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Approximate analytical solution for non-convective heat or mass transfer in composites of spherical particles

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INTRODUCTION

THE TRANSIENT, non-convective conduction of heat or diffusion of solute in composite media is important in several applications. In thermal storage in packed beds, for example, stratification in the non-flow mode deteriorates with time, i.e. the temperature gradient dissipates [1, 2]. Diffusion in arrested-flow chromatography also involves transient behavior as the stationary band of solute spreads in either direction in the column [3]. Other composite materials, e.g. cement with embedded gravel, are in the category studied here.

For isotropic composite media with different conductivity properties in the continuous and particle phases, relaxation to the quasi-steady state cannot be described by the simple effective conductivity equation, which for one-dimensional transport is

$$\partial A/\partial t = k_{\mathrm{eff}}\,\partial^2 A/\partial z^2 \tag{1}$$

where k_{eff} is the effective conductivity or diffusion coefficient, Kirkpatrick [4] showed that the relaxation to steady state for diffusion in a medium of randomly-distributed spherical traps could not be so represented. Park and McCoy [5] examined the conditions under which conduction or diffusion in a composite medium composed of widely-spaced, fixed spheres could be mathematically described by an effective conductivity or diffusivity. Criteria in terms of the Biot number, and the ratio of particle to external phase volumes were formulated for equilibration of particles with the surrounding material.

Our objective in this note is to develop an analytical approach for computing transient temperature or concentration profiles in both the continuous and particle phases for arbitrary initial conditions. The procedure makes use of the parabolic profile approximation for individual particles [6]. A restriction due to the uniform boundary conditions that are assumed for the surface of a particle is that the particles are small and spaced far apart. A Fourier transform solution allows the generation of spatial moments for an impulse response, which, being symmetrical, is modeled as a Gaussian profile. By utilizing the superposition principle resulting from the convolution of Fourier transforms, we express the response to a general initial condition. Results are presented for transient profiles in both the continuous and particle phase due to the impulse, pulse, step, and ramp initial conditions. After sufficient time has elapsed, the longitudinal profiles in the two phases become identical. For a composite medium the theory utilizes the superposition theory described by Crank [7] and by Carslaw and Jaeger [8], previously applied only to a single-phase medium, and now extended to the present two-phase composite.

THEORY

We consider a composite of equal-sized spheres in a homogeneous and continuous matrix. Table 1, defining pertinent dimensionless groups, shows the analogy between mass and heat transfer. With the analogy, the development shown below in terms of dimensionless quantities is applicable to both conduction and diffusion problems. An assumption in what follows is that the temperature or concentration at a particle surface is uniform. Ideally this holds exactly only for widely separated particles in a slight gradient field, but can be nearly true for packed beds if the gradient is not too large.

Table 1. Definition of dimensionless quantities for non-convective mass and heat transfer

Variables and parameters	Mass transfer	Heat transfer
A	$(c_i-c_b)/(c_0-c_b)$	$(T_s-T_b)/(T_0-T_b)$
C	$(c-c_b)/(c_0-c_b)$	$(T-T_b)/(T_0-T_b)$
x	r/R	r/R
y	z/R	z/R
τ	$D_i t/\beta R^2$	$\kappa_s t/R^2$
λ	$\beta D_v/\alpha D_i$	$\kappa_v/\alpha\kappa_s$
Bi	$k_p R/D_i$	$h_s R/k_s$

The mass or heat balance equation for the homogeneous material surrounding the spheres is, in dimensionless form

$$\lambda\,\partial^2 C/\partial y^2 - 3(\beta/\alpha)(1-\alpha)(\partial A/\partial x)_{x=1} = \partial C/\partial\tau. \tag{2}$$

The heat or mass diffusion balance equation for a particle is

$$\frac{1}{x^2}\frac{\partial}{\partial x}\left(x^2\frac{\partial A}{\partial x}\right) = \frac{\partial A}{\partial \tau}. \tag{3}$$

For initial conditions, we considered in our earlier work [5] an impulse of heat or mass with the magnitude T_0-T_b or c_0-c_b in the continuous phase. For the present study we consider a general initial condition for the continuous phase, i.e. $B(y)$

$$C(y,\tau=0) = B(y) \tag{4}$$

$$A(x,\tau=0) = 0. \tag{5}$$

The boundary conditions are

$$C(y\to\pm\infty,\tau) = 0 \tag{6}$$

$$(\partial A/\partial x)_{x=0} = 0 \tag{7}$$

$$(\partial A/\partial x)_{x=1} = Bi[C-(A)_{x=1}]. \tag{8}$$

In equation (6) we consider a medium that is very large relative to particle diameter, and in equation (7) we let the intraparticle profile be symmetric. Equation (8) equates the fluxes on the inner and outer sides of the particle surface. For non-flow conditions in packed beds Bi is usually taken to be infinite [9]. For some cases, however, Bi would be finite, for example, for fouled particles coated with a thin insulating or mass transfer resistant material.

As the exact solution to the preceding equations is an unwieldy infinite series ill-suited for integration, we invoke the parabolic profile assumption of Do and Rice [6], who showed that for $\tau > 0.05$

$$A = m_1 + m_2 x^2. \tag{9}$$

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NOMENCLATURE

a_1	parameter, defined by equation (19)
a_2	parameter, defined by equation (19)
$A(x, y, \tau)$	dimensionless concentration or temperature inside particles, defined in Table 1
$\bar{A}(y, \tau)$	volumetric mean of $A(x, y, \tau)$ for spherical particles
$\hat{A}(\tau)$	Fourier transform of $\bar{A}(y, \tau)$
$B(y)$	initial condition, $C(y, \tau = 0)$, equation (4)
$\hat{B}$	Fourier transform of $B(y)$
Bi	Biot number, defined in Table 1
$C(x, y, \tau)$	dimensionless concentration or temperature in continuous phase, defined in Table 1
c	concentration in continuous phase [mol m^{-3}]
c_1	constant, defined by equation (19)
c_2	constant, defined by equation (19)
c_b	concentration particle pores at $\tau = 0$ [mol m^{-3}]
c_i	concentration in particle pores [mol m^{-3}]
c_0	magnitude of concentration impulse [mol m^{-3}]
D_i	intraparticle diffusivity [m^2 s^{-1}]
D_v	effective diffusivity in continuous phase [m^2 s^{-1}]
E_1	parameter, defined by equation (19)
E_2	parameter, defined by equation (19)
h	constant, defined in equations (31) and (33)
h_s	fluid-to-particle heat transfer coefficient [W m^{-2} K^{-1}]
k_{ij}	defined by equations (16)–(18)
k_{eff}	effective thermal diffusivity or mass diffusivity [m^2 s^{-1}]
k_p	fluid-to-particle mass transfer coefficient [m s^{-1}]
k_s	thermal conductivity of particle [W m^{-1} K^{-1}]
Q	parameter, defined by equation (19)
r	radial coordinate in spherical particle [m]
R	radius of spherical particle [m]
T	temperature of continuous phase [K]
T_b	intraparticle temperature at $t = 0$ [K]
T_0	temperature of thermal impulse [K]
T_s	temperature of particle [K]
t	time [s]
$U(y)$	unit step function
x	dimensionless radial coordinate in spherical particle, defined in Table 1
y	dimensionless longitudinal coordinate, defined in Table 1
z	longitudinal coordinate in composite medium [m].

Greek symbols

α	volume fraction of continuous phase
β	porosity of particle (for diffusion)
γ	$\beta(1-\alpha)/\alpha$
$\delta(y)$	Dirac delta function
κ	dimensionless Fourier domain variable
κ_s	thermal diffusivity of particle [m^2 s^{-1}]
κ_v	effective thermal diffusivity of continuous phase [m^2 s^{-1}]
λ	ratio of diffusivities or conductivities, defined in Table 1
μ_{An}	dimensionless nth spatial moment, generated by $\hat{A}$, defined by equation (20)
μ_{Cn}	dimensionless nth spatial moment, generated by $\hat{C}$, defined by equation (21)
ξ	variable of integration in equations (27) and (28)
τ	dimensionless time, defined in Table 1
ϕ	$-k_{11}(1+\gamma)\tau$.

Tomida and McCoy [10] recently demonstrated that if this polynomial is extended indefinitely, the solution is exact. Following Do and Rice it is not difficult to show that

$$(\partial A/\partial x)_{x=1} = (5/(1+5/Bi))\exp(-15\tau/(1+5/Bi)) \quad (10)$$

$$\partial \bar{A}/\partial \tau = (15/(1+5/Bi))(C-\bar{A}) \quad (11)$$

in terms of $\bar{A}$, the volume average over the spherical particles.

The Fourier transforms for equations (2), (10), and (11) can be written as

$$\mathrm{d}\hat{A}/\mathrm{d}\tau = k_{11}\hat{A}+k_{12}\hat{C} \quad (12)$$

$$\mathrm{d}\hat{C}/\mathrm{d}\tau = k_{21}\hat{A}+k_{22}\hat{C} \quad (13)$$

and initial conditions (4) and (5) become

$$\hat{C}(\tau = 0) = \hat{B} \quad (14)$$

$$\hat{A}(\tau = 0) = 0. \quad (15)$$

The coefficients in equations (12) and (13) are given by

$$k_{11} = -k_{12} = -15/(1+5/Bi) \quad (16)$$

$$k_{21} = k_{11}\beta(1-\alpha)/\alpha \quad (17)$$

$$k_{22} = \lambda\kappa^2 - k_{21}. \quad (18)$$

The Fourier domain solution for equations (12)–(15) can easily be obtained as

$$\hat{A} = \hat{B}(a_1\,\mathrm{e}^{E_1\tau}+a_2\,\mathrm{e}^{E_2\tau}), \quad \hat{C} = \hat{B}(c_1\,\mathrm{e}^{E_1\tau}+c_2\,\mathrm{e}^{E_2\tau}) \quad (19)$$

where

$$E_1 = (k_{11}+k_{22})(1-Q)/2$$

$$E_2 = (k_{11}+k_{22})(1+Q)/2$$

$$Q = [1+4(k_{12}k_{21}-k_{11}k_{22})/(k_{11}+k_{22})^2]^{1/2}$$

$$a_1 = -a_2 = -\hat{B}/(f_1-f_2)$$

$$c_1 = \hat{B}-c_2 = \hat{B}f_1/(f_1-f_2)$$

$$f_1 = (-E_1+k_{11}+k_{21})/(-E_1+k_{12}+k_{22})$$

$$f_2 = (-E_2+k_{11}+k_{21})/(-E_2+k_{12}+k_{22}).$$

Spatial moments are generated by $\hat{A}$ and $\hat{C}$ according to

$$\mu_{An}(\tau) = \int_{-\infty}^{\infty} A(y)y^n\,\mathrm{d}y \Big/ \int_{-\infty}^{\infty} B(y)\,\mathrm{d}y = (-1)^n\left[\lim_{\kappa\to 0}\mathrm{d}^n\hat{A}/\mathrm{d}\kappa^n\right]\Big/\hat{B} \quad (20)$$

$$\mu_{Cn}(\tau) = \int_{-\infty}^{\infty} C(y)y^n\,\mathrm{d}y \Big/ \int_{-\infty}^{\infty} B(y)\,\mathrm{d}y = (-1)^n\left[\lim_{\kappa\to 0}\mathrm{d}^n\hat{C}/\mathrm{d}\kappa^n\right]\Big/\hat{B}. \quad (21)$$

From equations (12)–(21) the first three moments are obtained as follows:

$$\mu_{A0}(\tau) = (1-e^{-\phi})/(1+\gamma) \quad (22)$$

$$\mu_{C0}(\tau) = (1+\gamma e^{-\phi})/(1+\gamma) \quad (23)$$

$$\mu_{A1}(\tau) = \mu_{C1}(\tau) = 0 \quad (24)$$

$$\mu_{A2}(\tau) = \frac{2\lambda}{k_{11}}\frac{(1-\gamma)}{(1+\gamma)^3}(1-e^{-\phi})+\frac{2\lambda\tau}{(1+\gamma)^2}(1-\gamma e^{-\phi}) \quad (25)$$

$$\mu_{C2}(\tau) = \frac{-4\lambda}{k_{11}}\frac{\gamma}{(1+\gamma)^3}(1-e^{-\phi})+\frac{2\lambda\tau}{(1+\gamma)^2}(1+\gamma^2 e^{-\phi}) \quad (26)$$

where

$$\gamma = \beta(1-\alpha)/\alpha, \quad \phi = -k_{11}(1+\gamma)\tau$$

and k_{11} is given by equation (16). The second moment expressions in ref. [5] should be corrected to agree with these.

After approximating the developing profiles of $\bar{A}$ and C for impulse input ($B(y) = \delta(y)$) as Gaussian functions, we can obtain the general solutions using the convolution theorem [7, 11], i.e.

$$\bar{A}(y,\tau) = \int_{-\infty}^{\infty} B(y-\xi)\{\bar{A}(\xi,\tau)_{\text{impulse}}\}\,d\xi \quad (27)$$

$$C(y,\tau) = \int_{-\infty}^{\infty} B(y-\xi)\{C(\xi,\tau)_{\text{impulse}}\}\,d\xi \quad (28)$$

where the impulse responses are given as

$$\bar{A}_{\text{impulse}} = \frac{\mu_{A0}}{(2\pi\mu_{A2})^{1/2}}\exp(-y^2/2\mu_{A2}) \quad (29)$$

$$C_{\text{impulse}} = \frac{\mu_{C0}}{(2\pi\mu_{C2})^{1/2}}\exp(-y^2/2\mu_{C2}). \quad (30)$$

RESPONSES FOR SPECIFIC INITIAL CONDITIONS

We consider several generalized functions as initial conditions for $C(y,\tau)$:

the rectangular pulse

$$B(y) = [U\{-(y-h)\}-U\{-(y+h)\}]/2h; \quad (31)$$

the step

$$B(y) = U(-y); \quad (32)$$

the ramp

$$B(y) = \frac{1}{2h}\{-(y-h)\}[U\{-(y-h)\} - U\{-(y+h)\}]+U\{-(y+h)\}. \quad (33)$$

Now, from equations (21)–(27), responses for pulse, step, and ramp functions can be obtained as follows:

pulse responses

$$\bar{A}_{\text{pulse}} = \left(\frac{\mu_{A0}}{4h}\right)\left\{\text{erf}\frac{h-y}{(2\mu_{A2})^{1/2}}+\text{erf}\frac{h+y}{(2\mu_{A2})^{1/2}}\right\} \quad (34)$$

$$C_{\text{pulse}} = \left(\frac{\mu_{C0}}{4h}\right)\left\{\text{erf}\frac{h-y}{(2\mu_{C2})^{1/2}}+\text{erf}\frac{h+y}{(2\mu_{C2})^{1/2}}\right\}; \quad (35)$$

step responses

$$\bar{A}_{\text{step}} = \left(\frac{\mu_{A0}}{2}\right)\text{erfc}\frac{y}{(2\mu_{A2})^{1/2}} \quad (36)$$

$$C_{\text{step}} = \left(\frac{\mu_{C0}}{2}\right)\text{erfc}\frac{y}{(2\mu_{C2})^{1/2}}; \quad (37)$$

ramp responses

$$\bar{A}_{\text{ramp}} = \left(\frac{\mu_{A0}}{4h}\right)\left(\frac{2\mu_{A2}}{\pi}\right)^{1/2}\left[\exp\left\{-\frac{(y-h)^2}{2\mu_{A2}}\right\} - \exp\left\{-\frac{(y+h)^2}{2\mu_{A2}}\right\}\right]+\left(\frac{h-y}{2h}\right)\left(\frac{\mu_{A0}}{2}\right)\left\{\text{erf}\frac{h-y}{(2\mu_{A2})^{1/2}} + \text{erf}\frac{h+y}{(2\mu_{A2})^{1/2}}\right\}+\left(\frac{\mu_{A0}}{2}\right)\text{erfc}\frac{y+h}{(2\mu_{A2})^{1/2}} \quad (38)$$

$$C_{\text{ramp}} = \left(\frac{\mu_{C0}}{4h}\right)\left(\frac{2\mu_{C2}}{\pi}\right)^{1/2}\left\{\exp\left[-\frac{(y-h)^2}{(2\mu_{C2})}\right] - \exp\left[-\frac{(y+h)^2}{(2\mu_{C2})}\right]\right\}+\left(\frac{h-y}{2h}\right)\left(\frac{\mu_{C0}}{2}\right) \times\left\{\text{erf}\frac{h-y}{(2\mu_{C2})^{1/2}}+\text{erf}\frac{h+y}{(2\mu_{C2})^{1/2}}\right\}+\left(\frac{\mu_{C0}}{2}\right)\text{erfc}\frac{y+h}{(2\mu_{C2})^{1/2}}. \quad (39)$$

The rectangular pulse responses and the step responses are plotted in Figs. 1 and 2, respectively.

DISCUSSION

After the transient has passed, radial gradients within the particles subside as shown in Figs. 1 and 2, and a quasi-steady state spreading of the profiles continues. The relationship for the area under the profiles in Fig. 1 is given as

$$\int_{-\infty}^{\infty} C(y,\tau=0)\,dy = \int_{-\infty}^{\infty} C(y,\tau)\,dy + \frac{\beta(1-\alpha)}{\alpha}\int_{-\infty}^{\infty}\bar{A}(y,\tau)\,dy. \quad (40)$$

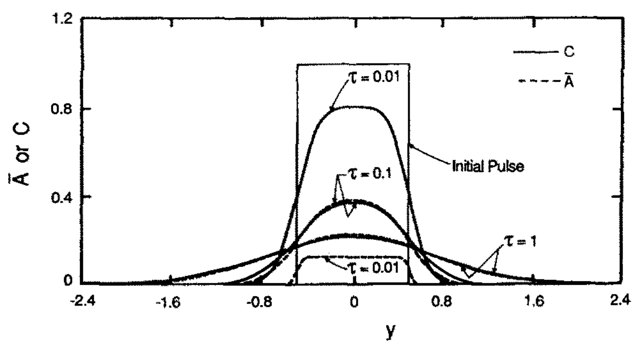

FIG. 1. Time dependence of profiles inside particle, $\bar{A}$, and in continuous phase, C, for $\lambda = 1.3$, $\beta(1-\alpha)/\alpha = 1.5$, $h = 0.5$, and $Bi = \infty$. Initial condition is a spatial rectangular pulse of tracer in the continuous phase.

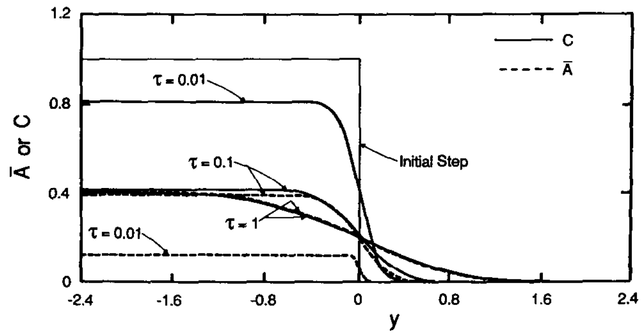

FIG. 2. Time dependence of profiles inside particle, $\bar{A}$, and in continuous phase, C, for $\lambda = 1.3$, $\beta(1-\alpha)/\alpha = 1.5$, and $Bi = \infty$. Initial condition is a spatial step of tracer in the continuous phase.

When time becomes infinite, C equals $\bar{A}$ and equation (40) becomes

$$\int_{-\infty}^{\infty} C(y,\tau=0)\,\mathrm{d}y = \left\{1+\frac{\beta(1-\alpha)}{\alpha}\right\}\int_{-\infty}^{\infty} C(y,\tau)\,\mathrm{d}y$$

$$= \left\{1+\frac{\beta(1-\alpha)}{\alpha}\right\}\int_{-\infty}^{\infty} \bar{A}(y,\tau)\,\mathrm{d}y. \quad (41)$$

The relative areas under the curves in Fig. 1 are due to transfer of heat or mass from the continuous phase to the particles, and are determined by the value, $\beta(1-\alpha)/\alpha = 1.5$. The asymptote on the negative y-axis in Fig. 2 for $\tau = 1$, which has the value $[1+\beta(1-\alpha)/\alpha]^{-1} = 0.4$, is likewise due to this transfer to the particles.

The rectangular pulse response, Fig. 1, resembles the impulse response in shape, and as time increases, the two responses become more alike. The ramp response resembles the step response, Fig. 2; and as time increases, these two also become more alike.

For times greater than the transient, an effective conduction or diffusion coefficient should apply. Expressions for such effective transport parameters have been developed by Maxwell [12] and by Jeffrey [13], for example. As the present model does not account for longitudinal gradients across the particles (only radial gradients are included), correct expressions for effective coefficients for densely packed spheres cannot be manifested by the present model. Thus, a restriction that holds for long time ($\tau \gg 1$) is that the volume fraction of the particle phase is very small compared to the continuous phase ($1-\alpha \ll 1$). This ensures that the contribution of the particle phase is negligible during the quasi-steady state transport process. This restriction is consistent with the boundary condition for radial symmetry, equations (7) and (8). A complete theory for the entire time domain for composite media conduction would include longitudinal, as well as radial, temperature gradients within the particles.

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