^\sigma - \sigma(\langle T_\sigma\rangle^\sigma)^3\boldsymbol{\lambda}\cdot\nabla\langle T_\sigma\rangle^\sigma - \sigma(\langle T_\sigma\rangle^\sigma)^2\mathbf{C}:\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma \quad (3\text{-}45)$$

In order to obtain an explicit expression for the area integral of $\boldsymbol{n}_\gamma$, we note that the volume fraction of the gas phase can be written as

$$\epsilon_\gamma = \frac{1}{V}\int_V \alpha_\gamma\, dV = \langle\alpha_\gamma\rangle \quad (3\text{-}46)$$

where $\alpha_\gamma = 1$ in the γ phase and $\alpha_\gamma = 0$ in the σ phase. The analogous form of eq 3-42 for a scalar leads to

$$\nabla\epsilon_\gamma = \nabla\langle\alpha_\gamma\rangle = \frac{1}{V}\int_{A_{\gamma e}}\alpha_\gamma\boldsymbol{n}_\gamma\, dA = \frac{1}{V}\int_{A_{\gamma e}}\boldsymbol{n}_\gamma\, dA \quad (3\text{-}47)$$

Substitution of this relation into eq 3-45 provides

$$\langle \boldsymbol{q}_\gamma^{R}\rangle^\gamma\cdot\nabla\epsilon_\gamma + \frac{1}{V}\int_{A_{\gamma e}}\tilde{\boldsymbol{q}}_\gamma^{R}\cdot\boldsymbol{n}_\gamma\, dA = -\sigma(\langle T_\sigma\rangle^\sigma)^3\mathbf{B}:\nabla\nabla\langle T_\sigma\rangle^\sigma - \sigma(\langle T_\sigma\rangle^\sigma)^3\boldsymbol{\lambda}\cdot\nabla\langle T_\sigma\rangle^\sigma - \sigma(\langle T_\sigma\rangle^\sigma)^3\mathbf{C}:\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma \quad (3\text{-}48)$$

At this point we *assume* that $\langle \boldsymbol{q}_\gamma^{R}\rangle^\gamma$ is proportional to the temperature gradient and write

$$\langle \boldsymbol{q}_\gamma^{R}\rangle^\gamma \sim -\mathbf{A}\cdot\nabla\langle T_\sigma\rangle^\sigma \quad (3\text{-}49)$$

In using the minus sign in this expression we have in mind that the net radiant energy transport will occur in the direction of decreasing temperature. Thus we expect that the diagonal elements of $\mathbf{A}$ will be positive and for an isotropic medium eq 3-49 would take the form

$$\langle \boldsymbol{q}_\gamma^{R}\rangle^\gamma \sim -A\nabla\langle T_\sigma\rangle^\sigma \quad (3\text{-}50)$$

where A is positive. We now ask what the assumption expressed by eq 3-49 tells us about the area integral of $\boldsymbol{q}_\gamma^{R}$ in eq 3-48. To begin with, it would seem to be consistent to assume that

$$\tilde{\boldsymbol{q}}_\gamma^{R} \sim \mathbf{D}\cdot\nabla\langle T_\sigma\rangle^\sigma \quad (3\text{-}51)$$

and we can use the divergence theorem to show that

$$\frac{1}{V}\int_{A_{\gamma e}}\tilde{\boldsymbol{q}}_\gamma^{R}\cdot\boldsymbol{n}_\gamma\, dA = \langle\nabla\cdot\tilde{\boldsymbol{q}}_\gamma^{R}\rangle - \frac{1}{V}\int_{A_{\gamma\sigma}}\tilde{\boldsymbol{q}}_\gamma^{R}\cdot\boldsymbol{n}_{\gamma\sigma}\, dA \quad (3\text{-}52)$$

In view of eq 3-51, we see that the first term on the right-hand side of eq 3-52 should be of the form $\nabla\cdot\mathbf{D}\cdot\nabla\langle T_\sigma\rangle^\sigma$. This encourages us to write

$$\frac{1}{V}\int_{A_{\gamma e}}\tilde{\boldsymbol{q}}_\gamma^{R}\cdot\boldsymbol{n}_\gamma\, dA \sim \nabla\cdot(\mathbf{D}\cdot\nabla\langle T_\sigma\rangle^\sigma) \quad (3\text{-}53)$$

Comparing eq 3-48, 3-49, and 3-53 *suggests* the separation

$$\langle \boldsymbol{q}_\gamma^{R}\rangle^\gamma\cdot\nabla\epsilon_\gamma \sim -\sigma(\langle T_\sigma\rangle^\sigma)^3\boldsymbol{\lambda}\cdot\nabla\langle T_\sigma\rangle^\sigma \quad (3\text{-}54)$$

$$\frac{1}{V}\int_{A_{\gamma e}}\boldsymbol{q}_\gamma^{R}\cdot\boldsymbol{n}_\gamma dA \sim -\sigma(\langle T_\sigma\rangle^\sigma)^3\mathbf{B}:\nabla\nabla\langle T_\sigma\rangle^\sigma - \sigma(\langle T_\sigma\rangle^\sigma)\mathbf{C}:\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma \quad (3\text{-}55)$$

and we conclude that $\boldsymbol{\lambda}$ is of the form

$$\boldsymbol{\lambda} = \nabla\epsilon_\gamma\cdot\mathbf{A} \quad (3\text{-}56)$$

This indicates that the *strictly anisotropic part* of the radiant energy source term given by eq 3-36 is proportional to $\nabla\epsilon_\gamma$, and we express that source term as

$$-\frac{1}{V}\int_{A_{\sigma\gamma}}\boldsymbol{q}_\sigma^{R}\cdot\boldsymbol{n}_{\sigma\gamma}\, dA = \sigma(\langle T_\sigma\rangle^\sigma)^3\mathbf{B}:\nabla\nabla\langle T_\sigma\rangle^\sigma + \sigma(\langle T_\sigma\rangle^\sigma)^3\nabla\epsilon_\gamma\cdot\mathbf{A}\cdot\nabla\langle T_\sigma\rangle^\sigma + \sigma(\langle T_\sigma\rangle^\sigma)^3\mathbf{C}:\nabla\langle T_\sigma\rangle^\sigma\nabla\langle T_\sigma\rangle^\sigma \quad (3\text{-}57)$$

One should be careful to note that the development given by eq 3-38 through 3-56 *suggests, but does not prove*, that $\boldsymbol{\lambda}$ is a linear function of $\nabla\epsilon_\gamma$. The precise functional dependence is contained in eq 3-23, 3-28, and 3-34; however, there seems to be no simple method of extracting more information about $\boldsymbol{\lambda}$ from these equations. It seems possible that $\mathbf{A}$ depends only on structural anisotropic effects, thus for a packed bed a spheres $\mathbf{A}$ would be an isotropic tensor.

4. Total Energy Transport

We are now in a position to return to our analysis of the solid and gas-phase energy transport equations given by eq 2-16 and 2-17. We begin by using a theorem presented by Gray (1975) which states that

$$\langle T\sigma\rangle^\sigma\nabla\epsilon_\sigma = \frac{1}{V}\int_{A_{\sigma\gamma}}(\tilde{T}_\sigma - T_\sigma)\boldsymbol{n}_{\sigma\gamma}\, dA \quad (4\text{-}1)$$

This result allows us to express the first term on the right-hand side of eq 2-16 as

$$\nabla\cdot\left\{k_\sigma\left[\nabla(\epsilon_\sigma\langle T_\sigma\rangle^\sigma) + \frac{1}{V}\int_{A_{\sigma\gamma}}T_\sigma\boldsymbol{n}_{\sigma\gamma}\, dA\right]\right\} = \nabla\cdot\left\{k_\sigma\left[\epsilon_\sigma\nabla\langle T_\sigma\rangle^\sigma + \frac{1}{V}\int_{A_{\sigma\gamma}}\tilde{T}_\sigma\boldsymbol{n}_{\sigma\gamma}\, dA\right]\right\} \quad (4\text{-}2)$$

We can make use of eq 3-19 to write

$$\frac{1}{V}\int_{A_{\sigma\gamma}}\tilde{T}_\sigma\boldsymbol{n}_{\sigma\gamma}\, dA = \frac{1}{V}\int_{A_{\sigma\gamma}}\boldsymbol{C}_\sigma\cdot\nabla\langle T_\sigma\rangle^\sigma\boldsymbol{n}_{\sigma\gamma}\, dA \quad (4\text{-}3)$$
$$= \left\{\frac{1}{V}\int_{A_{\sigma\gamma}}\boldsymbol{n}_{\sigma\gamma}\boldsymbol{C}_\sigma\, dA\right\}\cdot\nabla\langle T_\sigma\rangle^\sigma$$
$$= \mathbf{K}_{\sigma\gamma}\cdot\nabla\langle T_\sigma\rangle^\sigma$$

Use of eq 4-3 and 4-2 now allows us to express eq 2-16 in the form

$$\epsilon_\sigma\rho_\sigma(C_p)_\sigma\frac{\partial\langle T_\sigma\rangle^\sigma}{\partial t} = \nabla\cdot\{k_\sigma[\epsilon_\sigma\nabla\langle T_\sigma\rangle^\sigma + \mathbf{K}_{\sigma\gamma}\cdot\nabla\langle T_\sigma\rangle^\sigma]\} - \frac{1}{V}\int_{A_{\sigma\gamma}}(\boldsymbol{q}_\sigma + \boldsymbol{q}_\sigma^{R})\cdot\boldsymbol{n}_{\sigma\gamma}\, dA \quad (4\text{-}4)$$

Here it should be clear that the first term on the right-hand side of eq 4-4 can be expressed in terms of a solid phase *effective thermal conductivity tensor* which takes the form

$$\mathbf{K}_\sigma^{\text{eff}} = k_\sigma[\epsilon_\sigma\mathbf{U} + \mathbf{K}_{\sigma\gamma}] \quad (4\text{-}5)$$

The analysis leading to eq 4-4 can be repeated for the gas phase allowing us to express eq 2-17 in the form

$$\epsilon_\gamma \rho_\gamma (c_p)_\gamma \frac{\partial \langle T_\gamma \rangle^\gamma}{\partial t} = \nabla \cdot \{k_\gamma [\epsilon_\gamma \nabla \langle T_\gamma \rangle^\gamma + \mathbf{K}_{\gamma\sigma} \cdot \nabla \langle T_\gamma \rangle^\gamma]\} - \frac{1}{V} \int_{A_{\gamma\sigma}} \boldsymbol{q}_\gamma \cdot \boldsymbol{n}_{\gamma\sigma} \, dA \quad (4\text{-}6)$$

If the temperatures $\langle T_\sigma \rangle^\sigma$ and $\langle T_\gamma \rangle^\gamma$ need to be determined, then we must propose a representation for the nonradiative heat flux terms in eq 4-4 and 4-5. For a stagnant fluid in a porous media, this is usually not necessary because conduction dominates and the assumption of *local thermal equilibrium* is valid (Whitaker, 1980, section IIIC). In the event of significant convective transport in the gas phase, eq 4-6 can be modified following procedures outlined elsewhere (Whitaker, 1977a, section IVB). In that case, film heat transfer coefficients will be needed and the recent work of Schlünder (1978) should be consulted.

The assumption of local thermal equilibrium is best understood by defining a new spatial deviation according to

$$\langle T_\sigma \rangle^\sigma = \langle T \rangle + \hat{T}_\sigma \quad (4\text{-}7a)$$

$$\langle T_\gamma \rangle^\gamma = \langle T \rangle + \hat{T}_\gamma \quad (4\text{-}7b)$$

and noting that the assumption requires that

$$\frac{\partial \hat{T}_\sigma}{\partial t} \ll \frac{\partial \langle T \rangle}{\partial t} \text{ and } \nabla \hat{T}_\sigma \ll \nabla \langle T \rangle \quad (4\text{-}8)$$

along with comparable constraints for $\hat{T}_\gamma$. The spatial average temperature $\langle T \rangle$ is defined by eq 2-3 and can be explicitly represented as

$$\langle T \rangle = \epsilon_\sigma \langle T_\sigma \rangle^\sigma + \epsilon_\gamma \langle T_\gamma \rangle^\gamma \quad (4\text{-}9)$$

Imposing the assumption of local thermal equilibrium allows us to add eq 4-4 and 4-6 to obtain

$$\langle \rho \rangle C_p \frac{\partial \langle T \rangle}{\partial t} = \nabla \cdot \{\mathbf{K}_{\text{eff}} \cdot \nabla \langle T \rangle\} - \frac{1}{V} \int_{A_{\sigma\gamma}} \boldsymbol{q}_\sigma^{\text{R}} \cdot \boldsymbol{n}_{\sigma\gamma} \, dA \quad (4\text{-}10)$$

where C_p is the mass fraction weighted constant pressure heat capacity and $\mathbf{K}_{\text{eff}}$ is the effective thermal conductivity defined by

$$\mathbf{K}_{\text{eff}} = k_\sigma [\epsilon_\sigma \mathbf{U} + \mathbf{K}_{\sigma\gamma}] + k_\gamma [\epsilon_\gamma \mathbf{U} + \mathbf{K}_{\gamma\sigma}] \quad (4\text{-}11)$$

A few lines of analysis can be used to show that the assumption of local thermal equilibrium is consistent with

$$\tilde{T}_\sigma = \tilde{T}_\gamma \text{ over } A_{\sigma\gamma} \quad (4\text{-}12)$$

thus the term $\mathbf{K}_{\gamma\sigma} \cdot \nabla \langle T_\gamma \rangle^\gamma$ can be expressed as

$$\begin{aligned} K_{\gamma\sigma} \cdot \nabla \langle T_\gamma \rangle^\gamma &= \frac{1}{V} \int_{A_{\gamma\sigma}} \tilde{T}_\gamma \boldsymbol{n}_{\gamma\sigma} \, dA = \frac{1}{V} \int_{A_{\gamma\sigma}} \tilde{T}_\sigma \boldsymbol{n}_{\gamma\sigma} \, dA \\ &= -\frac{1}{V} \int_{A_{\sigma\gamma}} \tilde{T}_\sigma \boldsymbol{n}_{\sigma\gamma} \, dA \quad (4\text{-}13) \\ &= -\mathbf{K}_{\sigma\gamma} \cdot \nabla \langle T_\sigma \rangle^\sigma \end{aligned}$$

Since local thermal equilibrium is also consistent with $\nabla \langle T_\sigma \rangle^\sigma = \nabla \langle T_\gamma \rangle^\gamma$ we have

$$\mathbf{K}_{\gamma\sigma} = -\mathbf{K}_{\sigma\gamma} \quad (4\text{-}14)$$

and we can express the effective thermal conductivity as

$$\mathbf{K}_{\text{eff}} = (\epsilon_\sigma k_\sigma + \epsilon_\gamma k_\gamma) \mathbf{U} + (k_\sigma - k_\gamma) \mathbf{K}_{\sigma\gamma} \quad (4\text{-}15)$$

The assumption of local thermal equilibrium, which allowed us to combine eq 4-4 and 4-6 to obtain eq 4-10, has been considered at some length elsewhere (Whitaker, 1980, section IIIC). For practical purposes, the assumption is valid when the process is "slow" and when the characteristic length scales for the σ and γ phases are small compared to the characteristic length scale for the porous media. If we designate the characteristic time of the process as τ, the necessary constraints can be expressed as

$$\frac{\epsilon_\omega \rho_\omega (c_p)_\omega}{\tau (A_{\sigma\gamma}/V)} \left(\frac{\ell_\sigma}{k_\sigma} + \frac{\ell_\gamma}{k_\gamma} \right) \ll 1 \quad (4\text{-}16)$$

$$\frac{\epsilon_\omega k_\omega}{L^2 (A_{\sigma\gamma}/V)} \left(\frac{\ell_\sigma}{k_\sigma} + \frac{\ell_\gamma}{k_\gamma} \right) \ll 1 \quad (4\text{-}17)$$

where ω represents both σ and γ. The length L is indicated in Figure 2 and ℓ_σ and ℓ_γ are the characteristic lengths for the σ and γ phases. We can think of these as the particle size and pore size, respectively.

At this point we need only include our representation of the radiant energy source term given by eq 3-57 in order to obtain the final form of the thermal energy transport equation.

$$\langle \rho \rangle C_p \frac{\partial \langle T \rangle}{\partial t} = \nabla \cdot \{\mathbf{K}_{\text{eff}} \cdot \nabla \langle T \rangle\} + \sigma \langle T \rangle^3 \mathbf{B} : \nabla \nabla \langle T \rangle + \sigma \langle T \rangle^3 \nabla \epsilon_\gamma \cdot \mathbf{A} \cdot \nabla \langle T \rangle + \sigma \langle T \rangle^3 \mathbf{C} : \nabla \langle T \rangle \nabla \langle T \rangle \quad (4\text{-}18)$$

This result is similar to the energy equation obtained for combined conduction and radiation in an absorbing–emitting media (Siegel and Howell, 1972, Chapter 19) when the so-called "diffusion method" is used. In that case, the term involving $\nabla \epsilon_\gamma$ does not appear because there is only one phase. However, near solid boundaries the diffusion method does not apply because the radiation field is anisotropic.

Temperature Profiles

While we will avoid a detailed comparison between theory and experiment, it will be of interest to know something about the temperature profiles predicted by eq 4-18. In particular, it will be interesting to use eq 4-18 to model the absorbing-emitting gas which has been studied extensively. We can do this by thinking of the solid particles shown in Figure 1 as being arbitrarily small while requiring that ϵ_γ remain constant. If we then restrict our analysis to the steady state and consider temperature gradients which are small enough so that the last term in eq 4-18 can be dropped, we obtain

$$0 = \nabla \cdot \{\mathbf{K}_{\text{eff}} \cdot \nabla \langle T \rangle\} + \sigma \langle T \rangle^3 \mathbf{B} : \nabla \nabla \langle T \rangle + \sigma \langle T \rangle^3 A \nabla \epsilon_\gamma \cdot \nabla \langle T \rangle \quad (4\text{-}19)$$

Here we have in mind that the solid particles are spherical so that there is no structural anisotropy and the tensor $\mathbf{A}$ can be expressed as

$$\mathbf{A} = A\mathbf{U} \quad (4\text{-}20)$$

where A is a positive scalar.

We now consider the steady, one-dimensional heat conduction process illustrated in Figure 5. There we have shown an absorbing-emitting media in contact with a wall, and we have also illustrated several averaging volumes in the neighborhood of the wall. It should be understood that nothing in the theory restricts the location of the averaging volume; thus it need not be restricted to the absorbing-emitting phase. Indeed, if one wishes to determine $\langle T \rangle$ at the phase interface, an averaging volume must be placed with its centroid at the interface. This method of treating volume averaged quantities at a phase interface is sug-

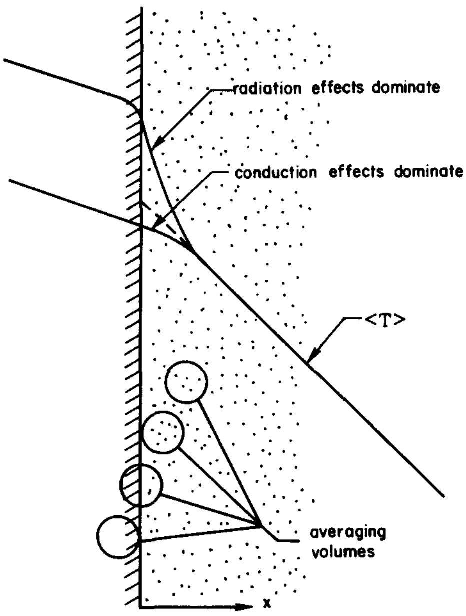

Figure 5. Heat conduction in an absorbing–emitting media.

gested by Slattery (1972, p 207).

The one dimensional form of eq 4-20 can be expressed as

$$0 = \frac{\partial}{\partial x}\left\{K_{\text{eff}}\frac{\partial\langle T\rangle}{\partial x}\right\} + \sigma\langle T\rangle^3 B\frac{\partial^2\langle T\rangle}{\partial x^2} + \sigma\langle T\rangle^3 A\left(\frac{\partial\epsilon_\gamma}{\partial x}\right)\frac{\partial\langle T\rangle}{\partial x} \quad (4\text{–}21)$$

or in expanded form as

$$0 = (K_{\text{eff}} + \sigma\langle T\rangle^3 B)\frac{\partial^2\langle T\rangle}{\partial x^2} + \left[\frac{K_{\text{eff}}}{\partial x} + \sigma\langle T\rangle^3 A\left(\frac{\partial\epsilon_\gamma}{\partial x}\right)\right]\frac{\partial\langle T\rangle}{\partial x} \quad (4\text{–}22)$$

The sign of the second derivative can be determined by arranging this result as

$$(K_{\text{eff}} + \sigma\langle T\rangle^3 B)\frac{\partial^2\langle T\rangle}{\partial_x{}^2} = -\left[\underset{(-)}{\frac{\partial K_{\text{eff}}}{\partial x}} + \sigma\langle T\rangle^3 A\underset{(+)}{\left(\frac{\partial\epsilon_\gamma}{\partial x}\right)}\right]\underset{(-)}{\frac{\partial\langle T\rangle}{\partial x}} \quad (4\text{–}23)$$

Under each term we have indicated the sign of the term in the region near the wall. In assigning $\partial K_{\text{eff}}/\partial x$ a negative value we have in mind the common situation in which the thermal conductivity of the wall is greater than the effective thermal conductivity of the absorbing–emitting media. Obviously $\partial\epsilon_\gamma/\partial x$ is positive in the region near the wall, and from eq 4-23 we deduce that

$$\frac{\partial^2\langle T\rangle}{\partial x^2} > 0 \quad \text{(owing to radiation effects)}$$

$$\frac{\partial^2\langle T\rangle}{\partial x^2} < 0 \quad \text{(owing to conduction effects)}$$

The uppermost curve shown in Figure 5 is similar to the exact solution for the temperature profile in an absorbing-emitting gas (Siegel and Howell, 1972, p 640) and it gives rise to the so-called temperature *slip coefficient*

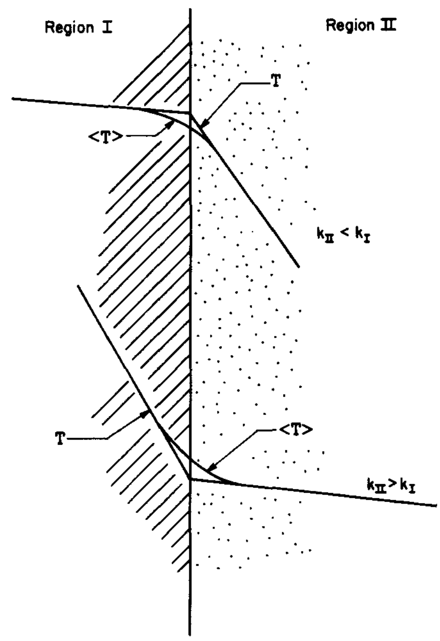

Figure 6. Temperature slip for conductive transport.

(Howell and Goldstein, 1969; Taitel and Hartnett, 1968). It seems unlikely that one would want to analyze heat transfer in an absorbing–emitting gas by means of the volume averaging method since the governing differential equations can be precisely formulated and solved numerically. On the other hand, this is not true of a dusty gas and the method presented here may be of value, provided the solid particles are large enough so that scattering effects can be neglected. In the case of packed beds and porous media, there is no other route to the formulation of governing differential equations and it is of interest to note that the uppermost curve shown in Figure 5 is precisely the type of profile measured experimentally by Hill and Wilhelm (1959).

In considering packed beds, we note that the transport process near the wall is complicated by the fact that the void fraction first *increases* as we approach the wall and then *decreases* as the averaging volume passes out of the bed and into the wall region. In general, the increase is small compared to the overall decrease which requires that the void fraction tend toward zero as the averaging volume passes into the wall. The lower temperature profile illustrated in Figure 5 may be somewhat unappealing since it would give rise to a negative wall heat transfer coefficient. While negative heat transfer coefficients have been observed (Hill and Wilhelm, 1959; Schlunder, 1978), they are not common. This suggests that the radiant energy transport term on the right-hand side of eq 4-23 dominates for most practical situations. That conductive effects can indeed give rise to negative heat transfer coefficients is easily seen by examining point and volume averaged temperature profiles for pure heat conduction in a composite slab. In Figure 6 we have illustrated two temperature profiles which indicate that the temperature slip coefficient *owing to conduction* can change sign depending on the ratio of thermal conductivities. Such an effect may have been observed by Hill and Wilhelm (1959), who found that wall heat transfer coefficients at a Calrod heater were significantly larger than those at a stainless steel wall.

While the use of heat transfer coefficients is an attractive method of overcoming the complexities that exist near phase boundaries, it may be more appropriate under some circumstances to work directly with all the terms in eq 4-23. This possibility is currently being explored.

5. Conclusions

The governing differential equations for conductive and radiative transport in a porous media have been derived directly from the associated point equations. The analysis gives rise to a radiant energy thermal conductivity tensor as expected; however, a convective-like radiant energy transport mechanism also appears. Arguments are presented that suggest that this term is proportional to the void fraction gradient; thus it will make an important contribution in nonhomogeneous porous media and at the bounding surfaces of packed beds.

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Nomenclature

A = area, m^2
$\mathbf{B}$ = linear portion of the radiant energy conductivity tensor, m
$\mathbf{C}$ = nonlinear portion of the radiant energy conductivity tensor, m
C_p = mass fraction weighted constant pressure heat capacity, kcal/kg K
c_p = consatnt pressure heat capacity, kcal/kg K
k = thermal conductivity, kcal/s m K
$\mathbf{K}_{eff}$ = effective thermal conductivity tensor, kcal/s m K
ℓ = characteristic length for a phase, m
L = characteristic length for the system, m
$\boldsymbol{n}$ = unit normal vector
$\boldsymbol{q}$ = heat flux vector, kcal/s m^2
$\boldsymbol{q}^R$ = radiant energy heat flux vector, kcal/s m^2
r_0 = radius of the averaging volume, m
$\mathbf{r}$ = position vector
T = temperature, K
t = time, s
$\mathbf{U}$ = unit tensor
V = averaging volume, m^3
V = volume of a phase, m^3

Greek Letters

α = reflectivity
ϵ = emissivity
$\epsilon_\sigma = V_\sigma/V$, volume fraction of the solid phase
$\epsilon_\gamma = V_\gamma/V$, volume fraction of the solid phase
ρ = reflectivity and mass density, kg/m^3
σ = Stefan–Boltzmann constant, kcal/s m^2 K^4
ρ = density, kg/m^3
λ = radiant energy transport vector
τ = characteristic time, s

Subscripts

σ = denotes a property of the solid phase
γ = denotes a property of the gas phase
$\sigma\gamma$ or $\gamma\sigma$ = denotes a property of the σ–γ interface

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