Longitudinal and Lateral Thermal Dispersion in Packed Beds

Part I: Theory

A new model is developed for the transient thermal response of a packed bed, using the method of spatial averaging. Equations for the average temperature of the fluid and the solid phase are derived from the point equations for thermal energy in each phase. The new model exhibits some unusual convective and dispersive coupling between the equations for the average fluid and solid temperatures. The response of the model equations to a pulse disturbance is analyzed. It is found that after a sufficiently long time has elapsed, the temperature pulses for the fluid and solid phases will be separated by a constant distance and will spread or disperse about their centroids at an equal rate. The pulse separation predicted by the new model equations is larger than that predicted using more conventional analyses of heat transfer in packed beds. Effective thermal conductivities measured under steady state conditions can differ significantly from those observed in transient experiments due to the spread in temperature pulses caused by heat exchange between phases. Estimates are made of the magnitude of the more important terms affecting longitudinal and lateral effective thermal conductivities under flow conditions, in order to make possible a direct comparison between theory and experiment in a companion paper.

J. LEVEC
Department of Chemistry and Chemical Technology
University of Ljubljana
Ljubljana, Yugoslavia
and
R. G. CARBONELL
Department of Chemical Engineering
North Carolina State University
Raleigh, NC 27695

SCOPE

There are many cases where a detailed knowledge of the thermal response of packed beds is desirable. In chemical reactor design it is important to know the thermal transport characteristics of the porous medium in order to make accurate predictions of the variations in reaction rate caused by inlet temperature disturbances (Froment and Bischoff, 1979). In the design of packed bed thermal storage systems, it is again desirable to have good estimates of heat transfer coefficients and effective thermal conductivities so that one can predict the time required to heat up the solid particles (Sáez and McCoy, 1982).

There are many different approaches to the study of the thermal behavior of packed beds, and these have been reviewed recently by Wakao et al. (1979). The models fall basically into two categories. The first type of model uses an equation for the average temperature of the fluid and an equation for the average temperature of the solid. These are coupled by a term for heat exchange between phases. The energy equation for each phase has its own effective thermal conductivity. This type of model was labeled the continuous solid phase model by Wakao et al., and has seen numerous recent applications (Dixon and Cresswell, 1979; Cresswell and Dixon, 1982; Vortmeyer and Berninger, 1982; Vormeyer, 1975). The second type of model also uses an equation for the average fluid temperature, but it couples this equation to the point thermal energy equation for heat conduction in a single particle. The particle is usually treated as being spherical with uniform flux boundary conditions along the surface. Wakao et al. labeled this the dispersion-concentric model, and one can also find recent examples of the use of this approach (Sáez and McCoy, 1982; Sagara et al., 1970). The continuous solid phase model is much easier to analyze since both fluid and solid phase temperature equations are functions only of bed position and time. In the dispersion-concentric model there is the additional variable of radial position inside the individual particles. In both of these types of model the choice of which value of effective thermal conductivity to use is not an easy one, and recent work has centered on the difference between axial effective conductivities under steady and transient conditions (Cresswell and Dixon, 1982; Vortmeyer and Berninger, 1982).

In this paper we develop a new model for the transport of thermal energy in a porous medium using the method of spatial averaging. Since the method of spatial averaging uses the exact point equations and boundary conditions to derive the equations for the average solid and fluid temperatures, it is a more rigorous analysis. However, it also leads to more complex equations with more parameters. In this development, some unusual convective and dispersive coupling terms arise, making the model equations look quite different from those used in previous studies. We investigate the physical nature of these new terms, and we

---

Work performed while the authors were at the Department of Chemical Engineering, University of California, Davis, CA 95616.

analyze the behavior of the model to pulse disturbances. We then make reasonable estimates of the factors influencing the separation of pulses in the fluid and solid phases and the longitudinal and lateral effective thermal conductivities under flow conditions. The results of this paper are compared directly to experimental measurements of pulse velocities, pulse separations, and effective thermal conductivities in Part II of this work.

CONCLUSIONS AND SIGNIFICANCE

The method of spatial averaging is used to develop transport equations for the average temperature of the fluid and solid phases in a packed bed (Eqs. 22 and 23). These equations have convective and dispersive coupling terms of a rather unusual nature, but which have proven to be necessary in obtaining an accurate representation of exact solutions for transient heat transfer problems in capillary tubes (Zanotti and Carbonell, 1983c). The response of the model equations to pulse disturbances is analyzed using the method of moments. It is found that for sufficiently long times (Eq. 35), the pulses of temperature in the fluid and solid phases will move at equal velocities given by Eq. 41. Their mean positions will differ by a constant distance which can be calculated using Eq. 57. The additional convective coupling terms can affect the magnitude of this pulse separation significantly. One can expect that experimental measurements of the distance separating fluid and solid temperature pulses will be larger than those predicted by the more traditional dispersive-concentric or continuous solid phase heat transfer models. For these long times the pulses in the fluid and solid phases will spread about their centroids at equal rates, so that the axial effective thermal conductivity will be given by Eq. 65. One can estimate the magnitude of the major contributions to the pulse separation and to the longitudinal effective thermal conductivity under transient conditions using results for heat conduction for the case of no fluid flow (Nozad, 1983), hydrodynamic dispersion coefficients from mass transfer experiments (Eidsath et al., 1983), effective diffusivities in packed beds (Ryan et al., 1981), and film heat transfer coefficients (Schlünder, 1978). It is found that longitudinal effective thermal conductivities under transient and steady-state conditions can differ significantly due to the spread in temperature pulses caused by heat conduction into the particles. If lateral effective thermal conductivities are computed from steady-state measurements, as is usually the case, one can derive a simple relation to estimate their magnitude from conductivities under no-flow conditions and lateral dispersivities from mass transfer experiments (Han et al., 1983). The results presented in this work are compared directly to experimental data in Part II of this work.

INTRODUCTION

In this paper we use the method of spatial averaging (Slattery, 1972) to derive appropriate forms for the transport equations for thermal energy of the fluid and solid phases in a porous medium. This approach has found a great number of applications recently to problems in diffusion and heat conduction in porous media (Ryan et al., 1981; Nozad, 1983) as well as in the dispersion of solutes in packed beds (Carbonell and Whitaker, 1983; Eidsath et al., 1983). By itself, the method of spatial averaging provides a convenient approach for deriving equations for macroscopic averages of a quantity from local or point equations in a multiphase system. It automatically incorporates the boundary conditions at phase interfaces into the averaged transport equations. However, it still leaves one with a closure problem, namely, how to represent the average fluxes from one phase to another, as well as the dispersive fluxes in the direction of flow and perpendicular to flow. For simple problems in diffusion, heat conduction, and dispersion of an inert solute, closure schemes have been developed which have led to transport equations of the same form as those derived using a more heuristic approach. With a particularly simple structural model of the porous medium, a two-dimensional spatially periodic array of particles, it has even been possible to make a priori calculations of the transport coefficients in the averaged equations. Effective diffusivities, effective thermal conductivities, and dispersion coefficients have all been computed with relatively good comparison with experimental data (Ryan et al., 1981; Nozad, 1983; Eidsath et al., 1983).

In more complex problems involving flow and mass exchange between phases, the closure schemes developed have resulted in rather nontraditional forms of the transport equations for the averaged phase properties (Zanotti and Carbonell, 1983a). The new equations exhibit some unusual convective and dispersive coupling terms which arise directly as a result of the closure scheme. The resulting equations have proven to be an excellent representation of the average system behavior when compared to direct numerical computation in one- and two-phase flow problems in capillary tubes (Zanotti and Carbonell, 1983b). Zanotti and Carbonell (1983c) have studied the role of these terms in controlling heat transfer processes in capillary tubes with conducting walls. In this paper we present a three-dimensional extension of the previous work in order to derive a model that can be used to make direct comparisons between theory and experiments for heat transfer in packed beds.

AVERAGED EQUATIONS

Consider a porous medium with a moving fluid phase β and a stationary solid phase σ. The thermal energy equation valid at each point in the fluid and solid phases takes the form

$$(\rho c_p)_\beta \left[\frac{\partial T_\beta}{\partial t} + \mathbf{v}_\beta \cdot \nabla T_\beta\right] = \nabla \cdot (k_\beta \nabla T_\beta) \qquad \text{in } V_\beta \qquad (1)$$

$$(\rho c_p)_\sigma \frac{\partial T_\sigma}{\partial t} = \nabla \cdot (k_\sigma \nabla T_\sigma) \qquad \text{in } V_\sigma \qquad (2)$$

The velocity $\mathbf{v}_\beta$ is the mass average velocity at each point in the fluid. Throughout the analysis the flow will be treated as incompressible and the density, heat capacity, and thermal conductivity of each phase as being independent of temperature. At the fluid-solid interface the jump boundary condition for thermal energy expresses the continuity of the conductive heat flux at the phase interface

$$\mathbf{n}_{\beta\sigma} \cdot k_\sigma \nabla T_\sigma = \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla T_\beta \qquad \text{on } A_{\beta\sigma}. \qquad (3)$$

Here $\mathbf{n}_{\beta\sigma}$ is a unit normal pointing from the fluid into the solid phase at each point on the interface. We also require that the temperature of the fluid and the solid be the same at the phase interface

$$T_\beta = T_\sigma \qquad \text{on } A_{\beta\sigma} \qquad (4)$$

We would like to derive equations for the intrinsic phase average temperatures in each phase

$$\langle T_\beta \rangle^\beta = \frac{1}{V_\beta}\int_{V_\beta} T_\beta dV; \qquad \langle T_\sigma \rangle^\sigma = \frac{1}{V_\sigma}\int_{V_\sigma} T_\sigma dV \qquad (5)$$

Here V_β and V_σ represent the volume of fluid and solid phases contained within an averaging volume $\mathcal{V}$ whose characteristic dimensions are larger than the characteristic lengths associated with the particles or the fluid spaces between particles. In order to derive equations for the quantities defined in Eq. 5, we use the spatial averaging theorem (Slattery, 1972), and follow the procedures already outlined in detail in recent papers by Carbonell and Whitaker (1983) and Zanotti and Carbonell (1983a). Equations 1 and 2 are formally integrated over the averaging volume $\mathcal{V}$ and the spatial averaging theorem is used to convert the averages of gradients to gradients of averages. The no-slip condition is imposed at the fluid-solid interface ($\mathbf{n}_{\beta\sigma}\cdot\mathbf{v}_\beta = 0$), and the volume fractions of fluid and solid, ϵ_β and ϵ_σ, are taken to be constants. We also define spatial deviations of the point temperatures and the point velocity from their average values

$$\begin{aligned} T_\sigma &= \tilde{T}_\sigma + \langle T_\sigma\rangle^\sigma &&\text{in } V_\sigma \\ T_\beta &= \tilde{T}_\beta + \langle T_\beta\rangle^\beta &&\text{in } V_\beta \\ \mathbf{v}_\beta &= \tilde{\mathbf{v}}_\beta + \langle \mathbf{v}_\beta\rangle^\beta &&\text{in } V_\beta \end{aligned} \tag{6}$$

The volume averages of all the spatial deviations are taken to be equal to zero. The quantity $\langle \mathbf{v}_\beta\rangle^\beta$ is the intrinsic phase average or interstitial average velocity of the fluid phase. The end results of the averaging step are two equations, one for $\langle T_\beta\rangle^\beta$ and one for $\langle T_\sigma\rangle^\sigma$

$$\begin{aligned} (\rho c_p)_\beta \left[\frac{\partial\langle T_\beta\rangle^\beta}{\partial t} + \langle \mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle T_\beta\rangle^\beta\right] &= \nabla\cdot\left\{k_\beta\nabla\langle T_\beta\rangle^\beta + \frac{k_\beta}{V_\beta}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{T}_\beta dA\right\} \\ &\quad - (\rho c_p)_\beta\nabla\cdot\langle\tilde{\mathbf{v}}_\beta\tilde{T}_\beta\rangle^\beta + \frac{1}{V_\beta}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{T}_\beta dA \end{aligned} \tag{7}$$

and

$$\begin{aligned} (\rho c_p)_\sigma\frac{\partial\langle T_\sigma\rangle^\sigma}{\partial t} &= \nabla\cdot\left\{k_\sigma\nabla\langle T_\sigma\rangle^\sigma + \frac{k_\sigma}{V_\sigma}\int_{A_{\beta\sigma}} \mathbf{n}_{\sigma\beta}\tilde{T}_\sigma dA\right\} \\ &\quad + \frac{1}{V_\sigma}\int_{A_{\beta\sigma}} \mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla\tilde{T}_\sigma dA \end{aligned} \tag{8}$$

The equations above require closure relations for three terms: (1) the thermal tortuosity terms involving the area integrals of the spatial deviations in temperature along the interface; (2) the hydrodynamic dispersion term, which is the volume average of the product of spatial deviations in velocity and temperature; and (3) the heat exchange term between phases, which is the area integral of the heat flux at the phase interface. These closure schemes can take the form of a relation between the spatial deviations $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ and the average temperatures $\langle T_\beta\rangle^\beta$ and $\langle T_\sigma\rangle^\sigma$.

Closure Scheme

We can derive the form of these relationships between the spatial deviations and the average temperatures, subject to some reasonable simplifying assumptions. This is done by subtracting the averaged equations, Eqs. 7 and 8, from the point equations, Eqs. 1 and 2, respectively. The result is a pair of transport equations for the spatial deviations $\tilde{T}_\beta$ and $\tilde{T}_\sigma$, shown in detail in Appendix A. The spatial deviations $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ will be functions that vary significantly over distances of the order of the characteristic lengths of the fluid pore spaces and solid particles ℓ_β and ℓ_σ. Any quantity averaged over the averaging volume will undergo significant variations over a length L_T which is characteristic of the distances over which gradients in the average temperature are occurring. In general, given a sufficiently long time since the generation of a disturbance in temperature, the length L_T will be much greater than both ℓ_β and ℓ_σ. Under these conditions, the equations for the spatial deviations can be considered quasi-steady, and we can neglect all gradients of averaged quantities relative to similar gradients of spatial deviations. The end result is the following set of equations for the spatial deviations

$$\begin{aligned} (\rho c_p)_\beta[\tilde{\mathbf{v}}_\beta\cdot\nabla\langle T_\beta\rangle^\beta + \mathbf{v}_\beta\cdot\nabla\tilde{T}_\beta] &= \nabla\cdot(k_\beta\nabla\tilde{T}_\beta) \\ &\quad - \frac{1}{V_\beta}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{T}_\beta dA \end{aligned} \tag{9}$$

and

$$0 = \nabla\cdot(k_\sigma\nabla\tilde{T}_\sigma) - \frac{1}{V_\sigma}\int_{A_{\beta\sigma}} \mathbf{n}_{\sigma\beta}\cdot k_\sigma\nabla\tilde{T}_\sigma dA \tag{10}$$

The constraints that need to be satisfied so that the above equations are valid are the quasi-steady constraints

$$\frac{\alpha_\beta t^*}{\ell_\beta^2}, \frac{\alpha_\sigma t^*}{\ell_\beta^2} \gg 1 \tag{11}$$

and the associated characteristic length constraint

$$L_T \gg \ell_\beta, \ell_\sigma \tag{12}$$

A discussion of how the form of Eqs. 9 and 10 is arrived at can be found in Appendix A.

By substituting the definitions of the spatial deviations, Eq. 6, into the boundary conditions in Eqs. 3 and 4, one can derive boundary conditions for the spatial deviations

$$\tilde{T}_\beta = \tilde{T}_\sigma + [\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta] \qquad \text{on } A_{\beta\sigma} \tag{13}$$

$$\begin{aligned} \mathbf{n}_{\beta\sigma}\cdot k_\beta\nabla\tilde{T}_\beta = \mathbf{n}_{\beta\sigma}\cdot k_\sigma\nabla\tilde{T}_\sigma + \mathbf{n}_{\beta\sigma}\cdot[k_\sigma\nabla\langle T_\sigma\rangle^\sigma \\ - k_\beta\nabla\langle T_\beta\rangle^\beta] \qquad \text{on } A_{\beta\sigma} \end{aligned} \tag{14}$$

In Eq. 9 the gradient of the average temperature in the fluid phase $\nabla\langle T_\beta\rangle^\beta$ appears as a linear source term in the $\tilde{T}_\beta$ equation. This gradient also influences the relationship between gradients of the spatial deviations in the boundary condition in Eq. 14. We also note that both the difference between solid and fluid temperatures $[\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta]$, and the gradient of the solid phase average temperature $\nabla\langle T_\sigma\rangle^\sigma$, are linear source terms in the boundary conditions in Eqs. 13 and 14. This same situation appeared in the analysis of Zanotti and Carbonell (1983a) for the case of mass transfer between two moving fluid phases in a porous medium. They found that for these linear source terms in the equations and boundary conditions one can obtain solutions to Eqs. 9 and 10 of the form

$$\tilde{T}_\beta = \mathbf{f}_\beta\cdot\nabla\langle T_\beta\rangle^\beta + \mathbf{g}_\beta\cdot\nabla\langle T_\sigma\rangle^\sigma + h_\beta[\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta] \tag{15}$$

and $$\tilde{T}_\sigma = \mathbf{f}_\sigma\cdot\nabla\langle T_\beta\rangle^\beta + \mathbf{g}_\sigma\cdot\nabla\langle T_\sigma\rangle^\sigma + h_\sigma[\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta] \tag{16}$$

where $\mathbf{f}$, $\mathbf{g}$, and h are functions of spatial position only. One can obtain equations and boundary conditions for $\mathbf{f}$, $\mathbf{g}$, and h by substituting Eqs. 15 and 16 in Eqs. 9, 10, 13, and 14. These equations are shown in Appendix A, together with a detailed discussion of their derivation.

Given that Eqs. 15 and 16 are an adequate representation of the relation between the spatial deviations and the average temperatures, we are in a position to obtain closure in the problem by substituting these representations into the averaged transport equations.

Transport Equations for the Averaged Temperatures

Equations 15 and 16 are used to evaluate the tortuosity terms, the hydrodynamic dispersion term, and the heat exchange contributions on the righthand side of Eqs. 7 and 8. For example, in the fluid phase thermal energy equation the tortuosity term can be written as

$$\begin{aligned} a_\beta\langle\mathbf{n}_{\beta\sigma}\tilde{T}_\beta\rangle_{\beta\sigma} = \underset{\sim}{\boldsymbol{\tau}}_{\beta\beta}\cdot\nabla\langle T_\beta\rangle^\beta + \underset{\sim}{\boldsymbol{\tau}}_{\beta\sigma}\cdot\nabla\langle T_\sigma\rangle^\sigma \\ + \mathbf{t}_\beta[\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta] \end{aligned} \tag{17}$$

where the thermal tortuosity tensors $\underset{\sim}{\boldsymbol{\tau}}$ and the tortuosity vector $\mathbf{t}_\beta$ are defined in Table 1. The hydrodynamic dispersion contribution in Eq. 7 can also be expanded in the form

TABLE 1. COEFFICIENTS OF TORTUOSITY, HYDRODYNAMIC DISPERSION, AND HEAT EXCHANGE

	Fluid Phase	Solid Phase
Tortuosity	$\boldsymbol{\tau}_{\beta\beta} = a_\beta \langle \boldsymbol{n}_{\beta\sigma} \boldsymbol{f}_\beta \rangle_{\beta\sigma}$	$\boldsymbol{\tau}_{\sigma\beta} = a_\sigma \langle \boldsymbol{n}_{\sigma\beta} \boldsymbol{f}_\sigma \rangle_{\beta\sigma}$
	$\boldsymbol{\tau}_{\beta\sigma} = a_\beta \langle \boldsymbol{n}_{\beta\sigma} \boldsymbol{g}_\beta \rangle_{\beta\sigma}$	$\boldsymbol{\tau}_{\sigma\sigma} = a_\sigma \langle \boldsymbol{n}_{\sigma\beta} \boldsymbol{g}_\sigma \rangle_{\beta\sigma}$
	$\boldsymbol{t}_\beta = a_\beta \langle \boldsymbol{n}_{\beta\sigma} h_\beta \rangle_{\beta\sigma}$	$\boldsymbol{t}_\sigma = a_\sigma \langle \boldsymbol{n}_{\sigma\beta} h_\sigma \rangle_{\beta\sigma}$
Hydrodynamic Dispersion	$\boldsymbol{D}_{\beta\beta} = -\langle \tilde{\boldsymbol{v}}_\beta \boldsymbol{f}_\beta \rangle^\beta$	
	$\boldsymbol{D}_{\beta\sigma} = -\langle \tilde{\boldsymbol{v}}_\beta \boldsymbol{g}_\beta \rangle^\beta$	
	$\boldsymbol{d}_\beta = -\langle \tilde{\boldsymbol{v}}_\beta h_\beta \rangle^\beta$	
Heat Exchange	$\boldsymbol{\xi}_{\beta\beta} = a_\beta \langle \boldsymbol{n}_{\beta\sigma} \cdot \nabla \boldsymbol{f}_\beta \rangle_{\beta\sigma}$	$\boldsymbol{\xi}_{\sigma\beta} = a_\sigma \langle \boldsymbol{n}_{\sigma\beta} \cdot \nabla \boldsymbol{f}_\sigma \rangle_{\beta\sigma}$
	$\boldsymbol{\xi}_{\beta\sigma} = a_\beta \langle \boldsymbol{n}_{\beta\sigma} \cdot \nabla \boldsymbol{g}_\beta \rangle_{\beta\sigma}$	$\boldsymbol{\xi}_{\sigma\sigma} = a_\sigma \langle \boldsymbol{n}_{\sigma\beta} \cdot \nabla \boldsymbol{g}_\sigma \rangle_{\beta\sigma}$
	$\gamma_\beta = k_\beta a_\beta \langle \boldsymbol{n}_{\beta\sigma} \cdot \nabla h_\beta \rangle_{\beta\sigma}$	$\gamma_\sigma = k_\sigma a_\sigma \langle \boldsymbol{n}_{\sigma\beta} \cdot \nabla h_\sigma \rangle_{\beta\sigma}$
Surface Area/ Volume	$a_\beta = A_{\beta\sigma}/V_\beta$	$a_\sigma = A_{\beta\sigma}/V_\sigma$

$$\langle \tilde{\boldsymbol{v}}_\beta \tilde{T}_\beta \rangle^\beta = \boldsymbol{D}_{\beta\beta} \cdot \nabla \langle T_\beta \rangle^\beta + \boldsymbol{D}_{\beta\sigma} \cdot \nabla \langle T_\sigma \rangle^\sigma + \boldsymbol{d}_\beta [\langle T_\sigma \rangle^\sigma - \langle T_\beta \rangle^\beta] \quad (18)$$

with the hydrodynamic dispersion tensors $\boldsymbol{D}$ and the vector $\boldsymbol{d}_\beta$ defined in Table 1. The heat exchange term is more complex since it involves the gradient of the spatial deviation

$$a_\beta \langle \boldsymbol{n}_{\beta\sigma} \cdot \nabla \tilde{T}_\beta \rangle_{\beta\sigma} = \boldsymbol{\xi}_{\beta\beta} \cdot \nabla \langle t_\beta \rangle^\beta + \boldsymbol{\xi}_{\beta\sigma} \cdot \nabla \langle T_\sigma \rangle^\sigma + \gamma_\beta [\langle T_\sigma \rangle^\sigma - \langle T_\beta \rangle^\beta] + \boldsymbol{\tau}_{\beta\beta} : \nabla\nabla \langle T_\beta \rangle^\beta + \boldsymbol{\tau}_{\beta\sigma} : \nabla\nabla \langle T_\sigma \rangle^\sigma + \boldsymbol{t}_\beta \cdot [\nabla \langle T_\sigma \rangle^\sigma - \nabla \langle T_\beta \rangle^\beta]. \quad (19)$$

Again, the terms $\boldsymbol{\xi}$ and γ_β are related to the closure functions in Table 1. In traditional heat transfer models, the heat flux between one phase and another is modeled by an overall heat transfer coefficient multiplied by the driving force $[\langle T_\sigma \rangle^\sigma - \langle T_\beta \rangle^\beta]$. The additional terms appearing in Eq. 19 would disappear or become unimportant for small gradients in the temperature of the fluid and solid phases. However, for short time periods after an inlet temperature disturbance, these gradients can be very large, and they can affect the velocity of temperature pulses moving through the porous medium through the $\boldsymbol{\xi}$ terms as we will see later. Both the tortuosity and the hydrodynamic dispersion terms are normally modeled as being proportional to the temperature gradients for systems where the fluid and solid are in thermal equilibrium. The last terms in Eqs. 17 and 18 represent the role of heat transfer in modifying the tortuosity and hydrodynamic dispersion contributions.

The thermal tortuosity and heat exchange terms in Eq. 8 can be expanded in an analogous fashion, and the results can be written as

$$a_\sigma \langle \boldsymbol{n}_{\sigma\beta} \tilde{T}_\beta \rangle_{\beta\sigma} = \boldsymbol{\tau}_{\sigma\beta} \cdot \nabla \langle T_\beta \rangle^\beta + \boldsymbol{\tau}_{\sigma\sigma} \cdot \nabla \langle T_\sigma \rangle^\sigma + \boldsymbol{t}_\sigma [\langle T_\sigma \rangle^\sigma - \langle T_\beta \rangle^\beta] \quad (20)$$

and

$$a_\sigma \langle \boldsymbol{n}_{\sigma\beta} \cdot \nabla \tilde{T}_\sigma \rangle_{\beta\sigma} = \boldsymbol{\xi}_{\sigma\beta} \cdot \nabla \langle T_\beta \rangle^\beta + \boldsymbol{\xi}_{\sigma\sigma} \cdot \nabla \langle T_\sigma \rangle^\sigma + \gamma_\sigma [\langle T_\sigma \rangle^\sigma - \langle T_\beta \rangle^\beta] + \boldsymbol{\tau}_{\sigma\beta} : \nabla\nabla \langle T_\beta \rangle^\beta + \boldsymbol{\tau}_{\sigma\sigma} : \nabla\nabla \langle T_\sigma \rangle^\sigma + \boldsymbol{t}_\sigma \cdot [\nabla \langle T_\sigma \rangle^\sigma - \nabla \langle T_\beta \rangle^\beta] \quad (21)$$

The expressions for $\boldsymbol{\tau}$, $\boldsymbol{\xi}$, and $\boldsymbol{t}_\sigma$ are also given in Table 1.

We can now substitute Eqs. 17 through 21 in Eqs. 7 and 8 and collect terms that are proportional to the first and second derivatives of the average temperatures and proportional to the temperature difference between fluid and solid. The end result is the final form of the transport equations for the average temperatures of the two phases

$$\frac{\partial \langle T_\beta \rangle^\beta}{\partial t} + \boldsymbol{U}_{\beta\beta} \cdot \nabla \langle T_\beta \rangle^\beta + \boldsymbol{U}_{\beta\sigma} \cdot \nabla \langle T_\sigma \rangle^\sigma = \boldsymbol{D}^*_{\beta\beta} : \nabla\nabla \langle T_\beta \rangle^\beta + \boldsymbol{D}^*_{\beta\sigma} : \nabla\nabla \langle T_\sigma \rangle^\sigma + \frac{\gamma_\beta}{(\rho c_p)_\beta} [\langle T_\sigma \rangle^\sigma - \langle T_\beta \rangle^\beta] \quad (22)$$

and

$$\frac{\partial \langle T_\sigma \rangle^\sigma}{\partial t} + \boldsymbol{U}_{\sigma\beta} \cdot \nabla \langle T_\beta \rangle^\beta + \boldsymbol{U}_{\sigma\sigma} \cdot \nabla \langle T_\sigma \rangle^\sigma = \boldsymbol{D}^*_{\sigma\beta} : \nabla\nabla \langle T_\beta \rangle^\beta + \boldsymbol{D}^*_{\sigma\sigma} : \nabla\nabla \langle T_\sigma \rangle^\sigma + \frac{\gamma_\sigma}{(\rho c_p)_\sigma} [\langle T_\sigma \rangle^\sigma - \langle T_\beta \rangle^\beta] \quad (23)$$

TABLE 2. CONVECTIVE AND DISPERSIVE COEFFICIENTS IN TRANSPORT EQUATIONS

Convective Coefficients	
Fluid	$\boldsymbol{U}_{\beta\beta} = \langle \tilde{\boldsymbol{v}}_\beta \rangle^\beta + \alpha_\beta (2\boldsymbol{t}_\beta - \boldsymbol{\xi}_{\beta\beta}) + \boldsymbol{d}_\beta$
	$\boldsymbol{U}_{\beta\sigma} = -\alpha_\beta (2\boldsymbol{t}_\beta + \boldsymbol{\xi}_{\beta\sigma}) - \boldsymbol{d}_\beta$
Solid	$\boldsymbol{U}_{\sigma\sigma} = -\alpha_\sigma (2\boldsymbol{t}_\sigma + \boldsymbol{\xi}_{\sigma\sigma})$
	$\boldsymbol{U}_{\sigma\beta} = \alpha_\sigma (2\boldsymbol{t}_\sigma - \boldsymbol{\xi}_{\sigma\beta})$
Dispersive Coefficients	
Fluid	$\boldsymbol{D}^*_{\beta\beta} = \alpha_\beta (\boldsymbol{I} + 2\boldsymbol{\tau}_{\beta\beta}) + \boldsymbol{D}_{\beta\beta}$
	$\boldsymbol{D}^*_{\beta\sigma} = \alpha_\beta (2\boldsymbol{\tau}_{\beta\sigma}) + \boldsymbol{D}_{\beta\sigma}$
Solid	$\boldsymbol{D}^*_{\sigma\sigma} = \alpha_\sigma (\boldsymbol{I} + 2\boldsymbol{\tau}_{\sigma\sigma})$
	$\boldsymbol{D}^*_{\sigma\beta} = \alpha_\sigma (2\boldsymbol{\tau}_{\sigma\beta})$

The convective coefficients $\boldsymbol{U}$ and the total dispersivities $\boldsymbol{D}^*$ are functions of the tortuosity coefficients, the hydrodynamic dispersion coefficients, and the heat exchange coefficients. The relationships are listed in Table 2. Note that even though the solid phase is not moving, the equation for the average solid phase temperature has convective-type terms due to the influence of temperature gradients on the heat exchange process. Furthermore, the fluid phase thermal energy equation contains terms that are proportional to the first and second derivatives of the solid phase temperature. The solid phase equation contains first and second derivatives of the fluid phase temperature. The coupling is much more complex than in traditional heat transfer models. For example, the continuous solid phase model described by Wakao et al. (1979) can be obtained from Eqs. 22 and 23 by letting

$$\boldsymbol{U}_{\beta\beta} = \langle \boldsymbol{v}_\beta \rangle^\beta, \qquad \boldsymbol{U}_{\beta\sigma} = 0, \qquad \boldsymbol{D}^*_{\beta\sigma} = 0 \quad (24)$$

and

$$\boldsymbol{U}_{\sigma\beta} = \boldsymbol{U}_{\sigma\sigma} = \boldsymbol{D}^*_{\sigma\beta} = 0 \quad (25)$$

In Table 2 we see that $\langle \boldsymbol{v}_\beta \rangle^\beta$ is the leading term in the definition of $\boldsymbol{U}_{\beta\beta}$. Dropping out the remaining terms indicated in Eqs. 24 and 25 is equivalent to neglecting some of the influence of heat exchange between phases on the velocity of the average temperature fields and neglecting the role of temperature gradients in one phase influencing the spread of the temperature field of the second phase.

In Appendix A, Table A1, we have listed the boundary conditions at the fluid-solid interface for the $\boldsymbol{f}$, $\boldsymbol{g}$, and h fields in both phases. Since the values of these functions and their derivatives are related at the phase interface, all the coefficients of tortuosity and heat exchange that are defined as averages over the interfacial area are also related. From the definitions in Table 1 and the boundary conditions in Appendix A we can derive the expressions shown in Table 3. It should be noted that the ratio of surface areas per unit volume can be related to the volume fraction ratio $a_\sigma/a_\beta = \epsilon_\beta/\epsilon_\sigma$ in Table 3. These equations will be useful in deriving results for the moment response of the model equations, Eqs. 22 and 23.

If one could solve the equations for the $\boldsymbol{f}$, $\boldsymbol{g}$, and h fields shown in Appendix A, one would be in a position to make a priori estimates of the transport parameters in Eqs. 22 and 23 since they are all ultimately related to area and volume averages of these closure functions. Zanotti and Carbonell (1983a) have presented a scheme for doing this in the case of spatially periodic models of the structure of the porous medium, and have applied the approach to a very simple case: laminar flow of a fluid in a cylindrical tube with conducting walls (Zanotti and Carbonell, 1983c). They found that the additional coupling terms in Eqs. 22 and 23 were not small, and that the heat transfer process between phases had a significant influence on the magnitude of terms such as $\boldsymbol{U}_{\beta\sigma}$ and $\boldsymbol{U}_{\sigma\beta}$. What remains to be seen is whether one can detect the influence of these

TABLE 3. RELATIONS BETWEEN COEFFICIENTS IN TABLE 1

Tortuosity	$a_\alpha \boldsymbol{\tau}_{\beta\beta} = -a_\beta \boldsymbol{\tau}_{\sigma\beta}$
	$a_\alpha \boldsymbol{\tau}_{\beta\sigma} = -a_\beta \boldsymbol{\tau}_{\sigma\sigma}$
	$a_\alpha \boldsymbol{t}_\beta = -a_\beta \boldsymbol{t}_\alpha$
Heat Exchange	$a_\alpha k_\beta \boldsymbol{\xi}_{\beta\beta} = -a_\beta k_\sigma \boldsymbol{\xi}_{\sigma\beta}$
	$a_\sigma k_\beta \boldsymbol{\xi}_{\beta\sigma} = -a_\beta k_\sigma \boldsymbol{\xi}_{\sigma\sigma}$
	$a_\sigma \gamma_\beta = -a_\beta \gamma_\sigma$

terms experimentally. In preparation for this, we study the predictions of Eqs. 22 and 23 for the case of pulse disturbances, and we estimate the contributions of the most important terms to the thermal dispersion process in packed beds.

RESPONSE OF MODEL EQUATIONS TO PULSE DISTURBANCES

In this section we analyze the response of model Eqs. 22 and 23 to a pulse disturbance in the temperature of one of the phases. Consider the case of one-dimensional flow along the z direction in an insulated system with no heat losses in the directions perpendicular to flow. Equations 22 and 23 would then reduce to the form

$$\frac{\partial\langle T_\beta\rangle^\beta}{\partial t} + U_{\beta\beta}\frac{\partial\langle T_\beta\rangle^\beta}{\partial z} + U_{\beta\sigma}\frac{\partial\langle T_\sigma\rangle^\sigma}{\partial z} = D^*_{\beta\beta}\frac{\partial^2\langle T_\beta\rangle^\beta}{\partial z^2} + D^*_{\beta\sigma}\frac{\partial^2\langle T_\sigma\rangle^\sigma}{\partial z^2} + \frac{\gamma_\beta}{(\rho c_p)_\beta}[\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta] \quad (26)$$

and

$$\frac{\partial\langle T_\sigma\rangle^\sigma}{\partial t} + U_{\sigma\beta}\frac{\partial\langle T_\beta\rangle^\beta}{\partial z} + U_{\sigma\sigma}\frac{\partial\langle T_\sigma\rangle^\sigma}{\partial z} = D^*_{\sigma\beta}\frac{\partial^2\langle T_\beta\rangle^\beta}{\partial z^2} + D^*_{\sigma\sigma}\frac{\partial^2\langle T_\sigma\rangle^\sigma}{\partial z^2} + \frac{\gamma_\sigma}{(\rho c_p)_\sigma}[\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta] \quad (27)$$

It is understood that the terms $U_{\sigma\beta}$, $D^*_{\beta\beta}$, etc. appearing in the equations above are the components of the respective vectors and tensors along the direction of flow. We have omitted all subscripts in order to simplify notation.

The response of Eqs. 26 and 27 to pulse disturbances can be analyzed by deriving expressions for the axial moments

$$M_{n\omega} = \int_{-\infty}^{+\infty} [\langle T_\omega\rangle^\omega - T_o]z^n dz; \qquad \omega = \beta,\sigma. \quad (28)$$

where $M_{n\omega}$ is the nth axial moment of the temperature field in phase ω, and T_o is the temperature of both the fluid and the solid at positive and negative infinity. The mean positions of the pulses in the fluid and solid phases are given by the first absolute moments of the temperature fields

$$\mu'_{1\omega} = M_{1\omega}/M_{o\omega}; \qquad \omega = \beta,\sigma. \quad (29)$$

The spreads of the temperature profiles relative to their mean positions are equal to the second central moments of the temperature distributions

$$\mu_{2\omega} = (M_{2\omega}/M_{o\omega}) - (\mu'_{1\omega})^2; \qquad \omega = \beta,\sigma. \quad (30)$$

One can derive equations for the moments $M_{n\omega}$ by multiplying Eqs. 26 and 27 by z^n, integrating from $-\infty$ to $+\infty$, and integrating by parts. It is assumed that at $+\infty$ and at $-\infty$ the temperature of both phases is T_o and that all derivatives of the average temperatures approach zero faster than z^n.

The equations for the zeroth moments are given by

$$\frac{dM_{o\beta}}{dt} = \frac{\gamma_\beta}{(\rho c_p)_\beta}[M_{o\sigma} - M_{o\beta}] \quad (31)$$

and

$$\frac{dM_{o\sigma}}{dt} = \frac{\gamma_\sigma}{(\rho c_p)_\sigma}[M_{o\sigma} - M_{o\beta}] \quad (32)$$

Since $\gamma_\sigma = -\gamma_\beta(\epsilon_\beta/\epsilon_\sigma)$ according to the relation in Table 3, we can solve Eqs. 31 and 32 to yield

$$\frac{M_{o\sigma}(t) - M_{o\beta}(t)}{M_{o\sigma}(0) - M_{o\beta}(0)} = \exp\left\{-\frac{\gamma_\beta}{(\rho c_p)_\beta}\left[\frac{1+K}{K}\right]t\right\} \quad (33)$$

where $M_{o\sigma}(0)$ and $M_{o\beta}(0)$ are the areas of the initial temperature pulses in the solid and fluid respectively, and K is the ratio of heat capacities

$$K = \frac{\epsilon_\sigma(\rho c_p)_\sigma}{\epsilon_\beta(\rho c_p)_\beta} \quad (34)$$

For times t, measured from the introduction of the pulse disturbance, that are long enough to satisfy the criterion

$$\frac{\gamma_\beta}{(\rho c_p)_\beta}\left[\frac{1+K}{K}\right]t \gg 1, \quad (35)$$

the areas under the curves of the pulses in the fluid and solid temperatures will be nearly equal

$$M_{o\sigma}(t) \simeq M_{o\beta}(t). \quad (36)$$

This is a condition where there is no net transfer of thermal energy between fluid and solid phases, but it does not imply that $\langle T_\sigma\rangle^\sigma = \langle T_\beta\rangle^\beta$ locally.

When Eq. 36 is satisfied, it is a simple matter to derive equations for the first absolute moments from the equations for $M_{1\sigma}$ and $M_{1\beta}$

$$\frac{d\mu'_{1\beta}}{dt} - (U_{\beta\beta} + U_{\beta\sigma}) = \frac{\gamma_\beta}{(\rho c_p)_\beta}[\mu'_{1\sigma} - \mu'_{1\beta}] \quad (37)$$

$$\frac{d\mu'_{1\sigma}}{dt} - (U_{\sigma\beta} + U_{\sigma\sigma}) = -\frac{\gamma_\beta}{(\rho c_p)_\sigma}\left(\frac{\epsilon_\beta}{\epsilon_\sigma}\right)[\mu'_{1\sigma} - \mu'_{1\beta}] \quad (38)$$

Solving Eqs. 37 and 38 simultaneously, and considering times long enough that Eq. 35 is satisfied, we can derive an expression for the separation between the mean pulse positions of the fluid and solid phases

$$\Delta = \mu'_{1\beta} - \mu'_{1\sigma} = \frac{(\rho c_p)_\beta}{\gamma_\beta}\left(\frac{K}{1+K}\right)[(U_{\beta\beta} + U_{\beta\sigma}) - (U_{\sigma\beta} + U_{\sigma\sigma})] \quad (39)$$

Note that this separation is a constant with time, and it implies that the two pulses in the fluid and solid are moving with the same velocity. Since the velocity of the pulse in each phase is defined as the time rate of change of the mean pulse position

$$u_\omega = \frac{d\mu'_{1\omega}}{dt}; \qquad \omega = \beta,\sigma \quad (40)$$

we can derive an expression for the final pulse velocity by substituting Eq. 39 into Eq. 37 or 38. The end result is given by

$$u = u_\beta = u_\sigma = \frac{\langle v_\beta\rangle^\beta}{1+K} \quad (41)$$

To derive Eq. 41 we used the definitions of $U_{\beta\beta}$, $U_{\beta\sigma}$, $U_{\sigma\sigma}$, and $U_{\sigma\beta}$ in Table 2, and the relations in Table 3.

When the constraint in Eq. 35 is satisfied, and consequently Eqs. 36 and 37 are valid, one can derive equations for the second central moments of the temperature pulses in the two phases

$$\frac{d\mu_{2\beta}}{dt} = 2(D^*_{\beta\beta} + D^*_{\beta\sigma}) + \frac{\gamma_\beta}{(\rho c_p)_\beta}(\mu_{2\sigma} - \mu_{2\beta}) - 2U_{\beta\sigma}\Delta + \frac{\gamma_\beta}{(\rho c_p)_\beta}\Delta^2 \quad (42)$$

and

$$\frac{d\mu_{2\sigma}}{dt} = 2(D^*_{\sigma\sigma} + D^*_{\sigma\beta}) - \frac{\gamma_\beta}{(\rho c_p)_\sigma}\left(\frac{\epsilon_\beta}{\epsilon_\sigma}\right)(\mu_{2\sigma} - \mu_{2\beta}) + \frac{\gamma_\beta}{(\rho c_p)_\sigma}\left(\frac{\epsilon_\beta}{\epsilon_\sigma}\right)\Delta^2 + 2U_{\sigma\beta}\Delta \quad (43)$$

Solving Eqs. 42 and 43, and considering long enough times so that Eq. 35 is satisfied, results in an expression for the difference between the spread of the two pulses relative to their centroids

$$\mu_{2\beta} - \mu_{2\sigma} = \left(\frac{K}{1+k}\right)\frac{(\rho c_p)_\beta}{\gamma_\beta}\left[\sum_\beta - \sum_\sigma\right] \quad (44)$$

where

$$\sum_\beta = 2(D^*_{\beta\beta} + D^*_{\beta\sigma}) + \Delta^2\frac{\gamma_\beta}{(\rho c_p)_\beta} - \Delta(2U_{\beta\sigma}) \quad (45)$$

and

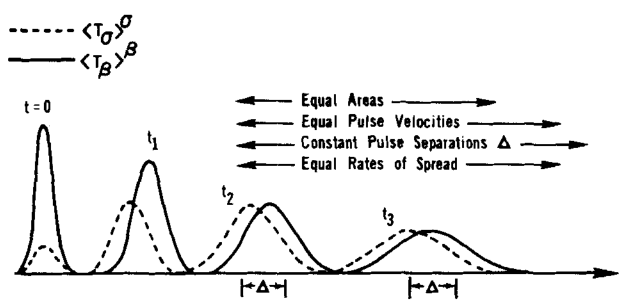

Figure 1. Response of fluid and solid phases to a pulse disturbance in temperature at time $t = 0$.

$$\sum_\sigma = 2(D^*_{\sigma\sigma} + D^*_{\sigma\beta}) + \Delta^2 \frac{\gamma_\beta}{(\rho c_p)_\beta}\left(\frac{\epsilon_\beta}{\epsilon_\sigma}\right) + \Delta(2U_{\sigma\beta}). \quad (46)$$

We can define a longitudinal effective thermal dispersivity for each phase in terms of the time rate of change of the spread of the pulses relative to the centroids

$$(\alpha^*_{zz}) = \frac{1}{2}\frac{d\mu_{2\omega}}{dt}; \qquad \omega = \beta,\sigma \quad (47)$$

Substituting Eq. 44 in Eqs. 42 and 43 results in identical expressions for the thermal dispersion coefficient in each phase

$$\alpha^*_{zz} = (\alpha^*_{zz})_\beta = (\alpha^*_{zz})_\sigma = \frac{1}{2}\left[\frac{K}{1+K}\sum_\sigma + \frac{1}{1+K}\sum_\beta\right]\cdot \quad (48)$$

These results for the thermal dispersivity are also independent of time.

The picture that emerges from the moment analysis is illustrated schematically in Figure 1. Initially a pulse of temperature is introduced in the fluid phase, resulting in slight heating of the solid phase. As time proceeds the fluid pulse will convect downstream and spread until its velocity and rate of spread in the axial direction becomes constant. The solid continues to heat up until the area of the solid and fluid pulses are equal. However, by this time the fluid and solid pulses are separated by a distance Δ, they are traveling at equal velocities, and they spread at equal rates. The separation distance Δ is influenced by the convective cross coupling terms $U_{\beta\sigma}$, $U_{\sigma\beta}$, and $U_{\sigma\sigma}$. These are the terms representing the role of heat exchange and temperature gradients on pulse velocities. Since the quantity Δ appears in the expression for α^*_{zz}, we see that the thermal dispersivity for long times will be dependent on the convective cross-coupling terms as well as the dispersive terms $D^*_{\beta\sigma}$ and $D^*_{\sigma\beta}$. If the time since the introduction of the disturbance is sufficiently large, both the fluid and solid temperature pulses may be analyzed by an equation of the form

$$\frac{\partial\langle T_\omega\rangle^\omega}{\partial t} + u_\omega \frac{\partial\langle T_\omega\rangle^\omega}{\partial z} = (\alpha^*_{zz})_\omega \frac{\partial^2\langle T_\omega\rangle^\omega}{\partial z^2}; \quad \omega = \beta,\sigma \quad (49)$$

if we recognize that the pulses will be separated by the distance Δ.

In Eq. 49 one would use the values of u_ω and $(\alpha^*_{zz})_\omega$ given in Eqs. 41 and 48 respectively. Now that we understand the nature of the model predictions qualitatively, we can attempt an evaluation of as many of the coefficients as possible in order to be able to make a comparison between theory and experiment.

EVALUATION OF THE PARAMETERS

From the experimental data, we will be able to calculate the velocity of pulses in the fluid and solid phases u_β and u_σ, the separation between pulses Δ, and the thermal dispersivity of both phases $(\alpha^*_{zz})_\beta$ and $(\alpha^*_{zz})_\sigma$ under conditions such that Eq. 35 is satisfied. If this is the case then we expect from Eq. 41 that

$$\frac{u_\beta}{u_\sigma} = 1 \quad (50)$$

and that the ratio of u to $\langle v_\beta\rangle^\beta$ be a function only of the ratio of heat capacities

$$\frac{u}{\langle v_\beta\rangle^\beta} = \frac{1}{1+K} \quad (51)$$

It is not hard to show that both the continuous solid phase model and the dispersion-concentric model used for heat transfer in packed beds (Wakao et al., 1979) predict the same values for the pulse velocities as given in Eqs. 50 and 51. However, as we will see now, the new model of Eqs. 26 and 27 provides an estimate of the pulse separation Δ which can be quite different from that given by previous theories.

We can divide Eq. 39 for the pulse separation Δ by the particle diameter, and introduce the definitions of $U_{\beta\beta}$, $U_{\beta\sigma}$, $U_{\sigma\sigma}$, and $U_{\sigma\beta}$ in Table 2 to obtain

$$\frac{\Delta}{d_p} = \frac{(\rho c_p)_\beta}{\gamma_\beta d_p}\left(\frac{K}{1+K}\right)\left[\langle v_\beta\rangle^\beta - \alpha_\beta(\xi_{\beta\beta} + \xi_{\beta\sigma})\left(\frac{1+K}{K}\right)\right]\cdot \quad (52)$$

Here we have used the relations in Table 3 to eliminate $\xi_{\sigma\beta}$ and $\xi_{\sigma\sigma}$ from the resulting expression. The coefficient γ_β is proportional to an overall heat transfer coefficient U which contains contributions from both the fluid phase resistance and the intraparticle resistance to heat transfer. By analogy to the results for a capillary tube model (Zanotti and Carbonell, 1983c) we write

$$\gamma_\beta = a_\beta U \quad (53)$$

where

$$\frac{1}{U} = \frac{1}{h_f} + A_\sigma\left(\frac{1}{a_\sigma k_\sigma}\right) \quad (54)$$

Here h_f is the fluid phase film heat transfer coefficient and a_β and a_σ are the surface area per unit volume of fluid and solid respectively, so that for spherical particles

$$a_\sigma = \frac{6}{d_p}; \qquad a_\beta = \left(\frac{6}{d_p}\right)\left(\frac{\epsilon_\sigma}{\epsilon_\beta}\right) \quad (55)$$

The coefficient A_σ is a geometrical coefficient for the heat conduction process inside the particles, and for spherical particles it takes on the value 3/5 (Green et al., 1964). The quantities $\xi_{\beta\beta}$ and $\xi_{\beta\sigma}$ defined in Table 1 have units of length^{-1}. We can write them as the product of a_β times dimensionless quantities

$$\xi_{\beta\beta} = a_\beta S_{\beta\beta}; \qquad \xi_{\beta\sigma} = a_\beta S_{\sigma\sigma} \quad (56)$$

where $S_{\beta\beta}$ and $S_{\sigma\sigma}$ are the terms in brackets in Table 1. Substituting Eqs. 53 through 56 in Eq. 52 we find

$$\frac{\Delta}{d_p} = \frac{1}{6}\frac{Pe_p}{Nu}\left(\frac{K}{1+K}\right) - \frac{(S_{\beta\beta} + S_{\beta\sigma})}{Nu}\cdot \quad (57)$$

Here we have defined an overall Nusselt number based on the overall heat transfer coefficient

$$\frac{1}{Nu} = \frac{1}{Nu_f} + \frac{A_\sigma}{6\kappa} = \frac{k_\beta}{Ud_p} \quad (58)$$

where Nu_f is the Nusselt number based on the film heat transfer coefficient

$$Nu_f = \frac{h_f d_p}{k_\beta},$$

and κ is the ratio of thermal conductivities

$$\kappa = k_\sigma/k_\beta. \quad (60)$$

The particle Peclet number is defined in terms of the hydraulic radius for the pores between particles (Eidsath et al., 1983)

$$Pe_p = \frac{\langle v_\beta\rangle^\beta d_p}{\alpha_\beta}\left(\frac{\epsilon_\beta}{\epsilon_\sigma}\right)\cdot \quad (61)$$

The Nusselt number Nu_f can be estimated from correlations such as those contributed by Schlünder (1978) and Whitaker (1972).

The first term on the righthand side of Eq. 57 is exactly the pulse separation predicted by Sáez and McCoy (1982) using the dispersion-concentric heat transfer model. This is also the identical separation predicted by the continuous solid phase model which neglects the terms $S_{\beta\beta}$ and $S_{\beta\sigma}$. As a result, we see that the second term in Eq. 57 represents the contribution of the additional convective coupling terms to the pulse separation, and it is exactly the quantity not accounted for in previous models. The best estimate for the quantity $S_{\beta\beta}$ can be derived from the capillary tube model (Zanotti and Carbonell, 1983c). By a rearrangement of the capillary tube results it is possible to show that

$$-\frac{S_{\beta\beta}}{Nu} = \frac{1}{216} Pe_p \left(\frac{\epsilon_\beta}{\epsilon_\sigma}\right); \qquad S_{\beta\sigma} = 0. \tag{62}$$

This would imply that in Eq. 57 we expect the measured value of Δ/d_p to be larger than that predicted by the traditional heat transfer models, and that this difference could be fairly large depending on the value of the Peclet number and the ratio of heat capacities.

We can follow a similar procedure in handling the longitudinal thermal dispersivity α_{zz}^* which for long times will be the same for both fluid and solid phases. First we combine Eqs. 45 and 46 with Eq. 48, then we multiply by the heat capacity of the bed

$$\langle\rho\rangle C_p = \epsilon_\sigma(\rho c_p)_\sigma + \epsilon_\beta(\rho c_p)_\beta. \tag{63}$$

We can then divide by the fluid phase thermal conductivity to obtain a dimensionless effective thermal conductivity in the axial direction

$$\begin{aligned} \frac{K_{zz}^*}{k_\beta} \equiv \frac{\alpha_{zz}^*\langle\rho\rangle C_p}{k_\beta} &= (\kappa\epsilon_\sigma + \epsilon_\beta) + 2\epsilon_\sigma\tau_{\sigma\sigma}(\kappa - 1) \\ &\quad + 2\epsilon_\beta\tau_{\beta\beta}(1 - \kappa) + \epsilon_\beta\left[\frac{D_{\beta\beta}}{\alpha_\beta} + \frac{D_{\beta\sigma}}{\alpha_\beta}\right] \\ &\quad + \Delta^2\frac{\epsilon_\beta\gamma_\beta}{k_\beta} + \Delta\left[\kappa\epsilon_\sigma\frac{U_{\sigma\beta}}{\alpha_\sigma} - \epsilon_\beta\frac{U_{\beta\sigma}}{\alpha_\beta}\right] \end{aligned} \tag{64}$$

In obtaining the equation above we have used the definitions of $D_{\beta\sigma}^*$, $D_{\beta\beta}^*$, $D_{\sigma\beta}^*$, and $D_{\sigma\sigma}^*$ in Table 2.

We now introduce into Eq. 64 the definitions of $U_{\sigma\beta}$ and $U_{\beta\sigma}$ found in Table 2, eliminate the term $(\xi_{\beta\beta} + \xi_{\beta\sigma})$ using Eq. 52, and use the definition of the Peclet number to obtain

$$\begin{aligned} \frac{K_{zz}^*}{k_\beta} &= (\kappa\epsilon_\sigma + \epsilon_\beta) + 2\epsilon_\sigma\tau_{\sigma\sigma}(\kappa - 1) \\ &\quad \left. + 2\epsilon_\beta\tau_{\beta\beta}(1 - \kappa)\right\} \begin{matrix}\text{Conduction}\\ \text{Contribution}\end{matrix} \\ &\quad \left. + \epsilon_\beta\left[\frac{D_{\beta\beta}}{\alpha_\beta} + \frac{D_{\beta\sigma}}{\alpha_\beta}\right]\right\} \begin{matrix}\text{Hydrodynamic}\\ \text{Dispersion}\\ \text{Contribution}\end{matrix} \\ &\quad + \epsilon_\sigma\left(\frac{\Delta}{d_p}\right) Pe_p\left[\left(\frac{K}{1 + K}\right) + D_\beta\right. \\ &\quad \left.\left. + \frac{12(1 - \kappa)\tau_\beta}{Pe_p}\right]\right\} \begin{matrix}\text{Heat}\\ \text{Exchange}\\ \text{Contribution}\end{matrix} \end{aligned} \tag{65}$$

In the equation above, we have used the definitions of $\boldsymbol{d}_\beta$ and $\boldsymbol{t}_\beta$ in Table 2 to write

$$\boldsymbol{d}_\beta = -\langle v_\beta\rangle^\beta \boldsymbol{D}_\beta; \qquad \boldsymbol{t}_\beta = a_\beta\boldsymbol{\tau}_\beta \tag{66}$$

where $\boldsymbol{D}_\beta$ and $\boldsymbol{\tau}_\beta$ are the dimensionless vectors

$$\boldsymbol{D}_\beta = -\langle\tilde{\boldsymbol{V}}h_\beta\rangle^\beta; \qquad \boldsymbol{\tau}_\beta = \langle\boldsymbol{n}_{\beta\sigma}h_\beta\rangle_{\beta\sigma}. \tag{67}$$

The quantity $\tilde{V}$ is the spatial deviation of the velocity, made dimensionless by dividing by $\langle v_\beta\rangle^\beta$. The quantities D_β and τ_β in Eq. 65 are the components of the vectors above along the flow direction.

We would like to be able to compare the prediction of Eq. 65 with experimental data for the longitudinal effective thermal conductivity under flow conditions. The first contribution on the righthand side of Eq. 65 is the purely conductive contribution, containing thermal tortuosity coefficients for the fluid and solid phases. The thermal conduction problem in porous media has been studied recently by Nozad (1983). A great amount of packed bed conduction data has been collected, and the results are presented in a figure of the effective thermal conductivity divided by the fluid phase thermal conductivity as a function of $\kappa = k_\sigma/k_\beta$. Even though the flow field will affect this tortuosity contribution to some extent, this should provide a reasonable estimate of the order of magnitude of this term

$$\begin{Bmatrix}\text{Conduction}\\ \text{Contribution}\end{Bmatrix} \simeq \frac{K_{\text{eff}}}{k_\beta} \tag{68}$$

The hydrodynamic dispersion contribution in Eq. 65 can be estimated from mass transfer data. Eidsath et al. (1983) have presented a collection of data on the longitudinal dispersivity for mass transfer of a nonreactive solute in packed beds, and have presented the results as the longitudinal dispersivity divided by the molecular diffusivity as a function of the Peclet number for mass transfer. The term in Eq. 65 is only the purely hydrodynamic contribution, and as a result one should correct the data collected by Eidsath et al. (1983) by subtracting from it the effect due to molecular diffusion only. This is usually represented as an effective diffusivity (Ryan et al., 1981) so that

$$\begin{Bmatrix}\text{Hydrodynamic}\\ \text{Dispersion}\\ \text{Contribution}\end{Bmatrix} \simeq \epsilon_\beta\left[\frac{D_{zz}^*}{\mathscr{D}} - \frac{D_{\text{eff}}}{\epsilon_\beta\mathscr{D}}\right] \tag{69}$$

From the results for heat transfer in a capillary tube, it is apparent that Eq. 69 will overestimate the hydrodynamic dispersion contribution (Zanotti and Carbonell, 1983c), since the heat conduction process at the fluid-solid interface tends to lower the magnitude of the hydrodynamic thermal dispersion coefficient.

Finally, we note from Eqs. 15 and 16 that under conditions where the spatial deviations in temperature are of the same order as those of the average temperatures, the coefficient h_β in Eq. 67 will be at most of order 1. When the spatial deviations in temperature are much smaller than the average temperatures, h_β will be a number much less than 1. This fixes the magnitude of the terms D_β and τ_β in Eq. 65 to the range between 0 and 1. For now we will assume that the spatial deviations are much smaller than the average, and we will let these two coefficients be zero. This provides an estimate for the third term on the righthand side of Eq. 65

$$\begin{Bmatrix}\text{Heat Exchange}\\ \text{Contribution}\end{Bmatrix} \simeq \epsilon_\sigma\left(\frac{\Delta}{d_p}\right) Pe_p\left(\frac{K}{1 + K}\right) \tag{70}$$

This term accounts for the spreading of the temperature field due to the time required to conduct thermal energy from the fluid into the solid and out again as the thermal pulse moves through the bed. Of course, the quantity Δ/d_p can be calculated using Eq. 57. As was mentioned previously, all the parameters in the first term on the righthand side of Eq. 57 can be calculated using existing correlations for the Nusselt number and knowing the ratio of thermal conductivities of the solid and fluid phases. If the second term in Eq. 57 is significant, one should see an important difference between experimentally measured values of Δ/d_p and the value computed using the first term in Eq. 57. As was also mentioned previously, this first term is the value of Δ/d_p predicted by the continuous solid phase model and the dispersive-concentric model for heat transfer in packed beds.

It is interesting to rewrite the long time constraint in Eq. 35 in terms which are more appealing for comparison with experimental data. If we let t in Eq. 35 be the axial distance from the bed entrance divided by the pulse velocity

$$t = z\Bigg/\left(\frac{\langle v_\beta\rangle^\beta}{1 + K}\right),$$

and substitute the definition for γ_β in terms of U in Eq. 53, we obtain

$$\frac{z}{d_p} \gg \frac{1}{6}\frac{Pe_p}{Nu}\frac{K}{(1 + K)^2} \tag{71}$$

Here we have made use of Eqs. 53, 55, 58, and 61. The equation above for the ratio of z/d_p indicates the ratio of column length to particle diameter required in order to achieve a condition where the pulse velocities in the fluid and solid phases are equal and where both fluid and solid pulses spread at the same rate about their centroids. Of course, Nu has a contribution from the film heat transfer resistance and from intraparticle conduction, as shown in Eq. 58.

LATERAL EFFECTIVE THERMAL CONDUCTIVITIES

Effective thermal conductivities perpendicular to the flow direction are normally measured under steady state conditions where the average temperature of the fluid and the solid are equal

$$\langle T_\beta \rangle^\beta = \langle T_\sigma \rangle^\sigma = \langle T \rangle .$$

Whitaker (1981) has derived the constraint required in order for this assumption to be valid

$$\epsilon_\sigma \left(\frac{d_p}{L_T}\right)^2 \left[1 + \frac{k_\sigma}{k_\beta}\right] \ll 1$$

This constraint is easily satisfied in the experiments described in Part II of this paper.

This condition of local thermal equilibrium greatly simplifies the analysis and interpretation of the terms that contribute to lateral effective thermal conductivities arising from the method of spatial averaging. If we take the volume average of the steady-state form of Eqs. 1 and 2, and assume local thermal equilibrium, we can add the averaged transport equations for the fluid and solid phases to yield

$$\epsilon_\beta(\rho c_p)_\beta \langle v_\beta \rangle^\beta \cdot \nabla \langle T \rangle = \nabla \cdot \left\{ (\epsilon_\beta k_\beta + \epsilon_\sigma k_\sigma) \nabla \langle T \rangle + \frac{(k_\beta - k_\sigma)}{\mathcal{V}} \int_{A_{\beta\sigma}} n_{\beta\sigma} \tilde{T}_\beta dA \right\} - \epsilon_\beta (\rho c_p)_\beta \nabla \cdot \langle \tilde{v}_\beta \tilde{T}_\beta \rangle^\beta \quad (72)$$

The spatial deviations in temperature and velocity are defined in Eq. 6. The closure scheme for this problem results in a very simple relation between the spatial deviation and the average temperatures. The local thermal equilibrium assumption reduces Eq. 15 to the form

$$\tilde{T}_\beta = f_\beta \cdot \nabla \langle T \rangle . \quad (73)$$

Substituting Eq. 73 in Eq. 72, expanding the terms in the gradients, and dividing by $\epsilon_\beta(\rho c_p)_\beta$ we obtain

$$\langle v_\beta \rangle^\beta \cdot \nabla \langle T \rangle = \underset{\sim}{\alpha}^* : \nabla\nabla \langle T \rangle \quad (74)$$

where

$$\underset{\sim}{\alpha}^* = \alpha_\beta (1 + \kappa \epsilon_\sigma / \epsilon_\beta) \underset{\sim}{I} + \alpha_\beta (1 - \kappa) \underset{\sim}{\tau}_{\beta\beta} + \boldsymbol{D}_{\beta\beta} . \quad (75)$$

This is an effective thermal dispersion coefficient under conditions of local thermal equilibrium. The first two terms represent contributions from conduction, while the last term is the hydrodynamic dispersion contribution. The definitions of the thermal tortuosity $\underset{\sim}{\tau}_{\beta\beta}$ and the hydrodynamic dispersion tensor $\boldsymbol{D}_{\beta\beta}$ are found in Table 1.

If we define the effective thermal conductivity tensor $\boldsymbol{K}^*$ by the relation

$$\boldsymbol{K}^* = \underset{\sim}{\alpha}^* \epsilon_\beta (\rho c_p)_\beta \quad (76)$$

we see that

$$\frac{\boldsymbol{K}^*}{k_\beta} = \left.(\epsilon_\beta + \kappa \epsilon_\sigma) \underset{\sim}{I} + \epsilon_\beta (1 - \kappa) \underset{\sim}{\tau}_{\beta\beta} \right\} \begin{array}{l} \text{Conductive} \\ \text{Contribution} \end{array} + \left.\epsilon_\beta \left\{ \frac{\boldsymbol{D}_{\beta\beta}}{\alpha_\beta} \right\} \right\} \begin{array}{l} \text{Hydrodynamic} \\ \text{Dispersion} \\ \text{Contribution} \end{array} \quad (77)$$

Note that even though Eqs. 77 and 65 are very similar in nature, they differ in a very important respect. The effective thermal conductivity in a transient problem contains a very significant contribution from heat exchange between phases. This is a pulse spread resulting from the time required to transfer heat by conduction into the particles, and it is represented by the third term in Eq. 65. This is also reflected in the difference in form of the conductive parts of Eqs. 65 and 77. The local thermal equilibrium assumption makes $\tau_{\sigma\sigma} = 0$, and eliminates the factor 2 from the conductive estimates. In addition, the term $D_{\beta\sigma}$ also becomes zero. This difference between transient and steady-state effective thermal conductivities has been pointed out in some of the recent work by Cresswell and Dixon (1982), and Vortmeyer and Berninger (1982).

If we wish to estimate the magnitude of lateral effective thermal conductivities, we can estimate the conductive contribution using the literature data collected by Nozad (1983) for heat conduction in packed beds under no-flow conditions. The hydrodynamic contribution can be estimated using the recent data of Han et al. (1983) for lateral dispersion in mass transfer experiments in packed beds, after correction for the diffusive contribution (Ryan et al., 1981)

$$\frac{K_{yy}^*}{k_\beta} \simeq \frac{K_{\text{eff}}}{k_\beta} + \epsilon_\beta \left[\frac{D_{yy}^*}{\mathcal{D}} - \frac{D_{\text{eff}}}{\epsilon_\beta \mathcal{D}} \right] . \quad (78)$$

The estimates from the above relation can then be compared directly to experimental results. This is done in Part II of this paper.

APPENDIX A

If we subtract Eq. 7 from Eq. 1 and Eq. 8 from Eq. 2 we obtain

$$(\rho c_p)_\beta \left[\frac{\partial \tilde{T}_\beta}{\partial t} + \tilde{v}_\beta \cdot \nabla \langle T_\beta \rangle^\beta + v_\beta \cdot \nabla \tilde{T}_\beta \right] = \nabla \cdot (k_\beta \nabla \tilde{T}_\beta) - \frac{1}{V_\beta} \int_{A_{\beta\sigma}} n_{\beta\sigma} \cdot k_\beta \nabla \tilde{T}_\beta dA - \nabla \cdot \left(\frac{k_\beta}{V_\beta} \int_{A_{\beta\sigma}} n_{\beta\sigma} \tilde{T}_\beta dA \right) + (\rho c_p)_\beta \nabla \cdot \langle \tilde{v}_\beta \tilde{T}_\beta \rangle^\beta \quad (A1)$$

and

$$(\rho c_p)_\sigma \frac{\partial \tilde{T}_\sigma}{\partial t} = \nabla \cdot (k_\sigma \nabla \tilde{T}_\sigma) - \frac{1}{V_\sigma} \int_{A_{\beta\sigma}} n_{\sigma\beta} \cdot k_\sigma \nabla \tilde{T}_\sigma dA - \nabla \cdot \left(\frac{k_\sigma}{V_\sigma} \int_{A_{\beta\sigma}} n_{\sigma\beta} \tilde{T}_\sigma dA \right) \quad (A2)$$

These are the transport equations for the spatial deviations $\tilde{T}_\beta$ and $\tilde{T}_\sigma$. In obtaining Eqs. A1 and A2 we have made use of the definitions in Eq. 6. The boundary conditions in Eqs. 13 and 14 apply to the spatial deviations. If we compare the time derivative terms to the heat conduction terms on the right hand side of Eqs. A1 and A2 we can make the problem quasi-steady if the condition of Eqs. 11 are satisfied. In deriving these constraints we have let t^* be the characteristic time for the motion of a pulse of temperature in the fluid and solid phases and we have let ℓ_β and ℓ_σ be the characteristic lengths for local temperature gradients in the fluid and solid respectively. For example, in Eq. A1 we can estimate that

$$\frac{\partial \tilde{T}_\beta}{\partial t} = 0 \left(\frac{\tilde{T}_\beta}{t^*} \right) \quad \text{and} \quad \nabla \cdot (k_\beta \nabla \tilde{T}_\beta) = 0 \left(\frac{k_\beta \tilde{T}_\beta}{\ell_\beta^2} \right) \quad (A3)$$

If the problem is quasi-steady, the time derivative is much smaller than the conductive term and the constraint in Eq. 11 must apply. All averaged quantities such as $\langle \tilde{v}_\beta \tilde{T}_\beta \rangle^\beta$ and the area integrals in Eqs. A1 and A2 must vary over distances L_T much greater than the characteristic lengths ℓ_β and ℓ_σ for variations in the spatial deviation fields. As a result, if we make order-of-magnitude estimates of the following terms in Eqs. A1 and A2

$$\nabla \cdot (k_\beta \nabla \tilde{T}_\beta) = 0(k_\beta \tilde{T}_\beta / \ell_\beta^2) \quad (A4)$$

$$\nabla \cdot (k_\beta a_\beta \langle n_{\beta\sigma} \tilde{T}_\beta \rangle_{\beta\sigma}) = 0(k_\beta \tilde{T}_\beta / \ell_\beta L_T) \quad (A5)$$

we see that the tortuosity term, Eq. A5, will be much less than the conductive term, Eq. A4, as long as

TABLE A1. GOVERNING EQUATIONS AND BOUNDARY CONDITIONS FOR THE CLOSURE FUNCTIONS

Fluid Phase (V_β)

$$(\rho c_p)_\beta[\tilde{v}_\beta + v_\beta \cdot \nabla f_\beta] = \nabla \cdot (k_\beta \nabla f_\beta) - a_\beta \langle n_{\beta\sigma} \cdot k_\beta \nabla f_\beta \rangle_{\beta\sigma}$$
$$(\rho c_p)_\beta v_\beta \cdot \nabla g_\beta = \nabla \cdot (k_\beta \nabla g_\beta) - a_\beta \langle n_{\beta\sigma} \cdot k_\beta \nabla g_\beta \rangle_{\beta\sigma}$$
$$(\rho c_p)_\beta v_\beta \cdot \nabla h_\beta = \nabla \cdot (k_\beta \nabla h_\beta) - a_\beta \langle n_{\beta\sigma} \cdot k_\beta \nabla h_\beta \rangle_{\beta\sigma}$$

Solid Phase (V_σ)

$$0 = \nabla \cdot (k_\sigma \nabla f_\sigma) - a_\sigma \langle n_{\sigma\beta} \cdot k_\sigma \nabla f_\sigma \rangle_{\beta\sigma}$$
$$0 = \nabla \cdot (k \cdot \nabla g_\sigma) - a_\sigma \langle n_{\sigma\beta} \cdot k_\sigma \nabla g_\sigma \rangle_{\beta\sigma}$$
$$0 = \nabla \cdot (k_\sigma \nabla h_\sigma) - a_\sigma \langle n_{\sigma\beta} \cdot k_\sigma \nabla h_\sigma \rangle_{\beta\sigma}$$

Boundary Conditions ($A_{\beta\sigma}$)

$$f_\beta = f_\sigma$$
$$g_\beta = g_\sigma$$
$$h_\beta = h_\sigma + 1$$
$$n_{\beta\sigma} \cdot k_\beta \nabla f_\beta = n_{\beta\sigma} \cdot k_\sigma \nabla f_\sigma - k_\beta n_{\beta\sigma}$$
$$n_{\beta\sigma} \cdot k_\beta \nabla g_\beta = n_{\beta\sigma} \cdot k_\sigma \nabla g_\sigma - k_\beta n_{\beta\sigma}$$
$$n_{\beta\sigma} \cdot k_\beta \nabla h_\beta = n_{\beta\sigma} \cdot k_\sigma \nabla h_\sigma$$

$$\ell_\beta \ll L_T \tag{A6}$$

Similarly, the dispersive term can be shown to be much less than the inertial term in $\tilde{T}_\beta$

$$v_\beta \cdot \nabla \tilde{T}_\beta = 0(\langle v_\beta \rangle^\beta \tilde{T}_\beta / \ell_\beta) \tag{A7}$$

$$\nabla \cdot \langle \tilde{v}_\beta \tilde{T}_\beta \rangle^\beta = 0(\langle v_\beta \rangle^\beta \tilde{T}_\beta / L_T) \tag{A8}$$

as long as Eq. A6 applies. Making the corresponding order-of-magnitude estimates on the solid phase equations, we can simplify Eqs. A1 and A2 to the form given in Eqs. 9 and 10. Note that a term such as $\tilde{v}_\beta \cdot \nabla \langle T_\beta \rangle^\beta$ cannot be neglected when compared to $v_\beta \cdot \nabla \tilde{T}_\beta$ based on the constraint in Eq. A6 for the simple reason that $\tilde{T}_\beta$ could be much less than $\langle T_\beta \rangle^\beta$. This is in fact the case for some dispersion problems in mass transfer (Carbonell and Whitaker, 1983).

We can obtain governing differential equations and boundary conditions for the functions f, g, and h in Eqs. 15 and 16 by substituting Eqs. 15 and 16 in Eqs. 9 and 10 and the boundary conditions in Eqs. 13 and 14. In carrying out the analysis, we neglect all derivatives of averaged quantities so that for example

$$\nabla \tilde{T}_\beta \simeq \nabla f_\beta \cdot \nabla \langle T_\beta \rangle^\beta + \nabla g_\beta \cdot \nabla \langle T_\sigma \rangle^\sigma + \nabla h_\beta [\langle T_\sigma \rangle^\sigma - \langle T_\beta \rangle^\beta]. \tag{A9}$$

This is consistent with our previous scaling arguments, since f, g, and h must vary over distances ℓ_β and ℓ_σ, which are much smaller than the distances over which the average temperatures undergo significant variations. After substitution in Eqs. 9, 10, 13, and 14, we collect all terms proportional to $\nabla \langle T_\beta \rangle^\beta$, all terms proportional to $\nabla \langle T_\sigma \rangle^\sigma$, and all terms proportional to $[\langle T_\sigma \rangle^\sigma - \langle T_\beta \rangle^\beta]$ so that the equations and boundary conditions are in the form

$$a_1 \cdot \nabla \langle T_\beta \rangle^\beta + a_2 \cdot \nabla \langle T_\sigma \rangle^\sigma + a_3 [\langle T_\sigma \rangle^\sigma - \langle T_\beta \rangle^\beta] = 0. \tag{A10}$$

We then require that a_1, a_2, and a_3 be zero. This results in the set of equations and boundary conditions for f, g, and h given in Table A1. Note that this in effect treats the sources of the spatial deviation fields as being independent, so that in order for one to solve Eqs. 9 and 10 one would have to provide values for the $\nabla \langle T_\beta \rangle^\beta$, $\nabla \langle T_\sigma \rangle^\sigma$, and $[\langle T_\sigma \rangle^\sigma - \langle T_\beta \rangle^\beta]$.

ACKNOWLEDGMENT

The authors wish to thank the Fulbright Foundation for the support of J. Levec. This work was also supported in part by NSF Grant ENG 79-13269 and Sandia National Laboratory in Livermore, CA.

NOTATION

a_ω = surface area per unit volume of phase ω

$A_{\beta\sigma}$ = interfacial area between fluid and particles

A_σ = geometrical parameter for solid phase conduction

c_p = heat capacity per unit mass of a phase

C_p = heat capacity per unit mass of packed bed

d_p = particle diameter

$\mathbf{d}_\omega$ = dispersivity vector for phase ω

D_{eff} = effective diffusivity of the porous medium

D^*_{zz} = longitudinal dispersion coefficient from mass transfer experiments

$\mathbf{D}_{\eta\omega}$ = hydrodynamic dispersion contribution to effective conductivity

$\mathbf{D}^*_{\eta\omega}$ = total dispersivity terms in the averaged equations

$\mathcal{D}$ = molecular diffusion coefficient

f_ω = closure function for spatial deviations in temperature

g_ω = closure function for spatial deviations in temperature

h_ω = closure function for spatial deviations in temperature

h_f = film heat transfer coefficient

k_ω = thermal conductivity of phase ω

K = ratio of heat capacities of solid to fluid

$\mathbf{K}^*$ = effective thermal conductivity tensor under flow conditions

$\mathbf{K}_{\text{eff}}$ = effective thermal conductivity tensor under no-flow condition

ℓ_ω = characteristic length for phase ω

L_T = characteristic length for gradients in the average temperature

$M_{n\omega}$ = nth axial moment of the temperature pulse in phase ω

$\mathbf{n}_{\eta\omega}$ = unit normal pointing from phase η to phase ω

Nu = Nusselt number based on an overall heat transfer coefficient

Nu_f = Nusselt number based on film heat transfer coefficient

Pe_p = Peclet number based on hydraulic radius of pore

t^* = characteristic time since temperature disturbance

$\mathbf{t}_\omega$ = tortuosity vector

T_o = bed temperature at $\pm\infty$

T_ω = point temperature in phase ω

$\tilde{T}_\omega$ = spatial deviation in temperature in phase ω

u_ω = pulse velocity for average temperature in phase ω

U = overall heat transfer coefficient

$\mathbf{U}_{\eta\omega}$ = convective coupling terms in the averaged equations

$\mathbf{v}_\beta$ = fluid velocity

$\tilde{\mathbf{v}}_\beta$ = spatial deviation in fluid velocity

V_ω = volume of phase ω in the averaging volume

$\mathcal{V}$ = volume of the averaging volume

y,z = lateral and longitudinal coordinates in the packed bed

Greek Letters

α_ω = thermal diffusivity of phase ω, $= k_\omega/(\rho c_p)_\omega$

$(\alpha^*_{zz})_\omega$ = longitudinal thermal dispersivity for phase ω

$\boldsymbol{\alpha}^*$ = thermal dispersivity tensor

ϵ_ω = volume fraction of phase ω

Δ = separation between pulses in fluid and solid

γ_ω = heat exchange coefficient in equation for phase ω temperature

$\boldsymbol{\tau}_{\eta\omega}$ = tortuosity tensor contribution to effective conductivity

κ = ratio of thermal conductivities of solid to fluid

ρ = density

$\langle \rho \rangle$ = average bed density $\epsilon_\beta \rho_\beta + \epsilon_\sigma \rho_\sigma$.

Σ_ω = contributions to total thermal dispersivity from phase ω

$\xi_{\eta\omega}$ = heat exchange contributions to pulse velocities

$\mu'_{1\omega}$ = first absolute moment of temperature pulse in phase ω

$\mu_{2\omega}$ = second central moment of temperature pulse in phase ω

Special Symbols

$\langle\ \rangle^\omega$ = intrinsic average in phase ω

$\langle\ \rangle_{\beta\sigma}$ = area average over the β-σ interface

Subscripts

η,ω = fluid and solid phases $\eta = \beta,\sigma$; $\omega = \beta,\sigma$, respectively

LITERATURE CITED

Carbonell, R. G., and S. Whitaker, "Dispersion in Pulsed Systems. II: Theoretical Developments for Passive Dispersion in Porous Media," *Chem. Eng. Sci.*, **38**, 1781 (1983).

Cresswell, D. L., and A. G. Dixon, "Reply to Comments by Vortmeyer and Berninger on the Paper: Theoretical Prediction of Effective Heat Transfer Parameters in Packed Beds [*AIChE J.*, **25**, 663, (1979)]," *AIChE J.*, **28**, 511 (1982).

Dixon, A. G., and D. L. Cresswell, "Theoretical Prediction of Effective Heat Transfer Parameters in Packed Beds," *AIChE J.*, **25**, 663 (1979).

Eidsath, A., et al., "Dispersion in Pulsed Systems. III: Comparison Between Theory and Experiment for Packed Beds," *Chem. Eng. Sci.*, **38**, 1803 (1983).

Froment, G. F., and K. B. Bischoff, *Chemical Reactor Analysis and Design*, J. Wiley and Sons, New York (1979).

Green, D. W., R. H. Perry, and R. E. Babcock, "Longitudinal Dispersion of Thermal Energy Through Porous Media with a Flowing Fluid," *AIChE J.*, **10**, 645 (1964).

Han, N., J. Bhakta, and R. G. Carbonell, "Longitudinal and Lateral Dispersion in Packed Beds: Effect of Column Length and Particle Size Distribution," *AIChE J.*, **31**(2), 277 (Feb., 1985).

Nozad, I., "Effective Thermal Conductivities for Two- and Three-Phase Systems: A Theoretical and Experimental Study," Ph.D. Thesis, Chem. Eng. Dept., Univ. of California, Davis (1983).

Ryan, D., R. G. Carbonell, and S. Whitaker, "A Theory of Diffusion and Reaction in Porous Media," *AIChE Symp. Ser.*, No. 202, **77**, 46 (1981).

Sáez, A. E., and B. J. McCoy, "Dynamic Response of a Packed Bed Thermal Storage System—A Model for Solar Air Heating," *Solar Energy*, **29**, 201 (1982).

Sagara, M., P. Schneider, and J. M. Smith, "The Determination of Heat Transfer Parameters for Flow in Packed Beds Using Pulse Testing and Chromatography Theory", *Chem. Eng. J.*, **1**, 47 (1970).

Schlünder, E. V., "Transport Phenomena in Packed Bed Reactors," *Chemical Reaction Engineering Reviews*, D. L. Houston and V. W. Weekman, Jr., Eds., ACS Symp. Ser. No. 72, Am. Chem. Soc., Washington, DC (1978).

Slattery, J. C., *Momentum, Energy, and Mass Transfer in Continua*, McGraw-Hill, New York (1972).

Vortmeyer, D., "Axial Heat Dispersion in Fixed Beds," *Chem. Eng. Sci.*, **30**, 999 (1975).

Vortmeyer, D., and R. Berninger, "Comments on the Paper: Theoretical Prediction of Effective Heat Transfer Parameters in Packed Beds by Anthony Dixon and D. L. Cresswell [*AIChE J.*, **25**, 663 (1979)]," *AIChE J.*, **28**, 508 (1982).

Wakao, N., S. Kaguei, and T. Funazkri, "Effect of Fluid Dispersion Coefficients on Particle-to-Fluid Heat Transfer Coefficients in Packed Beds," *Chem. Eng. Sci.*, **34**, 325 (1979).

Whitaker, S., "Heat and Mass Transfer in Granular Porous Media," *Advances in Drying*, A. S. Mujumdar, Ed., Ch. 2, Hemisphere Pub. Corp., New York, 1981.

Zanotti, F., and R. G. Carbonell, "Development of Transport Equations for Multiphase Systems. I: General Development for Two-Phase Systems," *Chem. Eng. Sci.*, **39**, 263 (1984).

———, "II: Application to One-Dimensional, Axi-Symmetric Flows of Two Phases," *Chem. Eng. Sci.*, **39**, 279 (1984).

———, "III: Application to Heat Transfer in Packed Beds," *Chem. Eng. Sci.*, **39**, 299 (1984).

Manuscript received April 11, 1983; revision received Feb. 15, 1984, and accepted Mar. 1, 1984.