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ANALYTICAL SOLUTIONS OF CONDUCTION/DIFFUSION EQUATION IN MEDIA CONTACTING A FINITE VOLUME SOLUTION AND THEIR TOPOLOGICAL RELATIONS

SOLUCIONES ANALÍTICAS DE LA ECUACIÓN DE CONDUCCIÓN/DIFUSIÓN EN UN MEDIO CONTACTANDO CON UNA SOLUCIÓN DE VOLUMEN FINITO Y SUS RELACIONES TOPOLÓGICAS

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Abstract

Topological relations between heat or mass transfer equations analytical solutions for media contacting a well stirred solution with finite volume were deduced for infinite flat slabs, infinite cylinders and spheres. Referred topological relations conduce to prediction heat or mass transfer properties in the averaged equations as function of thermal or mass diffusivity and medium size and geometry. As results corollary, the application of the analytical solutions for empirical evaluation of heat or mass diffusivity was detailed.

Keywords: analytical solution, heat conduction, diffusion, finite volume solution, topological relations, averaged equations.

Resumen

Las relaciones topológicas entre las soluciones analíticas de las ecuaciones de transferencia de calor o masa en medios contactando una solución bien mezclada de volumen finito fueron deducidas para placas planas infinitas, cilindros infinitos y esferas. Las relaciones topológicas referidas conducen a la predicción de propiedades de transferencia de calor o masa en ecuaciones promediadas como función de la difusividad térmica o másica y del tamaño y geometría del medio. Como corolario de los resultados se detalla la aplicación de las soluciones analíticas para la evaluación empírica de difusividades térmicas o másicas.

Palabras clave: solución analítica, conducción de calor, difusión, solución de volumen finito, ecuaciones promediadas, relaciones topológicas.

1 Introduction

Solid-fluid contact processes have several applications in Chemical Engineering. As examples, continuous solid-liquid extractors (Veloso *et al*., 2005), solid-supercritical CO2 column extractors (Perrut *et al*., 1997; Reverchon and Iacuzio 1997), osmotic dehydration (Medina-Vivanco *et al*. 2002, Khin *et al*. 2006), heterogeneous chemical reactors (Marroquin de la Rosa *et al*., 2002, Valdés-Parada *et al*. 2007, Hernández-Martínez *et al*. 2011) and air heating columns (Shou-Shing *et al*., 2002). It is important to remark that in any real solid-fluid process the medium particles have different geometries and sizes and therefore numerical solutions of constitutive equation, even with the modern methods and computational resources, are only approximations, because it is impossible to build a model for every single solid particle. Then, in solid-fluid process modeling, the medium geometry and size must be estimated from mathematical expectation of the whole particles which could have, with high probability, irregular geometry (Pacheco-Aguirre *et al*. 2015). The heat or mass transfer modeling in an irregular geometry may be performed by finite element or generalized finite

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differences (Pacheco-Aguirre *et al*. 2015). However, for process modeling, it is a common practice in chemical engineering the use of averaged equations in terms of external (in fluid phase) and internal (in the particles) heat or mass transfer coefficients (Perrut *et al*., 1997; Reverchon and Iacuzio 1997; Veloso *et al*., 2005). Internal mass transfer coefficients depend on internal solute diffusivity, a characteristic length for diffusion and the averaged geometry of particles (Espinoza-Pérez *et al*., 2007). The geometry effect on internal heat or mass transfer coefficient may be expressed in terms of topology. Therefore, in order to determine the topological relations of heat and mass transfer behavior in different geometries, their analytical solution in traditional geometries must be deduced and analyzed in topological point of view.

On this perspective the classical problem of heat conduction or solute diffusion in media contacting with a well stirred solution of finite volume with interfacial resistance represents the constitutive equations for any fluid-solid process. The problem, with negligible interfacial resistance (or conduction/diffusion controlled), was originally reported and analytically solved for an infinite sheet by Carslaw and Jaeger (1959). Analytical solutions of the mass transfer problem, with negligible interfacial resistance, were reported for infinite sheet, infinite cylinders and spheres, by Crank (1975). The problem solution for solid-liquid extraction has been reported by Mikhailov (1977) and Castillo-Santos *et al*., (2017). Crank (1975) solutions are classics and applied in osmotic dehydration (Medina-Vivanco *et al*. 2002, Khin *et al*. 2006) and solid-liquid extraction (Cacace and Mazza 2003; Espinoza-Pérez *et al*., 2007). However, Mikhailov (1977) solutions are expressed only for pointwise solute concentration and Castillo-Santos *et al*., (2017) solution is only for 1D rectangular geometry mass transfer equation.

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2 Problem formulation

2.1 Constitutive equations

Heat conduction or solute diffusion in media contacting with a finite volume of well-stirred solution in a solid-fluid operation may be described in a general coordinate system for heat transfer by,

$$\frac{\partial \Theta_\beta}{\partial t} = \alpha \nabla \cdot \nabla \Theta_\beta, \quad \text{in } \mathscr{V}_\beta \tag{1a}$$

$$-\mathbf{n} \cdot \alpha \rho_\beta C p_\beta \nabla \Theta_{\beta i} = h\left(\Theta_{\gamma i} - \Theta_\gamma\right), \quad \text{at } \mathscr{A}_{\beta\gamma} \tag{2a}$$

$$\Theta_{\gamma i} = \Theta_{\beta i}, \quad \text{at } \mathscr{A}_{\beta\gamma} \tag{3a}$$

$$\mathscr{V}_\gamma \rho_\gamma C p_\gamma \frac{\partial \Theta_\gamma}{\partial t} = h \mathscr{A}_{\beta\gamma}\left(\Theta_{\gamma i} - \Theta_\gamma\right), \quad \text{in } \mathscr{V}_\gamma \tag{4a}$$

And for mass transfer by,

$$\frac{\partial \Theta_\beta}{\partial t} = \alpha \nabla \cdot \nabla \Theta_\beta, \quad \text{in } \mathscr{V}_\beta \tag{1b}$$

$$-\mathbf{n} \cdot \alpha \nabla \Theta_{\beta i} = h \rho_\gamma \left(\Theta_{\gamma i} - \Theta_\gamma\right), \quad \text{at } \mathscr{A}_{\beta\gamma} \tag{2b}$$

$$\Theta_{\gamma i} = K_{eq} \Theta_{\beta i}, \quad \text{at } \mathscr{A}_{\beta\gamma} \tag{3b}$$

$$\mathscr{V}_\gamma \rho_\gamma \frac{\partial \Theta_\gamma}{\partial t} = h \rho_\gamma \mathscr{A}_{\beta\gamma}\left(\Theta_{\gamma i} - \Theta_\gamma\right), \quad \text{in } \mathscr{V}_\gamma \tag{4b}$$

Where α is thermal ($k/\rho_\beta C p_\beta$)) or mass diffusivity; h is heat or mass transfer interfacial coefficient; K_{eq} the distribution constant in mass transfer and Cp is heat capacity. The transfer surface ($\mathscr{A}_{\beta\gamma}$) can be expressed in terms of medium volume ($\mathscr{V}_\beta$),

$$\mathscr{A}_{\beta\gamma} = \frac{\theta \mathscr{V}_\beta}{\ell} \tag{5}$$

Particular forms of Eq. (5) are: infinite flat slab with transfer by both sides with ℓ as half thickness, $\theta = 1$; infinite cylinder with radius ℓ, $\theta = 2$; sphere with radius ℓ, $\theta = 3$. Moreover, the finite solution volume ($\mathscr{V}_\gamma$) and medium volume ($\mathscr{V}_\beta$) can be expressed as fraction of total system volume ($\mathscr{V} = \mathscr{V}_\gamma + \mathscr{V}_\beta$),

$$\mathscr{V}_\gamma = \varepsilon \mathscr{V}; \quad \mathscr{V}_\beta = (1-\varepsilon)\mathscr{V} \tag{6}$$

Then, Eqs. (1) to (4) may be written in dimensionless form as,

$$\frac{\partial \Psi_\beta}{\partial Fo} = \overset{\bullet}{\nabla} \cdot \overset{\bullet}{\nabla} \Psi_\beta, \quad \text{in } \mathscr{V}_\beta \tag{7}$$

$$-\mathbf{n} \cdot \overset{\bullet}{\nabla} \Psi_{\beta i} = Bi \Psi_{\beta i} + \frac{Bi}{\phi} \Psi_\gamma, \quad \text{at } \mathscr{A}_{\beta\gamma} \tag{8}$$

$$-\frac{1}{\theta} \frac{\partial \Psi_\gamma}{\partial Fo} = Bi \Psi_{\beta i} + \frac{Bi}{\phi} \Psi_\gamma, \quad \text{in } \mathscr{V}_\gamma \tag{9}$$

by introducing the following dimensionless variables and numbers,

$$\overset{\bullet}{\nabla} = \nabla \ell \quad Fo = \frac{\alpha t}{\ell^2}$$

for heat transfer

$$Bi = \frac{h\ell}{k} \quad \phi = \frac{m_\gamma C p_\gamma}{m_\beta C p_\beta}$$

$$\Psi_\beta = \frac{\Theta_\beta - \Theta_{\beta e}}{\Theta_{\beta 0} - \Theta_{\beta e}} \quad \Psi_\gamma = \frac{\Theta_\gamma - \Theta_{\gamma e}}{\Theta_{\gamma 0} - \Theta_{\gamma e}}$$

for mass transfer

$$Bi = \frac{hl}{\alpha} \frac{\rho_\gamma K_{eq}}{\rho_\beta} \quad \phi = \frac{m_{\gamma e} K_{eq}}{m_{\beta e}}$$

$$\Psi_\beta = \frac{m_{\beta e}\Theta_\beta - m_{\beta e}\Theta_{\beta e}}{m_{\beta 0}\Theta_{\beta 0} - m_{\beta e}\Theta_{\beta e}} \quad \Psi_\gamma = \frac{m_{\gamma e}\Theta_\gamma - m_{\gamma e}\Theta_{\gamma e}}{m_{\gamma 0}\Theta_{\gamma 0} - m_{\gamma e}\Theta_{\gamma e}}$$

The equilibrium temperature or equilibrium mass fraction are defined by the total heat balance or mass balance,

$$\Theta_{\beta e} = \frac{\phi \Theta_{\gamma 0} + \Theta_{\beta 0}}{1 + \phi} \text{ and } \Theta_{\gamma e} = \Theta_{\beta e} \text{ for heat transfer} \tag{10a}$$

$$\Theta_{\beta e} = \frac{\frac{m_{\gamma 0}}{m_{\beta e}}\Theta_{\gamma 0} + \frac{m_{\beta 0}}{m_{\beta e}}\Theta_{\beta 0}}{1 + \phi} \text{ and}$$

$$\Theta_{\gamma e} = K_{eq}\Theta_{\beta e} \text{ for mass transfer} \tag{10b}$$

Another result from heat or mass balance used in dimensionless Eqs. (7) to (9) is,

$$\Theta_{\gamma 0} - \Theta_{\gamma e} = -\frac{1}{\phi}\left(\Theta_{\beta 0} - \Theta_{\beta e}\right) \text{ for heat transfer} \tag{11a}$$

$$\frac{m_{\gamma 0}\Theta_{\gamma 0} - m_{\gamma e}\Theta_{\gamma e}}{m_{\beta 0}\Theta_{\beta 0} - m_{\beta e}\Theta_{\beta e}} = -1 \text{ for mass transfer} \tag{11b}$$

The above dimensionless analysis is not reported in Carslaw and Jaeger (1959) or Crank (1975), and it is extremely important because unifies the heat (Eqs. 1a-3a) and mass (Eqs. 1b-3b) transfer problem in Eqs. (7)-(9). It is important to note that mass transfer dimensionless variables considers that initial media mass ($m_{\beta 0}$) and initial solution mass ($m_{\gamma 0}$) may be differ of equilibrium ones ($m_{\beta e}$ and $m_{\gamma e}$). This is because in any solid-fluid (medium-solution) mass transfer process the solid phase retains fluid phase known as retained solution. Therefore, the final medium is a mixture of solid phase and retained solution called underflow (Castillo-Santos *et al*., 2016). The application of Eq. (10b) for equilibrium concentrations prediction requires the prediction of underflow mass at equilibrium which depend of specific retained fluid phase by inert solids in underflow (Castillo-Santos *et al*., 2016). In this work, only the result for dimensionless variables will be used.

2.2 *Constitutive equations for the three conventional geometries*

Eqs. (7) and (8) can be written in terms of 1D rectangular coordinate, 1D cylindrical coordinate and 1D spherical coordinate as is shown in the following paragraphs.

2.2.1 *Infinite flat slab with heat/mass transfer in both sides and ℓ as half thickness*

$$\frac{\partial \Psi_\beta}{\partial Fo} = \frac{\partial^2 \Psi_\beta}{\partial \xi^2} \text{ for } 0 \leqslant \xi \leqslant 1 \text{ and } Fo > 0 \tag{7a}$$

where $\xi = z/\ell$. Eqs. (7) and (8) are symmetric with respect to ξ and therefore $\partial\Psi_\beta/\partial\xi = 0$ at $\xi = 0$.

2.2.2 *Infinite cylinder with radius ℓ*

$$\frac{\partial \Psi_\beta}{\partial Fo} = \frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi \frac{\partial \Psi_\beta}{\partial \xi}\right) \text{ for } 0 \leqslant \xi \leqslant 1 \text{ and } Fo > 0 \tag{7b}$$

where $\xi = r/\ell$.

2.2.3 *Sphere with radius ℓ*

$$\frac{\partial \Psi_\beta}{\partial Fo} = \frac{1}{\xi^2}\frac{\partial}{\partial \xi}\left(\xi^2 \frac{\partial \Psi_\beta}{\partial \xi}\right) \text{ for } 0 \leqslant \xi \leqslant 1 \text{ and } Fo > 0 \tag{7c}$$

where $\xi = r/\ell$.

In the three cases the boundary condition at interface (Eq. 8) is expressed as,

$$-\frac{\partial \Psi_\beta}{\partial \xi} = Bi \Psi_{\beta i} + \frac{Bi}{\phi}\Psi_\gamma \text{ for } \xi = 1 \text{ and } Fo > 0 \tag{8a}$$

2.3 Space averaged equations

The same phenomena may be represented in terms of macroscopic heat or mass transfer and averaged temperature or solute concentration in underflow $\langle\theta\rangle_\beta = \int_{\mathscr{V}_\beta}\Theta_\beta d\mathscr{V} / \int_{\mathscr{V}_\beta} d\mathscr{V}$ (Castillo-Santos *et al.*, 2017).

Macroscopic heat balance in media and solution,

$$C_{p_\beta}\rho_\beta\mathscr{V}_\beta\frac{d\langle\Theta\rangle_\beta}{dt} = h_\beta\mathscr{A}_{\beta\gamma}\left(\Theta_{\beta i}-\langle\Theta\rangle_\beta\right),\ \text{in } \mathscr{V}_\beta \tag{12a}$$

$$C_{p_\gamma}\rho_\gamma\mathscr{V}_\gamma\frac{d\Theta_\gamma}{dt} = h_\gamma\mathscr{A}_{\beta\gamma}\left(\Theta_{\gamma i}-\Theta_\gamma\right),\ \text{in } \mathscr{V}_\gamma \tag{13a}$$

Macroscopic mass balances of extractable solids in media and solution,

$$\rho_\beta\mathscr{V}_\beta\frac{d\langle\Theta\rangle_\beta}{dt} = h_\beta\rho_\beta\mathscr{A}_{\beta\gamma}\left(\Theta_{\beta i}-\langle\Theta\rangle_\beta\right)\ \text{in } \mathscr{V}_\beta \tag{12b}$$

$$\rho_\gamma\mathscr{V}_\gamma\frac{d\Theta_\gamma}{dt} = h_\gamma\rho_\gamma\mathscr{A}_{\beta\gamma}\left(\Theta_{\gamma i}-\Theta_\gamma\right)\ \text{in } \mathscr{V}_\gamma \tag{13b}$$

In which the heat or mass transfer continuity at interface implies,

Heat transfer

$$h_\gamma\mathscr{A}_{\beta\gamma}\left(\Theta_{\gamma i}-\Theta_\gamma\right) = -h_\beta\mathscr{A}_{\beta\gamma}\left(\Theta_{\beta i}-\langle\Theta\rangle_\beta\right),\ \text{at } \mathscr{A}_{\beta\gamma} \tag{14a}$$

Mass transfer

$$h_\gamma\mathscr{A}_{\beta\gamma}\rho_\gamma\left(\Theta_{\gamma i}-\Theta_\gamma\right) = -h_\beta\mathscr{A}_{\beta\gamma}\rho_\beta\left(\Theta_{\beta i}-\langle\Theta\rangle_\beta\right),\ \text{at } \mathscr{A}_{\beta\gamma} \tag{14b}$$

h_γ is the same heat or mass transfer interface coefficient expressed in Eqs. (1) to (4) but particularly defined for fluid phase side; h_β is a heat or mass transfer interface coefficient in solid phase side, its implication and relation to constitutive equations will be discussed in deep in results section. Introducing the following dimensionless variables,

for heat transfer

$$\langle\Psi\rangle_\beta = \frac{\langle\Theta\rangle_\beta-\Theta_{\beta e}}{\Theta_{\beta 0}-\Theta_{\beta e}};\quad Bi=\frac{h_\gamma l}{k};\quad \Omega=\frac{h_\beta l\theta}{k}$$

for mass transfer

$$\langle\Psi\rangle_\beta = \frac{m_{\beta e}\langle\Theta\rangle_\beta - m_{\beta e}\Theta_{\beta e}}{m_{\beta 0}\Theta_{\beta 0}-m_{\beta e}\Theta_{\beta e}};Bi=\frac{h_\gamma l}{\alpha}\frac{\rho_\gamma K_{eq}}{\rho_\beta};\Omega=\frac{h_\beta l\theta}{\alpha}$$

Eqs. (9), (10) and (11) may be written as,

$$\frac{d\langle\Psi\rangle_\beta}{dFo} = \Omega\left(\Psi_{\beta i}-\langle\Psi\rangle_\beta\right) \tag{15}$$

$$\frac{d\Psi_\gamma}{dFo} = \frac{\theta Bi}{\phi}\left(\Psi_{\gamma i}-\Psi_\gamma\right) \tag{16}$$

$$\frac{\theta Bi}{\phi}\left(\Psi_{\gamma i}-\Psi_\gamma\right) = \Omega\left(\Psi_{\beta i}-\langle\Psi\rangle_\beta\right) \tag{17}$$

$$\Psi_{\gamma i} = -\phi\Psi_{\beta i} \tag{18}$$

3 Results

3.1 Analytical solutions of constitutive equations

Mikhailov (1977) presented an elegant analytical solution for mass transfer during solid-liquid extraction. The elegance lies in the fact that the solution (obtained by Laplace transform approach) was obtained for any geometry. However this solution is not referred for averaged media concentration $\langle\theta\rangle_\beta = \int_{\mathscr{V}_\beta}\Theta_\beta d\mathscr{V} / \int_{\mathscr{V}_\beta} d\mathscr{V}$ or for medium concentration Θ_γ. Therefore in this work the analytical solutions for the 3 conventional geometrics were deduced by Laplace transform in order to deduce the topological relation between them. Recently, Green´s function approaches have been reported for analytical solution of heat transfer problems with explicit function of time as boundary conditions (Chen *et al.*, 2017) or discontinuities at boundary conditions (Woodbury *et al.*, 2017). However for the present problem, in which the boundary condition (Eqs. 2) is coupled with an initial value problem (Eqs. 4), the classical Laplace approach (with natural application for initial value problems) is enough and the developed solution stages leads to topology relations between geometries.

Assuming homogeneous initial temperature or mass fraction, the initial conditions for Eqs. (7) to (9) are $\Psi_\beta = 1$ and $\Psi_\gamma = 1$ at $Fo = 0$. Applying the Laplace transform with respect to Fo to Eqs. (7a), (7b) and (7c),

$$\frac{d^2\Psi_\beta(s,\xi)}{d\xi^2} - s\Psi_\beta(s,\xi)+1=0 \tag{19a}$$

$$\xi^2\frac{d^2\Psi_\beta(s,\xi)}{d\xi^2}+\xi\frac{d\Psi_\beta(s,\xi)}{d\xi}-\left(s\xi^2+0\right)\Psi_\beta(s,\xi)+\xi^2=0 \tag{19b}$$

$$\xi^2\frac{d^2\Psi_\beta(s,\xi)}{d\xi^2}+2\xi\frac{d\Psi_\beta(s,\xi)}{d\xi}-\left(s\xi^2+0\right)\Psi_\beta(s,\xi)+\xi^2=0 \tag{19c}$$

where $\Psi_\beta(s,\xi)$ is the Laplace transform of $\Psi_\beta(Fo,\xi)$. The solutions of Eqs. (19) are,

$$\Psi_\beta(s,\xi) = C_1\cosh\left(\sqrt{s}\xi\right)+C_4\sinh\left(\sqrt{s}\xi\right)+\frac{1}{s} \tag{20a}$$

$$\Psi_\beta(s,\xi) = C_2 I_0\left(\sqrt{s}\xi\right) + C_5 K_0\left(\sqrt{s}\xi\right) + \frac{1}{s} \tag{20b}$$

$$\Psi_\beta(s,\xi) = C_3 i_0\left(\sqrt{s}\xi\right) + C_6 k_0\left(\sqrt{s}\xi\right) + \frac{1}{s} \tag{20c}$$

where I_0 and K_0 are the modified Bessel functions of first and second kind of order 0, and i_0 and k_0 are the modified spherical Bessel functions of first and second kind of order 0. By symmetry of Eq. (7a) $C_4 = 0$ and by the fact that Eqs. (19b) and (19c) must have a finite value in $\xi = 0$; $C_5 = 0$ and $C_6 = 0$. From Eqs. (8) and (9) it is evident that,

$$-\frac{1}{\theta}\frac{\partial \Psi_\gamma}{\partial Fo} = -\frac{\partial \Psi_\beta}{\partial \xi} \tag{21}$$

And therefore applying Eq. (21) in the Laplace transform of Eq. (9)

$$\Psi_\gamma(s) = \frac{1}{s} + \frac{C_1 \sinh\left(\sqrt{s}\right)}{\sqrt{s}} \tag{22a}$$

$$\Psi_\gamma(s) = \frac{1}{s} + \frac{2C_2 I_1\left(\sqrt{s}\xi\right)}{\sqrt{s}} \tag{22b}$$

$$\Psi_\gamma(s) = \frac{1}{s} + \frac{3C_3 i_1\left(\sqrt{s}\xi\right)}{\sqrt{s}} \tag{22c}$$

Applying Eqs. (20) and (21) in Eqs. (8),

$$-\frac{C_1\sqrt{s}\sinh\left(\sqrt{s}\right)}{Bi} = C_1\cosh\left(\sqrt{s}\right) + \frac{1}{s} + \frac{1}{\phi}\left(\frac{1}{s} + \frac{C_1\sinh\left(\sqrt{s}\right)}{\sqrt{s}}\right) \tag{23a}$$

$$-\frac{C_2\sqrt{s}I_1\left(\sqrt{s}\right)}{Bi} = C_2 I_0\left(\sqrt{s}\right) + \frac{1}{s} + \frac{1}{\phi}\left(\frac{1}{s} + \frac{2C_2 I_1\left(\sqrt{s}\xi\right)}{\sqrt{s}}\right) \tag{23b}$$

$$-\frac{C_3\sqrt{s}i_1\left(\sqrt{s}\right)}{Bi} = C_3 i_0\left(\sqrt{s}\right) + \frac{1}{s} + \frac{1}{\phi}\left(\frac{1}{s} + \frac{3C_3 i_1\left(\sqrt{s}\xi\right)}{\sqrt{s}}\right) \tag{23c}$$

From Eqs. (23),

$$C_\theta = \frac{\phi+1}{\phi}\frac{1}{s u_\theta(s)}, \text{ for } \theta = 1,2,3 \tag{24}$$

Where,

$$u_1(s) = -\frac{\sqrt{s}\sinh\left(\sqrt{s}\right)}{Bi} - \cosh\left(\sqrt{s}\right) - \frac{\sinh\left(\sqrt{s}\right)}{\phi\sqrt{s}} \tag{25a}$$

$$u_2(s) = -\frac{\sqrt{s}I_1\left(\sqrt{s}\right)}{Bi} - I_o\left(\sqrt{s}\right) - \frac{2I_1\left(\sqrt{s}\right)}{\phi\sqrt{s}} \tag{25b}$$

$$u_3(s) = -\frac{\sqrt{s}i_1\left(\sqrt{s}\right)}{Bi} - i_o\left(\sqrt{s}\right) - \frac{3i_1\left(\sqrt{s}\right)}{\phi\sqrt{s}} \tag{25c}$$

Then, applying the constant in Eqs. (20) and the residual theorem of Cauchy,

$$\Psi_\beta(Fo,\xi) = 1 + \lim_{s\to 0}\frac{s(1+\phi)\cosh\left(\sqrt{s}\xi\right)e^{sFo}}{\phi s u_1(s)} + \sum_{n=1}^{\infty}\lim_{s\to s_n}\frac{(s-s_n)}{u_1(s)}\frac{(1+\phi)\cosh\left(\sqrt{s}\xi\right)e^{sFo}}{\phi s} \tag{26a}$$

$$\Psi_\beta(Fo,\xi) = 1 + \lim_{s\to 0}\frac{s(1+\phi)I_0\left(\sqrt{s}\xi\right)e^{sFo}}{\phi s u_2(s)} + \sum_{n=1}^{\infty}\lim_{s\to s_n}\frac{(s-s_n)}{u_2(s)}\frac{(1+\phi)I_0\left(\sqrt{s}\xi\right)e^{sFo}}{\phi s} \tag{26b}$$

$$\Psi_\beta(Fo,\xi) = 1 + \lim_{s\to 0}\frac{s(1+\phi)i_0\left(\sqrt{s}\xi\right)e^{sFo}}{\phi s u_3(s)} + \sum_{n=1}^{\infty}\lim_{s\to s_n}\frac{(s-s_n)}{u_3(s)}\frac{(1+\phi)i_0\left(\sqrt{s}\xi\right)e^{sFo}}{\phi s} \tag{26c}$$

Where s_n are the roots of,

$$-\frac{\sqrt{s_n}\sinh\left(\sqrt{s_n}\right)}{Bi} - \cosh\left(\sqrt{s_n}\right) - \frac{\sinh\left(\sqrt{s_n}\right)}{\phi\sqrt{s_n}} = 0 \tag{27a}$$

$$-\frac{\sqrt{s_n}I_1\left(\sqrt{s_n}\right)}{Bi} - I_o\left(\sqrt{s_n}\right) - \frac{2I_1\left(\sqrt{s_n}\right)}{\phi\sqrt{s_n}} = 0 \tag{27b}$$

$$-\frac{\sqrt{s_n}i_1\left(\sqrt{s_n}\right)}{Bi} - i_o\left(\sqrt{s_n}\right) - \frac{3i_1\left(\sqrt{s_n}\right)}{\phi\sqrt{s_n}} = 0 \tag{27c}$$

for $n = 1,2,\ldots,\infty$.

Considering that $\lim_{x\to 0}\cosh(x) \to 1$, $\lim_{x\to 0} I_0(x) \to 1$, $\lim_{x\to 0} i_0(x) \to 1$, $\lim_{x\to 0}\frac{\sinh(x)}{x} \to 1$, $\lim_{x\to 0}\frac{I_1(x)}{x} \to \frac{1}{2}$ and $\lim_{x\to 0}\frac{i_1(x)}{x} \to \frac{1}{3}$ and applying L´Hôpital´s rule, Eqs. (27) can be written as,

$$\Psi_\beta(Fo,\xi) = \sum_{n=1}^{\infty}\frac{(1+\phi)\cosh\left(\sqrt{s_n}\xi\right)e^{s_n Fo}}{u_1'(s_n)\phi s_n} \tag{28a}$$

$$\Psi_\beta(Fo,\xi) = \sum_{n=1}^{\infty}\frac{(1+\phi)I_0\left(\sqrt{s_n}\xi\right)e^{s_n Fo}}{u_2'(s_n)\phi s_n} \tag{28b}$$

$$\Psi_\beta(Fo,\xi) = \sum_{n=1}^{\infty}\frac{(1+\phi)i_0\left(\sqrt{s_n}\xi\right)e^{s_n Fo}}{u_3'(s_n)\phi s_n} \tag{28c}$$

with

$$u_1{}'(s) = -\frac{\cosh\left(\sqrt{s}\right)}{2Bi} - \frac{\sinh\left(\sqrt{s}\right)}{2Bi\sqrt{s}} - \frac{\sinh\left(\sqrt{s}\right)}{2\sqrt{s}} - \frac{\cosh\left(\sqrt{s}\right)}{2\phi s} + \frac{\sinh\left(\sqrt{s}\right)}{2\phi s\sqrt{s}} \quad (29a)$$

$$u_2{}'(s) = -\frac{I_0\left(\sqrt{s}\right)}{2Bi} - \frac{I_1\left(\sqrt{s}\right)}{2\sqrt{s}} - \frac{I_2\left(\sqrt{s}\right)}{\phi s} \quad (29b)$$

$$u_3{}'(s) = -\frac{1}{Bi}\left(\frac{\sinh\left(\sqrt{s}\right)}{2\sqrt{s}} - \frac{\cosh\left(\sqrt{s}\right)}{2s} + \frac{\sinh\left(\sqrt{s}\right)}{2s\sqrt{s}}\right) - \frac{\cosh\left(\sqrt{s}\right) - \frac{\sinh\left(\sqrt{s}\right)}{\sqrt{s}}}{2s} - \frac{3}{\phi}\left(\frac{\sinh\left(\sqrt{s}\right)}{2s\sqrt{s}} - \frac{3}{2}\frac{\cosh\left(\sqrt{s}\right)}{s^2} - \frac{3}{2}\frac{\sinh\left(\sqrt{s}\right)}{s^2\sqrt{s}}\right) \quad (29c)$$

In Eq. (29c) was introduced the fact that: $i_0(x) = \frac{\sinh(x)}{x}$ and $i_1(x) = \frac{x\cosh(x)-\sinh(x)}{x^2}$.

Defining $\sqrt{s} = i\lambda$ and considering that $\sinh(iz) = i\sin(z)$, $\cosh(iz) = \cos(z)$ and $I_n(ix) = i^n J_n(x)$, Eqs. (26) are expressed in real dominion as,

$$\Psi_\beta(Fo,\xi) = 2\sum_{n=1}^{\infty}\frac{(1+\phi)\cos(\lambda_n\xi)e^{-\lambda_n^2 Fo}}{u_1'(\lambda_n)\phi\lambda_n^2} \quad (30a)$$

$$\Psi_\beta(Fo,\xi) = 2\sum_{n=1}^{\infty}\frac{(1+\phi)J_0(\lambda_n\xi)e^{-\lambda_n^2 Fo}}{u_2'(\lambda_n)\phi\lambda_n^2} \quad (30b)$$

$$\Psi_\beta(Fo,\xi) = 2\sum_{n=1}^{\infty}\frac{\sin(\lambda_n\xi)}{\lambda_n\xi}\frac{(1+\phi)e^{-\lambda_n^2 Fo}}{u_3'(\lambda_n)\phi\lambda_n^2} \quad (30c)$$

Where λ_n are the eigenvalues generated by the roots of,

$$\frac{\lambda_n\sin(\lambda_n)}{Bi} - \cos(\lambda_n) - \frac{\sin(\lambda_n)}{\phi\lambda_n} = 0 \quad (31a)$$

$$\frac{\lambda_n J_1(\lambda_n)}{Bi} - J_o(\lambda_n) - \frac{2J_1(\lambda_n)}{\phi\lambda_n} = 0 \quad (31b)$$

$$\frac{1}{Bi}\left(\cos(\lambda_n) - \frac{\sin(\lambda_n)}{\lambda_n}\right) + \frac{\sin(\lambda_n)}{\lambda_n} + \frac{3}{\phi}\left(-\frac{\cos(\lambda_n)}{\lambda_n^2} + \frac{\sin(\lambda_n)}{\lambda_n^3}\right) = 0 \quad (31c)$$

And,

$$u_1{}'(\lambda_n) = \frac{\cos(\lambda_n)}{Bi} + \frac{\sin(\lambda_n)}{Bi\lambda_n} + \frac{\sin(\lambda_n)}{\lambda_n} - \frac{\cos(\lambda_n)}{\phi\lambda_n^2} + \frac{\sin(\lambda_n)}{\phi\lambda_n^3} \quad (32a)$$

$$u_2{}'(\lambda_n) = \frac{J_0(\lambda_n)}{Bi} + \frac{J_1(\lambda_n)}{\lambda_n} + \frac{2J_2(\lambda_n)}{\phi\lambda_n^2} \quad (32b)$$

$$u_3{}'(\lambda_n) = \frac{1}{Bi}\left(\frac{\sin(\lambda_n)}{\lambda_n} + \frac{\cos(\lambda_n)}{\lambda_n^2} - \frac{\sin(\lambda_n)}{\lambda_n^3}\right) - \frac{1}{\lambda_n^2}\left(\cos(\lambda_n) - \frac{\sin(\lambda_n)}{\lambda_n}\right) + \frac{1}{\phi}\left(-\frac{3\sin(\lambda_n)}{\lambda_n^3} - \frac{9\cos(\lambda_n)}{\lambda_n^4} + \frac{9\sin(\lambda_n)}{\lambda_n^5}\right) \quad (32c)$$

Eq. (30a) is the analytical solution of Eqs. (7a), (8a) and (9); Eq. (30b) is the analytical solution of Eqs. (7b), (8a) and (9); and, Eq. (30c) is the analytical solution of Eqs. (7c), (8a) and (9). The mean temperature or concentration is obtained from,

$$\langle\Psi\rangle_\beta(Fo) = \frac{\int_0^1 \xi^{\theta-1}\Psi_\beta(\xi,Fo)\,d\xi}{\int_0^1 \xi^{\theta-1}d\xi} \quad (33)$$

Therefore,

$$\langle\Psi\rangle_\beta(Fo) = 2\sum_{n=1}^{\infty}\frac{(1+\phi)\sin(\lambda_n)e^{-\lambda_n^2 Fo}}{\phi u_1{}'(\lambda_n)\lambda_n^3} \quad (34a)$$

$$\langle\Psi\rangle_\beta(Fo) = 4\sum_{n=1}^{\infty}\frac{(1+\phi)J_1(\lambda_n)e^{-\lambda_n^2 Fo}}{\phi u_2{}'(\lambda_n)\lambda_n^3} \quad (34b)$$

$$\langle\Psi\rangle_\beta(Fo) = 6\sum_{n=1}^{\infty}\left(\frac{\sin(\lambda_n)}{\lambda_n^2} - \frac{\cos(\lambda_n)}{\lambda_n}\right)\frac{(1+\phi)e^{-\lambda_n^2 Fo}}{\phi u_3{}'(\lambda_n)\lambda_n^3} \quad (34c)$$

Finally, by applying Eq. (33) to Laplace transform of analytical solutions (Eqs. 20),

$$\langle\Psi\rangle_\beta(s) = \frac{\int_0^1\left(C_1\cosh\left(\sqrt{s}\xi\right) + \frac{1}{s}\right)d\xi}{\int_0^1 d\xi} = \frac{1}{s} + \frac{C_1\sinh\left(\sqrt{s}\right)}{\sqrt{s}} \quad (35a)$$

$$\langle\Psi\rangle_\beta(s) = \frac{\int_0^1\left(C_2 I_0\left(\sqrt{s}\xi\right) + \frac{1}{s}\right)\xi d\xi}{\int_0^1 \xi d\xi} = \frac{1}{s} + \frac{2C_2 I_1\left(\sqrt{s}\right)}{\sqrt{s}} \quad (35b)$$

$$\langle\Psi\rangle_\beta(s) = \frac{\int_0^1\left(C_3 i_0\left(\sqrt{s}\xi\right) + \frac{1}{s}\right)\xi^2 d\xi}{\int_0^1 \xi^2 d\xi} = \frac{1}{s} + \frac{3C_3 i_1\left(\sqrt{s}\right)}{\sqrt{s}} \quad (35c)$$

Which demonstrates (through Eqs. 22) that $\Psi_\gamma(s) = \langle\Psi\rangle_\beta(s)$. Therefore $\Psi_\gamma(Fo) = \langle\Psi\rangle_\beta(Fo)$ and the constitutive equations analytical solutions are complete. This result is not obvious from their differential form (Eqs. 7, 8 and 9).

3.2 Analytical solution of averaged equations

Eqs. (15) to (18) may be written,

$$\Psi_{\beta i} = -\frac{1}{\phi + \Omega\phi/(\theta Bi)}\Psi_\gamma + \frac{\Omega}{\theta Bi + \Omega}\langle\Psi\rangle_\beta \tag{36}$$

$$\frac{d\Psi_\gamma}{d\tau} = \frac{d\langle\Psi\rangle_\beta}{d\tau} \text{ or } \Psi_\gamma(Fo) = \langle\Psi\rangle_\beta(Fo) \tag{37}$$

Taking Laplace transform of Eqs. (15), solving for $\langle\Psi\rangle_\beta(s)$ (with Eq. 36 and 37) and taking the Laplace inverse the following result is obtained,

$$\langle\Psi\rangle_\beta(Fo) = \Psi_\gamma(Fo) = e^{-\Omega\left(1+\frac{1}{\phi+\Omega\phi/(\theta Bi)}-\frac{\Omega}{\theta Bi+\Omega}\right)Fo} \tag{38}$$

It will be demonstrated that Eq. (38) is valid for any geometry with the specific geometrical factor θ and topological factor Ω.

3.3 Mathematical properties

The main objective of this work is to deduce the topological relations of analytical solution between different geometries. However, as corollary of analytical solutions, some important mathematical properties must be discussed. Averaged analytical solutions of constitutive equations (Eqs. 34) behavior at different *Bi* numbers and different media/solute ratio (ϕ) are plotted with discontinuous lines in Fig. 1 to 3. It can be observed that the whole solutions in semi-log plot have a linear asymptotic behavior. This is as result of that eigenvalues generated by Eqs. (31) are categorized $\lambda_1 > \lambda_2 > \lambda_3 > \ldots$, and therefore Eqs. (34) have the following asymptotic limits,

$$\langle\Psi\rangle_\beta(Fo) = \Psi_\gamma(Fo) = Be^{-\lambda_1^2 Fo} = B\exp\left(-\frac{\lambda_1^2\alpha}{l^2}t\right) \tag{39}$$

This mathematical property has an important practical application: the estimation of mass diffusivity of thermal diffusivity from mass transfer or heat transfer experimental kinetics. In the case of mass transfer, Eqs. (34) for $Bi \to \infty$ (Crank 1975 solutions) has been applied for mass diffusivity estimation during osmotic drying (Medina-Vivanco *et al*. 2002), or during solid-liquid extraction kinetics (Cacace and Mazza, 2003; Espinoza-Pérez *et al*. 2007). Eq. (39) emphasizes the relevance of the first eigenvalue (λ_1), because represents the asymptotic slope of $\ln\langle\Psi\rangle_\beta$ or $\ln(\Psi_\gamma)$ vs Fo. As consequence, thermal or mass diffusivity (α) can be calculated from the slope (b) obtained by

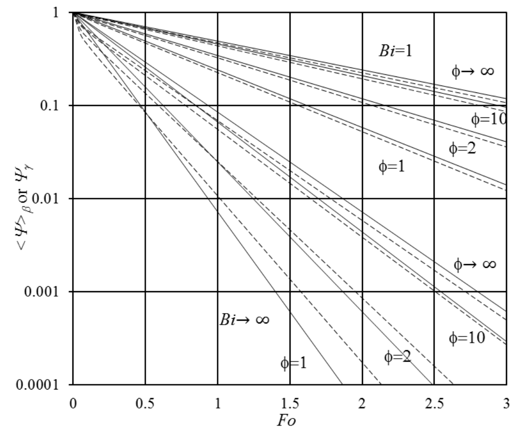

Fig. 1. Behavior of Eq. (34a) (discontinuous lines) and Eq. (38) (continuous lines) at different values of *Bi* and ϕ.

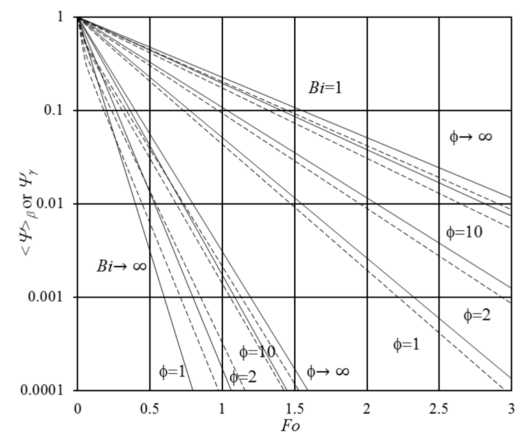

Fig. 2. Behavior of Eq. (34b) (discontinuous lines) and Eq. (38) (continuous lines) at different values of *Bi* and ϕ.

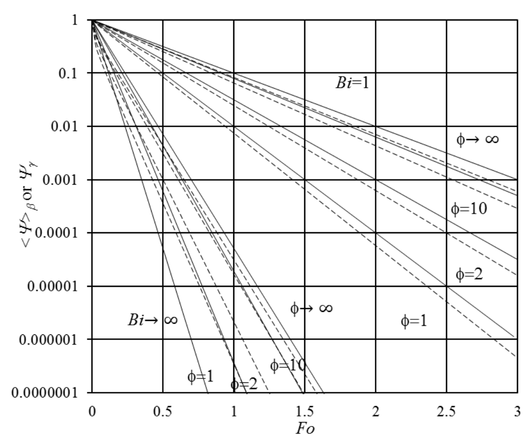

Fig. 3. Behavior of Eq. (34c) (discontinuous lines) and Eq. (38) (continuous lines) at different values of *Bi* and ϕ.

Table 1. First eigenvalue (λ_1) generated by Eqs. (31a) at different values of *Bi* and ϕ.

ϕ	*Bi*							
	0.1	0.5	1	4	6	10	50	∞
0.5	0.5386	1.1262	1.4672	2.0215	2.1089	2.1808	2.2675	2.2889
1	0.4398	0.9218	1.2078	1.7207	1.8145	1.8964	2.0016	2.0288
2	0.3809	0.7992	1.0499	1.5199	1.6122	1.6955	1.8069	1.8366
4	0.3478	0.73	0.9602	1.4007	1.4903	1.5725	1.685	1.7155
10	0.3262	0.685	0.9017	1.3214	1.4085	1.4892	1.6012	1.632
20	0.3187	0.6693	0.8813	1.2934	1.3795	1.4596	1.5712	1.602
∞	0.3111	0.6533	0.8603	1.2646	1.3496	1.4289	1.54	1.5708

Table 2. First eigenvalue (λ_1) generated by Eqs. (31b) at different values of *Bi* and ϕ.

ϕ	*Bi*							
	0.1	0.5	1	4	6	10	50	∞
0.5	0.7649	1.6212	2.1345	2.9246	3.0266	3.1035	3.1879	3.2075
1	0.6246	1.3273	1.7608	2.5477	2.6808	2.7899	2.9186	2.9496
2	0.5409	1.1509	1.5317	2.2734	2.416	2.5399	2.6955	2.7346
4	0.4938	1.0512	1.4012	2.1048	2.2485	2.3773	2.5453	2.5888
10	0.4632	0.9865	1.316	1.9906	2.1332	2.2635	2.4379	2.4839
20	0.4526	0.9639	1.2863	1.95	2.0919	2.2224	2.3985	2.4454
∞	0.4417	0.9408	1.2558	1.9081	2.049	2.1795	2.3572	2.4048

Table 3. First eigenvalue (λ_1) generated by Eqs. (31c) at different values of *Bi* and ϕ.

ϕ	*Bi*							
	0.1	0.5	1	4	6	10	50	∞
0.5	0.9391	2.0097	2.672	3.679	3.7915	3.8712	3.9536	3.972
1	0.7668	1.6449	2.2036	3.2487	3.4172	3.5485	3.6932	3.7264
2	0.6641	1.4261	1.9165	2.9146	3.1064	3.268	3.46	3.5059
4	0.6063	1.3025	1.7529	2.7042	2.9021	3.0765	3.2946	3.3485
10	0.5687	1.2222	1.6463	2.5603	2.7591	2.9392	3.1724	3.2316
20	0.5557	1.1942	1.609	2.5089	2.7075	2.889	3.127	3.1879
∞	0.5423	1.1656	1.5708	2.4556	2.6537	2.8363	3.0788	3.1416

the least square from experimental data of $\ln\langle\Psi\rangle_\beta$ or $\log(\Psi_\gamma)$ vs Fo in the linear zone in agreement with,

$$\alpha = -\frac{bl^2}{\lambda_1^2} \tag{40}$$

Then, the first eigenvalues at different values of *Bi* and ϕ are listed in Tables 1 (Eq. 31a), 2 (Eq. 31b) and 3 (Eq. 31c). Castillo-Santos *et al.*, (2017) applied this mathematical property for the empirical estimation of solutes mass diffusivity during solid-liquid extraction of vanilla.

Another mathematical property is that deduced solutions converge to the solutions reported by Crank (1975) when $Bi \to \infty$, which is easily verified with eigenvalues generators (Eqs 31),

$$\cos(\lambda_n) + \frac{\sin(\lambda_n)}{\phi\lambda_n} = 0 \text{ or } \tan(\lambda_n) = -\phi\lambda_n \tag{41a}$$

$$J_o(\lambda_n) + \frac{2J_1(\lambda_n)}{\phi\lambda_n} = 0 \text{ or } \phi\lambda_n J_o(\lambda_n) + 2J_1(\lambda_n) = 0 \tag{41b}$$

$$\frac{\sin(\lambda_n)}{\lambda_n} + \frac{3}{\phi}\left(-\frac{\cos(\lambda_n)}{\lambda_n^2} + \frac{\sin(\lambda_n)}{\lambda_n^3}\right) = 0$$
$$\text{or } \tan(\lambda_n) = \frac{3\lambda_n}{3+\phi\lambda_n^2} \tag{41c}$$

Finally deduced solutions converge to solutions of heat conduction or mass diffusion in a media with Cauchy boundary conditions when $\phi \to \infty$; and with Dirichlet boundary condition when $Bi \to \infty$ and $\phi \to \infty$. $Bi \to \infty$ implies that process is diffusion controlled (the heat or mass transfer rate is limited by diffusion within medium) and the interface temperature/concentration is equal to temperature/concentration at equilibrium $\Theta_{\beta i} = \Theta_{\beta e}$ or $\Psi_{\beta i} = 0$; and $\phi \to \infty$ implies that the mass relation solution/media tends to infinite, and therefore by Eqs. (11) $\Theta_{\gamma e} = \Theta_{\gamma 0}$.

3.4 Topological properties

Analytical solution of constitutive equations (Eqs. 34) may be represented for any dimensionless variable (Ψ) and for any of the studied geometries (θ) as,

$$\Psi_\theta = B_\theta \sum_{n=1}^{\infty} B_{n\theta} e^{-\lambda_{\theta n}^2 Fo} \quad (42)$$

Defining, T a topological space that contends the empty set and the whole possible values of $Fo > 0$, that is $T = \{\emptyset, [0, \infty)\}$; P_1 a topological space that contends the empty set and the whole possible values of Ψ_1 (rectangular) for $Fo > 0$, that is $P_1 = \{\emptyset, (0, 1]\}$; P_2 a topological space that contends the empty set and the whole possible values of Ψ_2 (cylindrical) for $Fo > 0$, that is $P_2 = \{\emptyset, (0, 1]\}$ and P_3 a topological space that contends the empty set and the whole possible values of Ψ_3 (spherical) for $Fo > 0$, that is $P_3 = \{\emptyset, (0, 1]\}$. Under above definition, Eq. (42) is a map,

$$f_\theta : T \to P_\theta, \quad \forall \theta = 1, 2, 3 \quad (43)$$

It is evident from Eq. (42) that f_θ are continuous ($f_\theta(Fo) = \lim_{x \to Fo} f_\theta(x)\ \forall Fo \in T\ \wedge \forall \theta = 1, 2, 3$) and bijective (($f_\theta(Fo_1) = f_\theta(Fo_2)) \leftrightarrow (Fo_1 = Fo_2) \wedge P_\theta = \mathrm{Im}(T)\ \forall \theta = 1, 2, 3$). As consequence the following maps exist and are bijective,

$$f_\theta^{-1} : P_\theta \to T \quad \forall \theta = 1, 2, 3 \quad (44)$$

Then, the following maps exist and are continuous and bijective,

$$f_{ij} = f_i\left(f_j^{-1}\left(\Psi_j\right)\right) : P_j \to P_i \quad \forall i, j = 1, 2, 3 \quad (45)$$

f_{ij} is therefore an homeomorphism between P_i and P_j. That is, any average solution of constitutive equation in any (rectangular, cylindrical or spherical) 1D coordinate has one and only one equivalent averaged solution in any other (rectangular, cylindrical or spherical) 1D coordinate. It is possible to obtain f_{ij} in the asymptotic zone of Eq. (42),

$$\Psi_\theta = B_\theta B_{1\theta} e^{-\lambda_{\theta 1}^2 Fo} \quad (46)$$

$$\Psi_i = B_i B_{1i} \left(\frac{\Psi_j}{B_j B_{1j}}\right)^{\frac{\lambda_{i1}^2}{\lambda_{j1}^2}} = f_{ij} \quad (47)$$

The existence of f_{ij} for any combination of 1D rectangular, cylindrical or spherical solution allows the conjecture on the homeomorphism existence between others geometries. Eq. (47) emphasize the relevance of the first eigenvalue in the topology of asymptotic solutions. Like it was discussed at the end of section 3.3., Eqs. (31) under Dirichlet boundary condition ($Bi \to \infty$ and $\phi \to \infty$) converge to,

$$J_{-1/2}(\lambda_n) = 0 \quad \text{1D rectangular} \quad (48a)$$

$$J_o(\lambda_n) = 0 \quad \text{1D cylindrical} \quad (48b)$$

$$J_{1/2}(\lambda_n) = 0 \quad \text{1D spherical} \quad (48c)$$

In Eqs. (48) it was taken into account that $\cos(\lambda) = \sqrt{\pi\lambda/2} J_{-1/2}(\lambda)$ and $\sin(\lambda) = \sqrt{\pi\lambda/2} J_{1/2}(\lambda)$. Therefore, $J_\nu(\lambda_n) = 0$ with $\nu = [-1/2, 1/2]$ where ν is a continuous metric that indicates how the constitutive analytical solution of heat and mass transfer equations under Dirichlet boundary is topologically transformed from a plane sheet ($\nu = -1/2$) to a sphere ($\nu = 1/2$), passing by a large cylinder ($\nu = 0$). In other words ν is a continuous metric that indicate the analytical solution asymptotic slope (in semilog representation) of a figure that deform from a plane sheet to a sphere. As example of the ν behavior, their values for a long square parallelepiped, a cube and a cubic cylinder (a cylinder with same diameter and height) will be calculated as follows.

Under Dirichlet boundary condition ($Bi \to \infty$ and $\phi \to \infty$) there is not effect of solution (liquid phase), and therefore the superposition principle applies. Therefore the asymptotic analytical solutions of a long square parallelepiped, a cube and a cubic cylinder are respectively,

$$\Psi_{\text{long square parallelepiped}} = (B_1 B_{11})^2 e^{-\left(\lambda_{11}^2 + \lambda_{11}^2\right) Fo} \quad (46a)$$

$$\Psi_{\text{cube}} = (B_1 B_{11})^3 e^{-\left(\lambda_{11}^2 + \lambda_{11}^2 + \lambda_{11}^2\right) Fo} \quad (46b)$$

$$\Psi_{\text{cubic cylinder}} = B_1 B_{11} B_2 B_{21} e^{-\left(\lambda_{11}^2 + \lambda_{21}^2\right) Fo} \quad (46c)$$

Where λ_{11} and λ_{21} are the first eigenvalues for 1D rectangular coordinate (Eq. 48a) and 1D cylindrical coordinate (Eq. 48b) respectively under Dirichlet boundary condition ($Bi \to \infty$ and $\phi \to \infty$). From Eqs. (48),

Square long parallelepiped:

$$J_\nu\left(\sqrt{\frac{\pi^2}{4} + \frac{\pi^2}{4}}\right) = 0 \to \nu = -0.1172 \to -\frac{1}{2} < \nu < 0 \quad (48d)$$

Cube:

$$J_\nu\left(\sqrt{\frac{\pi^2}{4} + \frac{\pi^2}{4} + \frac{\pi^2}{4}}\right) = 0 \to \nu = 0.2092 \to 0 < \nu < \frac{1}{2} \quad (48e)$$

Cubic cylinder:

$$J_\nu\left(\sqrt{\frac{\pi^2}{4}+2.4048^2}\right)=0\rightarrow\nu=0.3125\rightarrow0.2092<\nu<\frac{1}{2} \quad (48f)$$

Therefore the square long parallelepiped analytical solution is topologically located between plane sheet and long cylinder; cube analytical solution is topologically located between long cylinder and sphere; and, cubic cylinder analytical solution is topologically located between cube and sphere. More complex geometries topology equivalence may be calculated form asymptotic slopes of numerical solution of deformed geometries evaluated by the method proposed by Pacheco-Aguirre *et al*., (2015).

The relation of topology transformation represented in Eqs. (48) with averaged equations will be deduced in the following paragraphs.

Taking the derivative of Eq. (46),

$$\frac{d\Psi_\theta}{dFo}=-B_\theta B_{1\theta}\lambda_{\theta 1}^2 e^{-\lambda_{\theta 1}^2 Fo}=-\lambda_{\theta 1}^2\langle\Psi\rangle_\beta \quad (49)$$

Or by analogy to Eq. (15),

$$\frac{d\langle\Psi\rangle_\beta}{dFo}=-\Omega\langle\Psi\rangle_\beta \quad (50)$$

Eq. (49) if fully analog to (15) when $Bi\rightarrow\infty$ because like it was detailed at the end of section 3.3, $Bi\rightarrow\infty$ implies that process is diffusion controlled (the heat or mass transfer rate is limited by diffusion within medium) and the interface temperature/concentration is equal to temperature/concentration at equilibrium $\Theta_{\beta i}=\Theta_{\beta e}$ or $\Psi_{\beta i}=0$. Comparing Eq. (49) with (15) or (50): $\Omega=\lambda_{\theta 1}^2$ and the internal heat or mass transfer coefficient in averaged equations is,

$$h_\beta=\frac{\Omega k}{l\theta}\ \text{(Heat transfer)} \quad h_\beta=\frac{\Omega\alpha}{l\theta}\text{(Mass transfer)} \quad (51)$$

Eq. (51) demonstrates that internal heat or mass transfer coefficient used in averaged equations may be represented in terms of heat conductivity or mass diffusivity and geometric characteristics through the topological factor $\Omega=\lambda_{\theta 1}^2$ and the geometric relation θ (Eq. 5) in the adequate geometry. In agreement with Eq. (50), the topological factor can be calculated when process is diffusion controlled ($Bi\rightarrow\infty$) and the solution/media relation tends to infinite ($\phi\rightarrow\infty$). That is, the averaged internal mass transfer coefficients may be predicted with Eq. (51) in which the geometric factors are independent of Bi and ϕ numbers (under Dirichlet boundary condition). The effect of Bi and ϕ numbers are included in analytical (Eq. 38) or numerical (Eqs. 15 to 18) solutions of averaged equations. From Eqs. (48) or Tables 1, 2 and 3, the topological and geometric factors for some geometries are: 1D rectangular ($\Omega=\pi^2/4$, $\theta=1$); 1D cylindrical ($\Omega=2.4084^2$, $\theta=2$), 1D spherical ($\Omega=\pi^2$, $\theta=3$), square long parallelepiped ($\Omega=\pi^2/2$, $\theta=2$), cube ($\Omega=3\pi^2/4$, $\theta=3$) and cubic cylinder ($\Omega=\pi^2/4+2.4048^2$, $\theta=3$).

The analytical solution of averaged equations (Eq. 38) with the above values and different Bi and ϕ values are plotted as continuous lines in Figs. 1, 2 and 3. Some deviations with respect to constitutive solutions (discontinuous lines) are observed mainly in spherical results (Fig. 3). However, in general, averaged solutions with topological factors taken at $Bi\rightarrow\infty$ and $\phi\rightarrow\infty$, follows the same tendency of constitutive solution, and the divergence is increasing at $\Psi<0.01$ which implies that temperature or concentration have been reached 99% of their equilibrium value. This demonstrate that differential equations (12) and (13) with interface continuity (14) in which medium heat or mass transfer coefficient is calculated with Eq. (51) represent an acceptable approximation of constitutive equations solution. It is important to remark that any solution (numerical or analytical) will be only an approximation of process behavior because the model only can use the mathematical expectation for particles sizes and geometries. Present study provides theoretical support of the use of Eqs. (12), (13) and (14), which have been used for continuous contact solid-liquid extractors modeling (Veloso *et al*., 2005) and supercritical fluid extraction columns modeling (Perrut *et al*., 1997; Reverchon and Iacuzio 1997).

Conclusion

The Laplace transform procedure, applied for to deduce the analytical solution of heat conduction or solute diffusion in media contacting a well stirred solution with finite volume equations in 1D rectangular, 1D cylindrical and 1D spherical coordinates, demonstrated that topological relation under Dirichlet boundary condition between different geometries are expressed in terms of Bessel function of the first kind order (Eqs. 48). By analogy with analytical solution of the averaged heat or mass transfer equations, it was demonstrated that internal transfer coefficient in medium may be predicted from heat conduction or mass diffusivity, characteristic conduction/diffusion length and the topological factor calculated under Dirichlet boundary condition, through Eq. (51). Additionally, the mathematical properties of analytical solutions show how they can be used for thermal or mass diffusivity estimation from experimental kinetics through Eqs. (39) and (40).

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Nomenclature

$\mathscr{A}$ transfer surface, m^2
b kinetic slope, s^{-1}
B any constant
Cp heat capacity, J/kgK
h interfacial heat transfer coefficient, W/m^2K or interfacial mass transfer coefficient, m/s
i integer index
j integer index
k heat conductivity, W/mK
K distribution constant, kg/kg
ℓ characteristic length, m
m mass, kg
$\mathbf{n}$ unit vector normal to transfer surface, Dimensionless
P topological space
r cylindrical or spherical radial coordinate, m
t time, s
T topological space
$\mathscr{V}$ volume, m^3
z rectangular coordinate, m

Greek symbols
α heat or mass diffusivity, m^2/s
ε system porosity, m^2/s
λ eigenvalues of analytical solution
θ geometric factor
Θ temperature, K or mass fraction, kg/kg
ν order of Bessel function of the first kind and topologic metric
ρ density, kg/m^3

Sub-symbols
β in the media
γ in the solution

Dimensionless groups
Bi Biot number
Fo Fourier number
ϕ heat or mass balance relations
Ψ temperature or mass fraction, dimensionless
ξ dimensionless coordinate
$\dot{\nabla}$ a linear map of gradient operator
Ω media heat or mass transfer dimensionless coefficient

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