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Topics in Heat and Mass Transfer in Porous Media: Cross-Diffusion, Thermophoresis and Reactive Surfaces

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1. Introduction

Coupled heat and mass transfer by natural convection in a fluid-saturated porous medium is a dynamic domain of research, due to many important engineering and geophysical applications, see the books by (Nield & Bejan, 2006), (Ingham & Pop, 1998; 2002; 2005), (Pop & Ingham, 2001), (Ingham et al., 2004) where a comprehensive account of the available information in the field is presented.

In the present context, the following assumptions will be used: a) the fluid and the porous medium are in local thermodynamic equilibrium; b) the flow is laminar, steady and two-dimensional; c) the porous medium is isotropic and homogeneous; d) the properties of the fluid and porous medium are constants; e) the Boussinesq approximation is valid and the boundary-layer approximation is applicable.

Thermal diffusion (thermodiffusion or Soret effect) corresponds to species differentiation developing in an initial homogeneous mixture submitted to a thermal gradient, (Soret, 1880). The energy flux caused by a composition gradient is called Dufour (diffusion-thermo) effect. These effects are considered as second order phenomena, on the basis that they are of smaller order of magnitude than the effects described by Fourier's and Fick's laws, but they may become significant in clear fluids, according to (Eckert & Drake, 1972), but also in porous media in areas such geosciences or hydrology, see (Benano-Melly et al., 2001) and the references quoted there. Consequently, Dufour and Soret effects on convective flows in porous media have been analyzed in a growing body of literature in the last years. However, the majority of the papers issued in the journals, in the last period, do not offer unfortunately a physical basis to calculate Dufour and Soret coefficients.

Restricting our considerations to porous media, let us refer further to the textbook by (Nield & Bejan, 2006) where some basic information are given on pages 42-44. According to the references quoted there

- In most liquid mixtures the Dufour effect is inoperative, but that this may not be the case in gases (Platten & Legros, 1984). This fact was confirmed also by (Mojtabi & Charrier-Mojtabi, 2000), who found that in liquids the Dufour coefficient is an order of magnitude smaller than the Soret effect.

- A not encouraging conclusion was drawn by these later authors, (Mojtabi and Charrier-Mojtabi, 2000), in the sense that for saturated porous media, the phenomenon of cross

diffusion is complicated due to the interaction between the fluid and the porous matrix. This is the reason why accurate values of these coefficients are not available.

(Benano-Melly et al, 2001) analyzed the problem of thermal diffusion in binary fluid mixtures, lying within a porous medium and subjected to a horizontal thermal gradient. The reader is directed to the references quoted in that paper for related information concerning the measurements and the Dufour coefficient.

Another possibility to deal with these effects is to use the theory of thermodynamics of irreversible processes, like in (Li et al., 2006) who considered a strongly endothermic chemical reaction system in a porous medium formed by spherical carbonate pellets in a reactor. However, orders of magnitude are given for these coefficients, in dimensional form, without physical justification and results are reported taking these coefficients as equal. For other references along this direction, the interested reader may consult those presented in the 9th chapter from the book by (Ingham and Pop, 2005).

In a general form the energy and concentration equations are expressed as

$$\frac{(\rho c)_m}{(\rho c)_f}\frac{\partial T}{\partial t} + \mathbf{V}\cdot\nabla T = \nabla\cdot\left(D_T\nabla T + D_{TC}\nabla C\right) \tag{1a}$$

$$\frac{(\rho c)_m}{(\rho c)_f}\frac{\partial T}{\partial t} + \mathbf{V}\cdot\nabla T = \nabla\cdot\left(D_T\nabla T + D_{TC}\nabla C\right) \tag{1b}$$

see (Nield and Bejan, 2006), where ϕ is the porosity of the medium, $D_T = k_m/(\rho c)_f$ is the thermal diffusivity, $D_C = D_m$ is the mass diffusivity, while D_{TC}/D_T and D_{CT}/D_C may be considered as Dufour and Soret coefficients (numbers) of the porous medium. In the last time, basically in all papers dealing with this subject, the previous equations were used in the form

$$u\frac{\partial T}{\partial x} + v\frac{\partial T}{\partial y} = \alpha_m\frac{\partial^2 T}{\partial y^2} + \frac{D_m}{C_s}\frac{k_T}{C_p}\frac{\partial^2 C}{\partial y^2} \tag{2a}$$

$$u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} = D_m\frac{\partial^2 C}{\partial y^2} + \frac{D_m k_T}{T_m}\frac{\partial^2 T}{\partial y^2} \tag{2b}$$

where α_m is the thermal diffusivity, C_p and C_s are the specific heat at constant pressure and concentration susceptibility and k_T is the thermal diffusion ratio. It seems that this form originates from a paper by (Kafoussias & Williams, 1995), where Dufour and Soret effects have been introduced in a free convection boundary-layer past a vertical plate in a viscous fluid

The recent literature offers a couple of papers, where the Dufour and Soret effects are quantified by dimensionless parameters, resulted from a non-dimensionalization procedure, associated usually with the search for similarity solutions of the governing equations of momentum, energy and mass transfer (which are partial differential equations).

1.1 Vertical plate, Darcy model

The Darcy law applies when the Reynolds number is less than 1 (Bear, 1988), otherwise non-Darcy models must be used. Consequently, the basic equations of motion are, in the Darcy formulation

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{3}$$

$$u = \frac{gK}{\upsilon}\left[\beta_T\left(T - T_\infty\right) + \beta_C\left(C - C_\infty\right)\right] \tag{4}$$

1.1.1 Prescribed wall temperature and concentration

The boundary conditions of the problem are

$$y = 0: \ v = 0, \ T = T_w, \ C = C_w \tag{5a}$$

$$y \to \infty: \ u \to 0, \ T \to T_\infty, \ C \to C_\infty \tag{5b}$$

(Anghel et al., 2000) looked for the free convection past this common geometry, by using then by (Bejan & Khair, 1985)

$$\psi = \alpha_m Ra_x^{1/2} f(\eta), \ \theta = \left(T - T_\infty\right)/\left(T_w - T_\infty\right), \ \phi = \left(C - C_\infty\right)/\left(C_w - C_\infty\right), \ \eta = \frac{y}{x}Ra_x^{1/2} \tag{6}$$

where $Ra_x = gK\beta_T\left(T_w - T_\infty\right)x/\left(\nu\alpha_m\right)$ is the local Rayleigh number. In order to stay close to (Bejan & Khair, 1985), the stream function ψ is defined as $u = -\partial\psi/\partial y$, $v = \partial\psi/\partial x$. The governing equations become

$$f' = -\theta - N\phi \tag{7}$$

$$\theta'' - \frac{1}{2}f\theta' + D_f\phi'' = 0 \tag{8}$$

$$\frac{1}{Le}\phi'' - \frac{1}{2}f\phi' + S_r\theta'' = 0 \tag{9}$$

where Le, D_f and S_r are Lewis, Dufour and Soret numbers, respectively

$$Le = \frac{\alpha_m}{D_m}, \ D_f = \frac{D_m k_T\left(C_w - C_\infty\right)}{C_s C_p \alpha_m\left(T_w - T_\infty\right)}, \ S_r = \frac{D_m k_T\left(T_w - T_\infty\right)}{\alpha_m T_m\left(C_w - C_\infty\right)} \tag{10a}$$

while

$$N = \frac{\beta_C\left(C_w - C_\infty\right)}{\beta_T\left(T_w - T_\infty\right)} \tag{10b}$$

is the sustentation parameter, which measures the relative importance of mass and thermal diffusion in the buoyancy-driven flow. We notice that N it is positive for thermally assisting flows, negative for thermally opposing flows and zero for thermal-driven flows. The transformed boundary conditions are

$$f(0) = 0, \ \theta(0) = 1, \ \phi(0) = 1 \tag{11a}$$

$$f' \to 0 \, , \, \theta \to 0 \, , \, \phi \to 0 \, , \text{ as } \eta \to \infty \qquad (11b)$$

We notice that the problem reduces to that formulated by (Bejan and Khair, 1985) when $D_f = 0$ and $S_r = 0$. The parameters of engineering interest are the local Nusselt and the Sherwood numbers, which are given by the expressions

$$Nu_x / Ra_x^{1/2} = -\theta'(0) \, , \, Sh_x / Ra_x^{1/2} = -\phi'(0) \qquad (12)$$

Three cases were considered by (Anghel et al., 2000):
- Case I: $Le = 1$, $N = 1$, $(D_f, S_r) = (\,(0.05, 1.2), (0.075, 0.8), (0.03, 2.), (0.037, 1.6), (0.6, 0.1)\,)$
- Case II: $Le = 1$, $N = 1$, $D_f = 0.15$, $S_r = 0.4$
- Case III: $Le = 1$, $(N, D_f, S_r) = (\,(0.2, 0.15, 0.4), (0.5, 0.075\ 0.8), (0.8, 0.03, 2.0)\,)$.

Many other subsequent papers used these combinations of Dufour and Soret coefficients. (Postelnicu, 2004a) extended the work by (Anghel et al., 2000), by including the effects of a magnetic field, such as Eq. (7) becomes

$$\left(1 + M^2\right)f' = -\theta - N\phi \qquad (13)$$

where M is the magnetic parameter, defined as $M^2 = K\sigma\mu_e^2 H_0^2 / \mu$ The parameters involved in the present problem are M, Le, N, D_f and S_r.

Table 1 presents local Nusselt and Sherwood numbers calculated for each set of parameters. Figs 1 and 2 show the dimensionless velocity, temperature and concentration when $M = 0$ and 1, for the following values of the parameters: $N = 1$, $D_f = 0$, $S_r = 0$, and $Le = (1, 2, 4, 6, 8, 10, 100)$. We remark that as M increases, the thickness of the hydrodynamic/concentration boundary layer increases.

M	Le	N	D_f	S_r	$Nu_x / Ra_x^{1/2}$	$Sh_x / Ra_x^{1/2}$
0	1	0.2	0.15	0.4	0.46331	0.38100
1	1	0.2	0.15	0.4	0.32762	0.26942
2	1	0.2	0.15	0.4	0.20723	0.17044
0	1	0.5	0.075	0.8	0.55508	0.28764
1	1	0.5	0.075	0.8	0.39250	0.20339
2	1	0.5	0.075	0.8	0.24825	0.12866
0	1	0.8	0.03	2.0	0.67028	-0.13736
1	1	0.8	0.03	2.0	0.47936	-0.09712
2	1	0.8	0.03	2.0	0.29976	-0.06142

Table 1. Values of Nusselt and Sherwood numbers in case III

To this end, we notice that, as remarked by Magyari (2010), if one defines a modified Rayleigh number as

$$Ra_{x,M} = gK\beta_T \left(T_w - T_\infty \right)x / \left(\nu\alpha_m\right) / \left(1 + M^2\right) = Ra_x / \left(1 + M^2\right) \qquad (14)$$

then the magnetic parameter is eliminated from the analysis and Eqs. (8-9) and (13) reduces to (7-9). One obtains the wall gradients $\theta'(0;M)$ and $\phi'(0;M)$ for non-zero M, which can be calculated from their counterparts $\theta'(0;0)$ and $\phi'(0;0)$ for $M = 0$ by the relationships
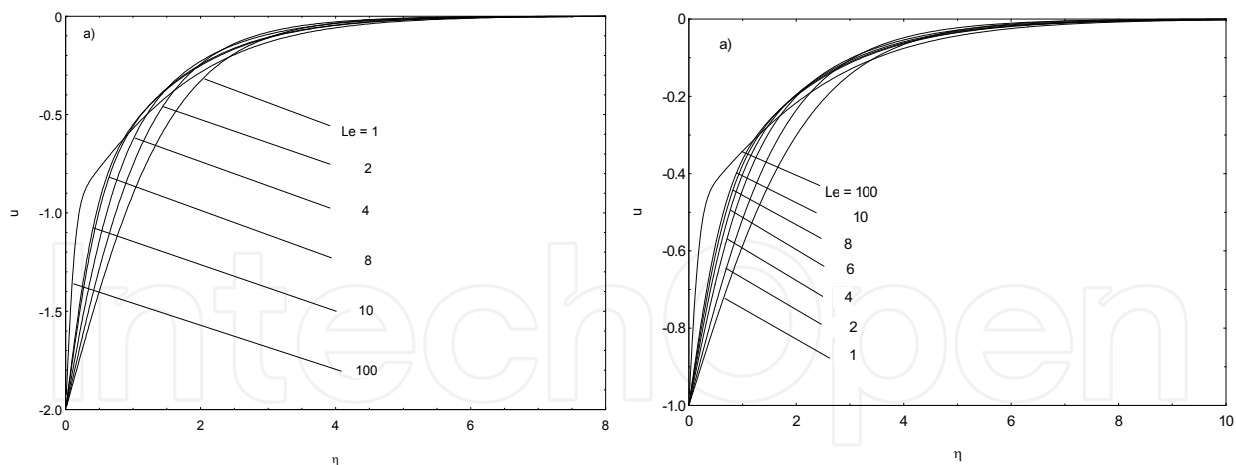
Fig. 1. Variations of velocity across the boundary layer for $N = 1$, $D_f = 0$, $S_r = 0$: $M = 0$ (left), $M = 1$ (right)
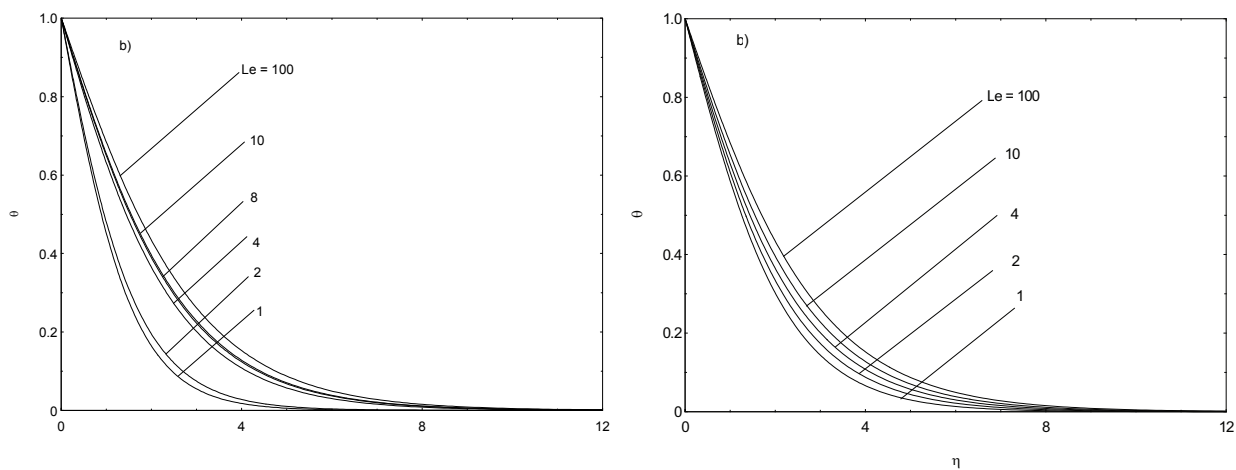
Fig. 2. Variations of temperature across the boundary layer for $N = 1$, $D_f = 0$, $S_r = 0$: $M = 0$ (left), $M = 1$ (right)
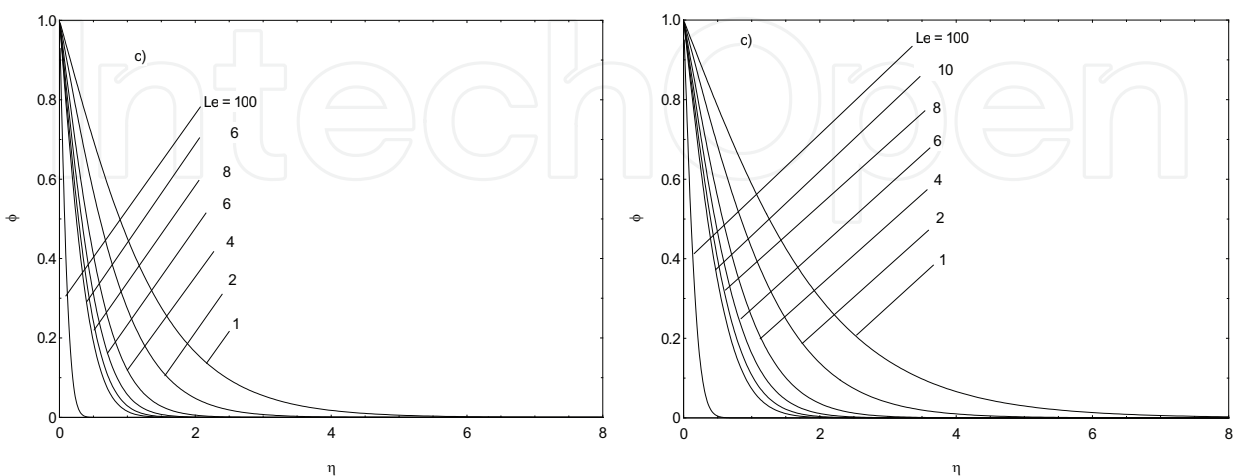
Fig. 3. Variations of the concentration across the boundary layer for $N = 1$, $D_f = 0$, $S_r = 0$: $M = 0$ (left), $M = 1$ (right)

$$\theta'(0;M) = \frac{\theta'(0;0)}{\sqrt{1+M^2}} \quad , \quad \phi'(0;M) = \frac{\phi'(0;0)}{\sqrt{1+M^2}} \tag{15}$$

1.1.2 Prescribed wall heat and mass fluxes

At our best knowledge, in a single paper by (Lakshmi Narayana & Murthy, 2007), both Soret and Dufour effects have been considered in a free convection boundary layer along a vertical surface placed in porous medium, subject to wall heat and mass fluxes. In a paper by (Magyari & Postelnicu, 2010a), there is performed a thorough analysis of how wall heat and mass fluxes can be prescribed in order to get similarity solutions.

1.1.3 Other contributions for vertical flows

(Partha et al., 2006) looked for the effect of double dispersion, thermal-diffusion and diffusion-thermo effects in free convection heat and mass transfer in a non-Darcy electrically conducting fluid saturating a porous medium. In a related paper, (Lakshmi Narayana & Murthy, 2006) studied the Soret and Dufour effects in a doubly stratified Darcy porous medium.

More effects, besides thermal-diffusion and diffusion-thermo phenomena, such as thermal dispersion and temperature-dependent viscosity have been introduced by (Afify, 2007a) and (Afify, 2007b) in the analysis of non-Darcy MHD free convection past a vertical isothermal surface embedded in a porous medium. Unfortunately, this kind of approaches seems to be of marginal interest for practical applications, due to the large number of parameters.

(Lakshmi Narayana et al. 2009a; b) analyzed cross-diffusion effects on free convection of Non-Newtonian power-law fluids from a vertical flat plate in saturated porous media.

1.2 Other geometries

- Hiemenz flow with cross-diffusion through a porous medium was analyzed by (Tsai and Huang, 2009), where, by combining also various other effects, such as variable viscosity, heat source, radiation and chemical reaction. Moreover, both wall-temperature and wall-concentration are taken as power-law functions of the coordinates along the plate. The number of problem parameters is well above 10, while their impact on the relevant quantities (skin-friction, Nusselt and Sherwood numbers, velocity, temperature and concentration profiles in the boundary layer) is presented in 7 tables and 8 figures.
- (Cheng, 2009) studied the Soret and Dufour effects on the boundary layer flow due to natural convection heat and mass transfer over a downward-pointing vertical cone in a porous medium saturated with Newtonian fluids. Constant wall temperature and concentration boundary conditions were considered in that paper and similarity equations have been obtained and solved by a cubic spline collocation method.
- Another variation on geometry can be found in the very recent paper by (Rathish Kumar and Krishna Murthy, 2010), on a free convection flow from a corrugated vertical surface in a non-Darcy porous medium, under constant wall temperature and concentration boundary conditions. They used for Forchheimer extended non-Darcy model and performed a similarity transformation followed by a wavy to flat surface transformation. The resulting equations were solved having as parameters Grashof and Lewis numbers, buoyancy ratio, wavy wall amplitude, Soret and Dufour numbers. Comparisons of local and average Nusselt and Sherwood numbers have been presented.

1.3 Mixed convection

Mixed convection in the presence of Soret and Dufour effects was tackled by (Chamkha and Ben-Nakhi, 2008). Additional effects included in that paper were MHD, radiation and permeability of the plate (placed in a porous medium). This time, the set of governing equation is no more reduced to ordinary differential equations, but to partial ones, of parabolic type, through appropriate transformation of variables. (Beg, Bakier and Prasad, 2009) presented a numerical study of magnetohydrodynamic heat and mass transfer from a stretching surface placed in a porous medium with Soret and Dufour effects.

1.4 Stagnation-point flows

Consider the natural convection in a two dimensional stagnation-point flow in a fluid saturated porous medium. The temperature and concentration of the ambient medium are T_∞ and C_∞, respectively, where the wall temperature and concentration are such that $T_w > T_\infty$ and $C_w > C_\infty$. The x-coordinate is measured along the body surface and the y-coordinate normal to it. The momentum equation takes the form

$$u = \frac{gK}{\nu}\left[\beta_T\left(T - T_\infty\right) + \beta_C\left(C - C_\infty\right)\right]S(x) \tag{16}$$

where S is the shape factor. In general $S(x) = \sin\gamma$, where γ is the angle between the outward normal from the body surface and the downward vertical. For a two dimensional stagnation-point flow, $S(x) = x/l$ where l is an appropriate length scale. (Postelnicu, 2010) considered also the effect of blowing/suction, therefore the boundary conditions of the problem are as in (5), except for $v = v_w$, where v_w is the suction/injection velocity.

In order to get similarity solutions, the stream function is expressed as $\psi = xf(y)$, using now the more common definition $u = \partial\psi/\partial y$, $v = -\partial\psi/\partial x$, the governing equations become after non-dimensionalization

$$f' = \theta + N\phi \tag{17}$$

$$\theta'' + f\theta' + D_f\phi'' = 0 \tag{18}$$

$$\frac{1}{Le}\phi'' + f\phi' + S_r\theta'' = 0 \tag{19}$$

where primes denote differentiation with respect to y. The transformed boundary conditions are

$$f(0) = f_w, \ \theta(0) = 1, \ \phi(0) = 1 \tag{20a}$$

$$\theta \rightarrow 0, \ \phi \rightarrow 0 \text{ as } y \rightarrow \infty \tag{20b}$$

Besides the numerical attack of the problem (17-20), in (Postelnicu, 2010a) it was performed also an asymptotic analysis, for large suction rates.

1.5 Effect of a chemical reaction

Another situation which can arise in practice is a chemical reaction produced in the porous medium. In engineering applications, when chemical reactions occur, they can be either

homogeneous or heterogeneous. Homogeneous chemical reactions occur uniformly in the domain of a given phase, while heterogeneous reactions develop along the boundary of a phase.

Some principles on the modeling of a chemical reaction in a porous medium are discussed by (Nield and Bejan, 2006), pages 38-39. The rate equation for a reagent of concentration C is: $dC_m / dt = -k_m C_m^n$, where $C_m = C/m$ is the concentration in moles per unit volume of the fluid mixture, m denotes the molar mass of the reagent and n is the order of the reaction. Further, the rate coefficient k is in general a function of the temperature, described for instance by the Arrhenius equation. However, in many studies k is considered as a constant. In his book, (Probstein, 1994) stated that most known chemical reactions are of first and second order.

Several recent papers related to this topic have been published. (El-Amin et al. 2008) studied the effects of chemical reaction and double dispersion on the non-Darcy free convection and heat and mass transfer, for constant temperature and concentration at the wall. (Chamkha et al. 2010) carried-out an unsteady analysis of natural convective power-law fluid flow past a vertical plate embedded in a non-Darcian porous medium in the presence of a first order homogeneous reaction.

Let us focus on the chemical reaction in the presence of cross-diffusion effects for natural convection boundary layer flow along a vertical flat plate. Besides Eqs. (2a, 3, 4) which keep their forms, now Eq. (2b) is modified as follows

$$u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} = D_m \frac{\partial^2 C}{\partial y^2} + \frac{D_m k_T}{T_m}\frac{\partial^2 T}{\partial y^2} - K_1 \left(C - C_\infty\right)^n \tag{21}$$

The nondimensionalization scheme id the same as in (6), to give same Eqs. (7) and (8), while the concentration equation becomes

$$\frac{1}{Le}\phi'' + f\phi' - \gamma\phi^n + S_r\theta'' = 0 \tag{22}$$

where again primes denote differentiation with respect to η, while Le, D_f, S_r and N are Lewis, Dufour, Soret numbers and sustentation parameter as defined previously. Further, in order to get similarity solutions, the constant dimensionless chemical reaction parameter $\gamma = K_1 x^2 / \left(\alpha_m Ra_x\right)$ was introduced in Eq. (22). The transformed boundary conditions are precisely (11). Local Nusselt number and local Sherwood number are given by the same expressions as in (12). The problem has been solved numerically by (Postelnicu, 2007a), using a version of the Keller-box method adapted to solve ordinary differential equations was used.

The parameters involved in the present problem are Le, N, D_f, S_r, γ and n, the last two quantities pertaining to the chemical reaction. As expected, the Sherwood number is much more sensitive than the Nusselt number to the variation of parameters γ and n.

In Figures 3 and 4 Nusselt and Sherwood local numbers vs γ are plotted for $D_f = 0.6$, $S_r = 0.1$, $Le = 1$, $N = 1$ and $n = (1, 2, 3)$. Then, Fig. 5 depicts the concentration profiles when $D_f = 0.6$, $S_r = 0.1$, $Le = 1$ and $N = 1$, for various combinations of n and γ. Another case with nonzero Dufour and Soret numbers was considered in Fig. 6: $D_f = 0.15$, $S_r = 0.4$, $Le = 1$ and $N = 1$, using the same combinations of n and γ, as in Fig. 4. The general behaviour is similar to that depicted in Fig. 4, but now we remark the strong overshoot when $n = 2$ and $\gamma = 1$.
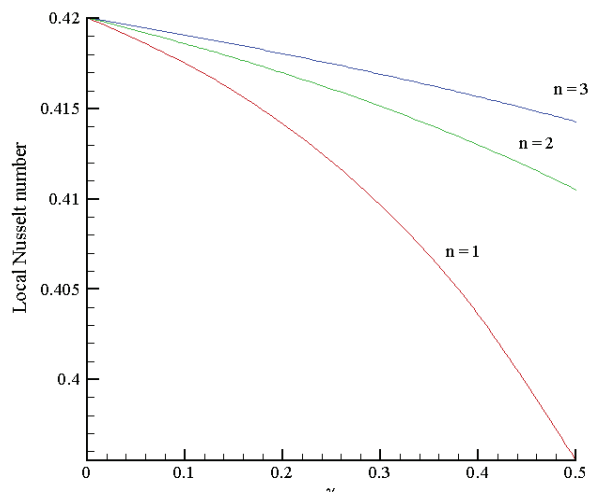
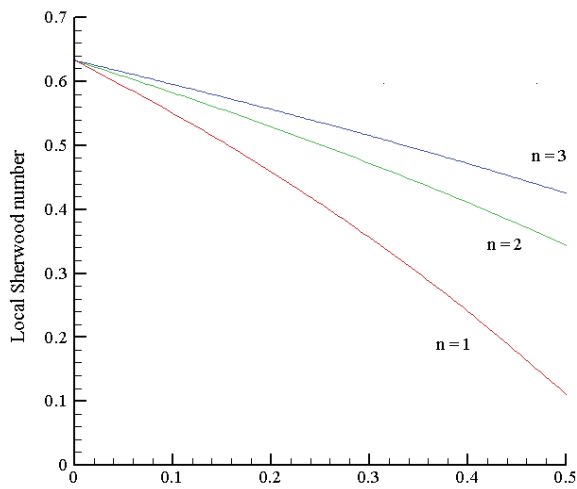Fig. 3. Nusselt number variation with γ for D_f = 0.6, S_r = 0.1, Le = 1, N = 1 and n = (1, 2, 3)

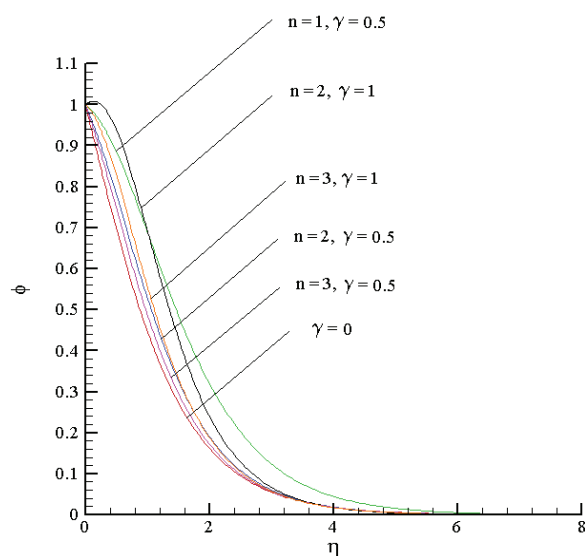Fig. 4. Sherwood number variation with γ for D_f = 0.6, S_r = 0.1, Le = 1, N = 1 and n = (1, 2, 3)

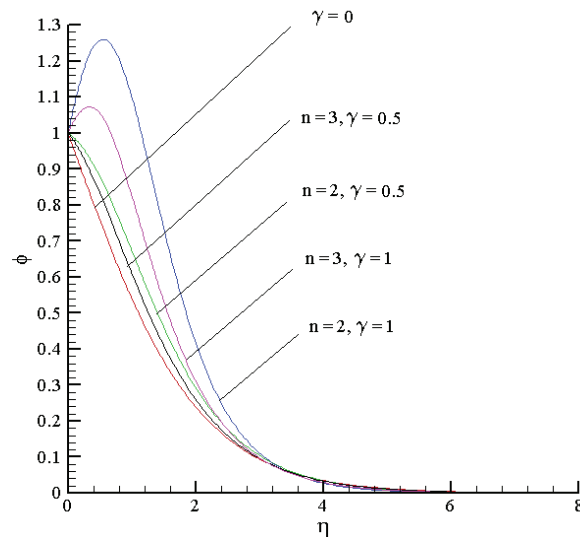Fig. 5. Concentration profiles for D_f = 0.6, S_r = 0.1, Le = 1 and N = 1

Fig. 6. Concentration profiles for $D_f = 0.15$, $S_r = 0.4$, Le = 1 and $N = 1$

The present problem subject to boundary conditions of prescribed wall heat and mass fluxes is under investigation in a paper by (Magyari and Postelnicu, 2010b).

2. Mass transfer (only) with chemical reaction

In this section we will analyze the convective diffusive-transport with chemical reaction in natural convection in fluid saturated porous medium. A vertical plate is composed of a chemical species maintained at a given concentration and immersed in a fluid-saturated porous medium. Far away from the plate the concentration is constant, at a value C_∞ The species on the plate is first transferred from the plate to the adjacent medium. Following (Postelnicu, 2009a), the basic equations in the boundary layer approximation are

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{23}$$

$$u = \frac{gK}{\upsilon}(C - C_\infty) \tag{24}$$

$$u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} = D_m\frac{\partial^2 C}{\partial y^2} + \dot{C}''' \tag{25}$$

where x and y are the coordinates along and normal to the plate, respectively, the orientation of the x-axis being upwards. The reaction-rate term is modelled by a power-law model

$$\dot{C}''' = -k(C - C_\infty)^n \tag{26}$$

where k is the reaction-rate constant and n is the order of the reaction. The boundary conditions are

$$u = v = 0 \text{, } C = C_0(x) \text{, at } y = 0 \tag{27}$$

Similarity solution is sought in the form

$$\psi = \alpha Ra_{x,C}^{1/2} f(\eta) \text{, } \eta = \frac{y}{x} Ra_{x,C}^{1/2} \text{, } \phi = \frac{C - C_\infty}{C_0 - C_\infty} \tag{28}$$

where $Ra_{x,C} = gK\beta(C - C_\infty)x / (\upsilon D_m)$ is the concentration Rayleigh number. Using (28), the problem transforms to

$$f' = \phi \tag{29}$$

$$\frac{1}{Le}\phi'' + f\phi' - \frac{k}{D_m} \cdot \frac{x^2}{Ra_{x,C}}(C - C_\infty)^n \phi^n = 0 \tag{30}$$

The last term in (30) can be rewritten as

$$\varepsilon(x) = \frac{k}{D_m} \cdot \frac{x^2}{Ra_{x,C}}(C - C_\infty)^n \phi^n = \frac{k\upsilon(C - C_\infty)^{n-1} x}{gK_C\beta} \phi^n \tag{31}$$

and, on physical basis, this quantity is small. The boundary conditions are

$$f(0) = 0 \text{, } \phi(0) = 1 \text{, } \phi(\infty) = 0 \tag{32}$$

Since we are considering a regular perturbation problem, there is no need for matching of layers or for multiple scales. The unknown functions of the problem are expanded as follows

$$f(\eta) = f_0(\eta) + \varepsilon f_1(\eta) + \dots \text{, } \phi(\eta) = \phi_0(\eta) + \varepsilon\phi_1(\eta) + \dots \tag{33}$$

and retaining the terms up to the first order, we obtain the following problems]

$$f_0' = \phi_0 \text{, } \frac{1}{Le}\phi_0'' + f_0\phi_0' = 0 \tag{34a}$$

$$f_0(0) = 0 \text{, } \phi_0(0) = 1 \text{, } \phi_0(\infty) = 0 \tag{34b}$$

$$f_1' = \phi_1 \text{, } \frac{1}{Le}\phi_1'' + f_0\phi_1' + \phi_0'f_0 - \phi_0^n = 0 \tag{35a}$$

$$f_1(0) = 0 \text{, } \phi_1(0) = 0 \text{, } \phi_1(\infty) = 0 \tag{35b}$$

Two parameters Le and n are involved in the present problem. A quantity which dictates on the final solution is the small parameter ε.

Le = 0.1 $f_0''(0) = -0.19948$		Le = 1 $f_0''(0) = -0.62756$		Le = 10 $f_0''(0) = -1.98450$		Le = 100 $f_0''(0) = -6.27554$	
n	$f_1''(0)$	n	$f_1''(0)$	n	$f_1''(0)$	n	$f_1''(0)$
1	-0.218055	1	-0.69979	1	-2.17852	1	-6.53320
2	-0.13900	2	-0.43593	2	-1.32077	2	-3.62634
3	-0.10427	3	-0.32418	3	-0.95866	3	-2.42976
4	-0.08407	4	-0.25950	4	-0.74983	4	-1.75969
5	-0.07066	5	-0.21659	5	-0.61186	5	-1.331435

Table 2. Dimensionless wall shear-stress for $n = (1, ..., 5)$ and Le = 0.1, 1, 10, 100
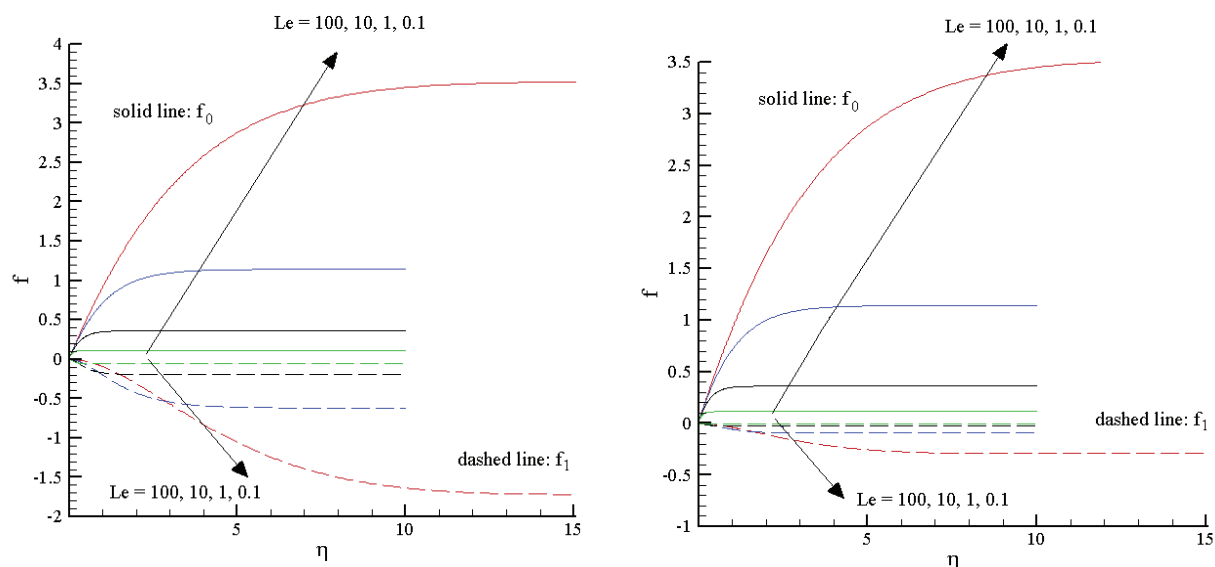
Fig. 7. Dimensionless stream function when n = 1 and n = 3

In Fig. 7 there is shown the variation of the dimensionless stream function across the boundary layer, when $n = 1$ and 3, for Le = 0.1, 1, 10 and 100. Figs. 8 and 9 depict the velocity profiles across the boundary layer for $n = 1$ and 3. It is worth to remark that the dimensionless velocity is equal to the dimensionless concentration according to Eq. (7).

It is readily seen from Table 2 and Fig. 7 that as n increases, the impact of the first order solution on the zeroth order solution (which describes the situation without reaction) decreases. In clear fluids, there are regions close to the wall where the flow accelerates, see (Aris, 1965). A similar behaviour is observed for porous media, see for instance Figs. 8 and 9.

A final comment is on the small parameter ε. From our Table 1 and from the figures it is seen that the order of magnitude of the first order solution is roughly the same as that of the zeroth order solution. So, a choice of a maximum 0.01 should be appropriate, in order to get appropriate results. On the other hand, the definition of ε given in (8) does not give us much chances to calculate it on a physical basis. So, it was decided to show graphically the stream function and velocity across the boundary layer for the zeroth and first order solutions.
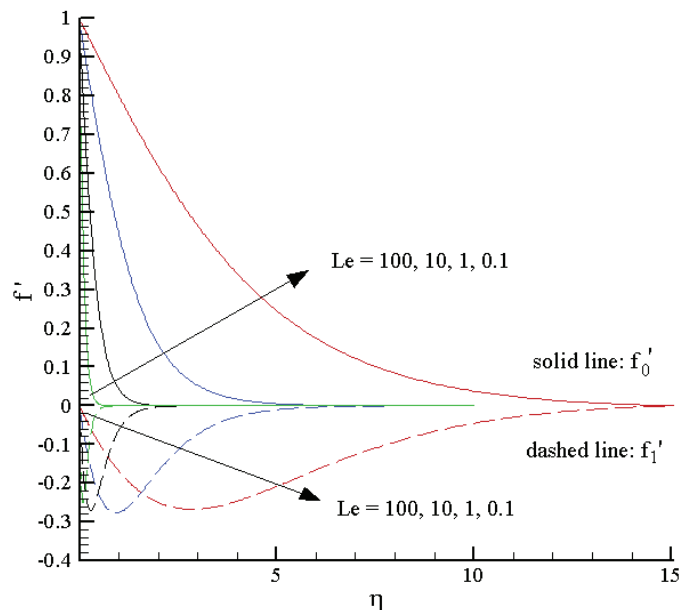
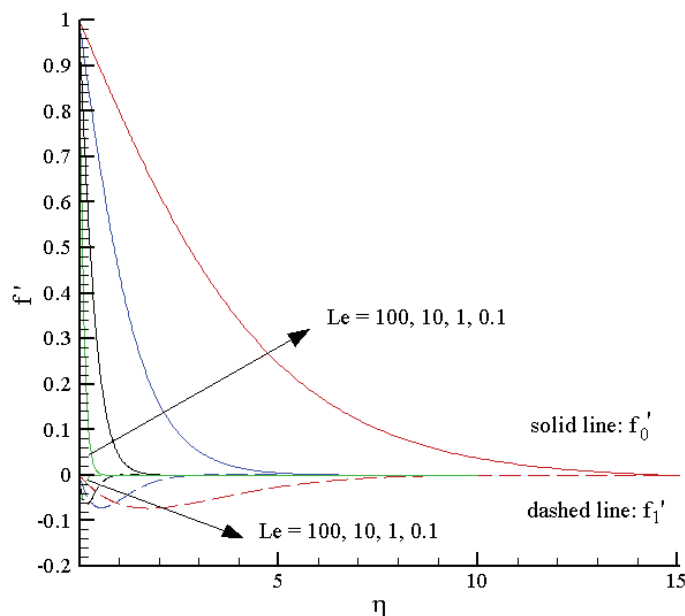Fig. 8. Velocity profiles, n = 1, zeroth and first order solutions

Fig. 9. Velocity profiles, n = 3, zeroth and first order solutions

3. Effects of thermophoresis particle deposition in free convection boundary layers

In the phenomenon of thermophoresis small sized (submicron) particles suspended in an isothermal gas acquire velocities relative to the gas in the direction of decreasing temperature. Thermophoresis is important when the particle sizes are small and the

temperature gradients are large. When the wall is cold, the particles tend to deposit on the surface, while when the wall is hot the particles tend to repel from that surface.

3.1 Vertical plate
(Chamka and Pop, 2004) and (Chamka et al, 2006) looked to the effect of thermophoresis particle deposition in free convection boundary layer from a vertical flat plate embedded in a porous medium, without and with heat generation or absorption, respectively.

3.2 Horizontal plate
We are going into details by using the paper by (Postelnicu, 2007b), where it was analyzed the effect of thermophoresis particle deposition in free convection from a horizontal flat plate embedded in a porous medium. The plate is held at constant wall temperature T_w and constant wall concentration C_w. The temperature and concentration of the ambient medium are T_∞ and C_∞, respectively. The x-coordinate is measured along the plate from its leading edge, and the y-coordinate normal to it. The following assumptions are used for the present physical model: a) the fluid and the porous medium are in local thermodynamic equilibrium; b) the flow is laminar, steady-state and two-dimensional; c) the porous medium is isotropic and homogeneous; d) the properties of the fluid and porous medium are constants; e) the Boussinesq approximation is valid and the boundary-layer approximation is applicable.

In-line with these assumptions, the governing equations describing the conservation of mass, momentum, energy and concentration can be written as follows

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{36}$$

$$u = -\frac{K}{\mu}\frac{\partial p}{\partial x}, \quad v = -\frac{K}{\mu}\left(\frac{\partial p}{\partial y} + \rho g\right) \tag{37}$$

$$u\frac{\partial T}{\partial x} + v\frac{\partial T}{\partial y} = \alpha_m \frac{\partial^2 T}{\partial y^2} \tag{38}$$

$$u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} + \frac{\partial(v_T C)}{\partial y} = D_m \frac{\partial^2 C}{\partial y^2} \tag{39}$$

together with the Boussinesq approximation $\rho = \rho_\infty\left[1 - \beta_T\left(T - T_\infty\right) - \beta_C\left(C - C_\infty\right)\right]$, where the thermophoretic deposition velocity in the y-direction is given by

$$v_T = -k\frac{v}{T}\frac{\partial T}{\partial y} \tag{40}$$

where k is the thermophoretic coefficient. We remark that only the velocity component given by (40) is to be considered within the boundary-layer framework. The boundary conditions are

$$y = 0 \; : \; T = T_w \, , \; C = C_w \, , \; v = 0 \tag{41a}$$

$$y \to \infty : u \to 0 \, , \; T \to T_\infty \, , \; C \to C_\infty \tag{41b}$$

Introducing the stream function ψ in the usual way, in order to identically satisfy the continuity equation, and using the dimensionless quantities

$$\psi = \alpha_m Ra_x^{1/3} f(\eta) \, , \; \theta(\eta) = \frac{T - T_\infty}{T_w - T_\infty} \, , \; \phi(\eta) = \frac{C - C_\infty}{C_w - C_\infty} \, , \; \eta = Ra_x^{1/3} \frac{y}{x} \tag{42}$$

equations (36-39) become

$$f'' - \frac{2}{3}\eta\theta' - \frac{2}{3}N\eta\phi' = 0 \tag{43}$$

$$\theta'' + \frac{1}{3}f\theta' = 0 \tag{44}$$

$$\frac{1}{Le}\phi'' + \frac{1}{3}f\phi' + \frac{k\,\mathrm{Pr}}{N_t + \theta}\left(\theta'\phi' + \theta''\phi - \frac{\phi}{N_t + \theta}\theta'^2\right) = 0 \tag{45}$$

where the sustentation parameter N, the thermophoresis parameter N_t, the local Rayleigh number Ra_x and the Prandtl number Pr are defined as follows

$$N = \frac{\beta_C(C_w - C_\infty)}{\beta_T(T_w - T_\infty)} \, , \; N_t = \frac{T_\infty}{T_w - T_\infty} \, , \; Ra_x = \frac{\rho_\infty g \beta_T K(T_w - T_\infty)x}{\mu\alpha} \, , \; \mathrm{Pr} = \frac{\nu}{\alpha_m} \tag{46}$$

The set of ordinary differential equations (43-45) must be solved along the following boundary conditions

$$f(0) = 0 \, , \; \theta(0) = 1 \, , \; \phi(0) = 1 \tag{47a}$$

$$f'(\infty) = 0 \, , \; \theta(\infty) = 0 \, , \; \phi(\infty) = 0 \tag{47b}$$

Of technical interest is the thermophoretic deposition velocity at the wall, which is given by the expression $V_{tw} = -\dfrac{k\,\mathrm{Pr}}{1 + N_t}\theta'(0)$. Some graphs are reproduced below, from the paper by (Postelnicu, 2007b).

Fig. 10 shows the effects of N on concentration profiles for $k = 0.5$, $N_t = 100$, when Le = 10. In comparison with the vertical case, Fig. 2 from (Chamka and Pop, 2004), the behaviour of the concentration profiles shown in our Fig. 2 is quite similar.

The effects of Le and N on thermophoretic deposition velocity V_{tw} can be seen in Fig. 11 when $k = 0.5$ and $N_t = 100$. Once again, it is instructive to compare our results with those obtained by Chamka and Pop (2004), see Fig. 1 from that paper, where the parameters have the same values as ours. The general behaviour is the same, but the values of V_{tw} are larger in present case. In Fig. 12 there is represented the thermophoretic deposition velocity as a function of k and N when Le = 10 and $N_t = 100$. Similar plots may be obtained for other

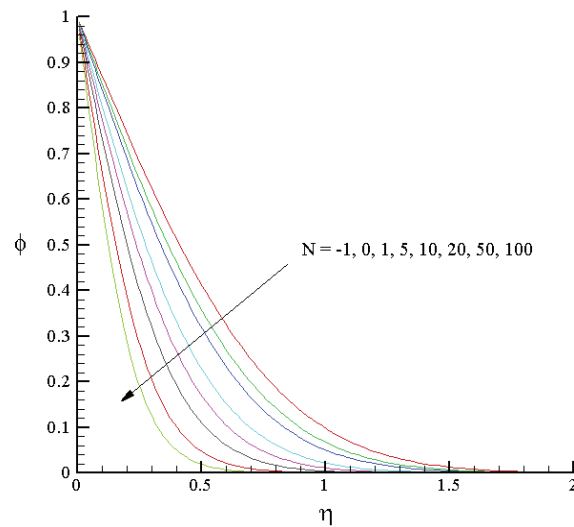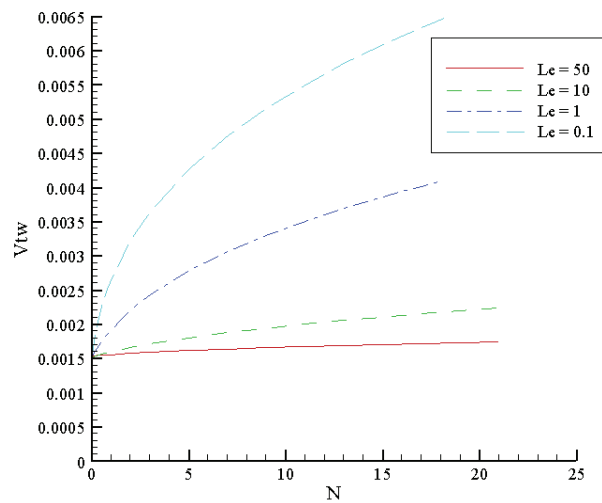Fig. 10. Effects of N on concentration profiles, Le =10, k = 0.5, N_t = 100

Fig. 11. Effects of Le and N on thermophoretic deposition velocity, k = 0.5, N_t = 100
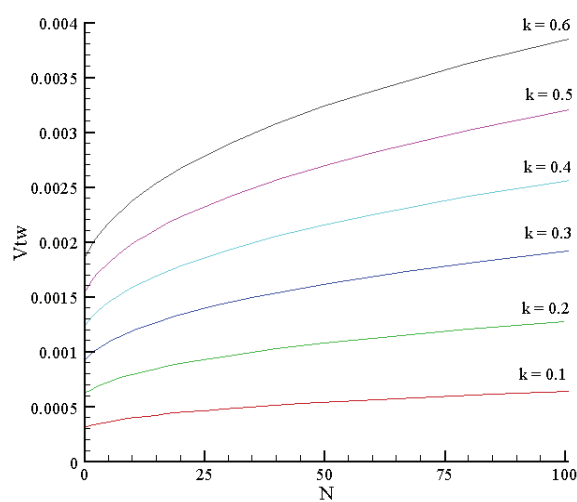

Fig. 12. Effects of k and N on thermophoretic deposition velocity, Le = 10, N_t = 100

values of the Lewis number. The thermophoretic deposition velocity increases as k increases, at a fixed value of N, as in the vertical case.

The problem may be extended on many directions, but the first one seems to be to consider a power law variation of the wall temperature with x: $T = T_w \pm Ax^\lambda$, where the "+" and "-" signs are for a heated plate facing upward and for a cooled plate facing downward respectively and A is a positive constant, but the general behaviour portrayed previously remains.

3.3 Other contributions

In a paper by (Chamkha et al., 2004), the steady free convection over an isothermal vertical circular cylinder embedded in a fluid-saturated porous medium in the presence of the thermophoresis particle deposition effect was analyzed.

The effect of suction / injection on thermophoresis particle deposition in a porous medium was studied by Partha (2009). Using again the boundary layer assumptions, but with a non-Darcy formulation, he found that the heat transfer is intensified when second order effects (thermal dispersion and cross-diffusion) are present.

Very recently, (Postelnicu, 2010b) analyzed thermophoresis particle deposition in natural convection over inclined surfaces in porous media. In this case, Eqs. (37) must be replaced with

$$\frac{\partial u}{\partial y} = \frac{g\beta_T K}{\upsilon}\left(\frac{\partial T}{\partial y}\sin\delta - \frac{\partial T}{\partial x}\cos\delta\right) + \frac{g\beta_C K}{\upsilon}\left(\frac{\partial C}{\partial y}\sin\delta - \frac{\partial C}{\partial x}\cos\delta\right) \tag{48}$$

where the angle of inclination of the plate with respect to horizontal is denoted by δ. The problem is no longer amenable to a set of ordinary differential equations, but partial ones, as follows

$$f'' - \frac{2}{3}\left(\theta' + N\phi'\right) = \xi\left(\theta' + N\phi' - \frac{1}{3}\frac{\partial\theta}{\partial\xi} - \frac{1}{3}N\frac{\partial\phi}{\partial\xi}\right) \tag{49a}$$

$$\theta'' + \frac{1}{3}f\theta' = \frac{1}{3}\xi\left(f'\frac{\partial\theta}{\partial\xi} - \theta'\frac{\partial f}{\partial\xi}\right) \tag{49b}$$

$$\frac{1}{Le}\phi'' + \frac{1}{3}f\phi' + \frac{k\text{Pr}}{N_t+\theta}\left(\theta'\phi' + \theta''\phi - \frac{\phi\theta'^2}{N_t+\theta}\right) = \frac{1}{3}\xi\left(f'\frac{\partial\phi}{\partial\xi} - \phi'\frac{\partial f}{\partial\xi}\right) \tag{49c}$$

subject to the boundary conditions which are essentially (47), at every ξ. The streamwise variable ξ is defined as $\xi = \left(Ra_x \cos\delta\right)^{1/3}\tan\delta$, where the local Rayleigh number Ra_x is defined as in (46). This system of partial differential equations is of parabolic type and may be solved by one of the well-known appropriate numerical methods, such as the Keller-box method, Local Nonsimilarity Method, etc. Aiming to throw some insight on the application of the last method to the present problem, we will refer shortly to this aspect.

This method was introduced by (Sparrow et al., 1970), then applied to thermal problems by (Sparrow & Yu, 1971), where a good description of the algorithm may be found. In the so-

called 2-equations model, one neglects in a first step the first-order derivatives with respect to ξ in Eqs. (49). In the second step, there is performed the differentiation of (49) with respect to ξ and the second-order derivatives $\partial^2 / \partial \xi^2$ are neglected. Proceeding so and introducing the notations

$$F = \frac{\partial f}{\partial \xi} \, , \, \Theta = \frac{\partial \theta}{\partial \xi} \text{ and } \Phi = \frac{\partial \phi}{\partial \xi} \, ,$$

we get the system of equations

$$f'' - \frac{2}{3}(\theta' + N\phi') = \xi\left(\theta' + N\phi' - \frac{1}{3}\Theta - \frac{1}{3}N\Phi\right) \tag{50a}$$

$$\theta'' + \frac{1}{3}f\theta' = \frac{1}{3}\xi(f'\Theta - \theta'F) \tag{50b}$$

$$\frac{1}{Le}\phi'' + \frac{1}{3}f\phi' + \frac{k\Pr}{N_t + \theta}\left(\theta'\phi' + \theta''\phi - \frac{\phi\theta'^2}{N_t + \theta}\right) = \frac{1}{3}\xi(f'\Phi - \phi'F) \tag{50c}$$

$$f'' - \frac{2}{3}(\theta' + N\phi') = \xi\left(\theta' + N\phi' - \frac{1}{3}\frac{\partial\Theta}{\partial\xi} - \frac{1}{3}N\frac{\partial\Phi}{\partial\xi}\right) \tag{50d}$$

$$\Theta'' + \frac{1}{3}f\Theta' + \frac{1}{3}\theta'F = \frac{1}{3}\xi(f'\Theta - \theta'F) + \frac{1}{3}\xi(F'\Theta - F\Theta') \tag{50e}$$

$$\frac{1}{Le}\Phi'' + \frac{1}{3}\xi(F\Phi' - F'\Phi) + \frac{1}{3}f\Phi' + \frac{2}{3}\varphi'F - \frac{1}{3}f'\Phi + \frac{k\Pr}{N_t + \theta}(\theta'\Phi' + \varphi'\Theta' + \theta''\Phi) \tag{50f}$$

$$- \frac{k\Pr}{(N_t + \theta)^2}\left[(\theta'\varphi' + \theta''\varphi)\Theta + 2\varphi\theta'\Theta' + (\theta')^2\Phi\right] + \frac{2k\Pr}{(N_t + \theta)^3}\varphi\theta'\Theta = 0$$

that must be solved along the boundary conditions

$$f(\xi,0) = 0 \, , \, \theta(\xi,0) = 1 \, , \, \phi(\xi,0) = 1 \, , \, F(\xi,0) = 0 \, , \, \Theta(\xi,0) = 0 \, , \, \Phi(\xi,0) = 0 \tag{51}$$

$$f'(\xi,\infty) = 0 \, , \, \theta(\xi,\infty) = 0 \, , \, \phi(\xi,\infty) = 0 \, , \, F'(\xi,\infty) = 0 \, , \, \Theta(\xi,\infty) = 0 \, , \, \Phi(\xi,\infty) = 0 \tag{52}$$

Now the problem was reduced to the set of differential ordinary equations (50) that must be solved subject to the boundary conditions (51) and (52) by any standard numerical method.

4. Convective flows on reactive surfaces in porous media

This kind of chemical reactions may undergo throughout the volume of (porous) region, or along interfaces / boundaries of this region. Real-world applications include chemical engineering systems, contaminant transport in groundwater systems, or geothermal processes. The catalytic systems are modeled usually by including the description of the

reaction kinetics of the catalytic process and the transport of momentum, heat, and mass coupled to this process. Concerning the transport phenomena, access to the catalyst is determined by the transport of mass and energy in a reactor. In heterogeneous catalysis, the access to the catalyst is maximised through the use of porous structures. Examples of catalytic surface reactions are methane/ammonia and propane oxidation over platinum, see for instance (Song et al., 1991) and (Williams et al, 1991). Our interest in the present section is related to the chemical reactions which take place along interfaces / boundaries of the flow region.

4.1 External flows

It is now recognized that chemical reactions affect buoyancy driven flows at least in two directions: the transition from conduction-reaction regimes to conduction-convection-reaction regimes and the influence of natural convection on the development of the chemical reaction.

Models for convective flows on reactive surfaces in porous media have been proposed for external flows by (Merkin and Mahmood, 1998), (Mahmood and Merkin, 1999), (Minto et al., 1998), (Ingham et al., 1999). In these studies bifurcation diagrams were presented for various combinations of the problem parameters and hysteresis bifurcation curves were identified, whenever they exist.

The study by (Merkin and Mahmood, 1998) was extended by (Postelnicu, 2004b) for porous media saturated with non-Newtonian fluids. We shall follow this later author and we will focus on the free convection near a stagnation point of a cylindrical body in a porous medium saturated with a non-Newtonian fluid. We point-out that many fluids involved in practical applications present a non-Newtonian behaviour. Such practical applications in porous media could be encountered in fields like ceramics production, filtration and oil recovery, certain separation processes, polymer engineering, petroleum production.

The fluid which saturates the porous medium is considered of power-law type. The governing equations of this process are

$$\frac{\partial u^*}{\partial x^*} + \frac{\partial v^*}{\partial y^*} = 0 \tag{53a}$$

$$\left(u^*\right)^n = \frac{gK^*(n)\beta}{v^*}(T - T_\infty)\frac{x^*}{l} \tag{53b}$$

$$u^*\frac{\partial T}{\partial x^*} + v^*\frac{\partial T}{\partial y^*} = \alpha_m \frac{\partial^2 T}{\partial y^{*2}} \tag{53c}$$

$$u^*\frac{\partial C}{\partial x^*} + v^*\frac{\partial C}{\partial y^*} = D_m \frac{\partial^2 C}{\partial y^{*2}} \tag{53d}$$

in standard notations, where stars mean dimensional quantities. The x and y-coordinates are taken along the body surface and normal to it, respectively. Moreover, the flow velocity and the pores of the porous medium are assumed to be small so that Darcy's model can be used. The modified permeability $K^*(n)$ is given by

- $K^*(n) = \dfrac{6}{25}\left(\dfrac{n\phi}{3n+1}\right)^n \left(\dfrac{\phi d}{3(1-\phi)}\right)^{n+1}$, according to (Christopher and Middleman, 1965);

- $K^*(n) = \dfrac{2}{\phi}\left(\dfrac{d\phi^2}{8(1-\phi)}\right)^{n+1} \dfrac{6n+1}{10n-3}\left(\dfrac{16}{75}\right)^{\frac{3(10n-3)}{10n+11}}$, according to (Darmadhikari and Kale, 1985),

where d is the particle diameter and ϕ is the porosity.
Heat is released by the first order reaction

$$A \rightarrow B + heat \text{ , rate} = k_0 C \exp\left(-\frac{E}{RT}\right) \tag{54}$$

with a heat of reaction $Q > 0$ which is taken from the body surface into the surrounding fluid-porous medium by conduction. We notice that (54) describes an exothermic catalytic reaction, of Arrhenius type, where the reactant A is converted to the inert product B. Here E is the activation energy, R is the universal gas constant, k_0 is the rate constant, T is the temperature and C is the concentration of reactant A within the convective fluid. This reaction scheme is a realistic one and has been used in the past in modelling of combustion processes, and also for reactive processes in porous media.
The boundary conditions are

$$v^* = 0 \text{ , } k_m \frac{\partial T}{\partial y^*} = -k_0 Q C \exp\left(-\frac{E}{RT}\right), \; D_m \frac{\partial C}{\partial y^*} = k_0 C \exp\left(-\frac{E}{RT}\right), \text{ on } y^* = 0 \text{ , } x^* \geq 0 \tag{55a}$$

$$v^* \rightarrow 0 \text{ , } T \rightarrow T_\infty \text{ , } C \rightarrow C_\infty \text{ as } y^* \rightarrow \infty \text{ , } x^* \geq 0 \tag{55b}$$

Using the stream function: $u^* = \partial \psi^* / \partial y^*$, $v^* = -\partial \psi^* / \partial x^*$, we proceed to render the problem in non-dimensional form by introducing the following quantities

$$x = \frac{x^*}{l} \text{ , } y = \sqrt{Ra}\frac{y^*}{l} \text{ , } \psi = \frac{1}{\sqrt{Ra}}\frac{\psi^*}{\alpha_m} \text{ , } \theta = \frac{T-T_\infty}{RT_\infty^2 l} \text{ , } \varphi = \frac{C}{C_\infty} \tag{56}$$

where $Ra = \left(\dfrac{gK^*(n)\beta RT_\infty^2 l^n}{v^* \alpha_m^n}\right)^{1/n}$ is the Rayleigh number and l is a length scale. We obtain

$$\left(\frac{\partial \psi}{\partial y}\right)^n = x\theta \tag{57a}$$

$$\frac{\partial \psi}{\partial y}\frac{\partial \theta}{\partial x} - \frac{\partial \psi}{\partial x}\frac{\partial \theta}{\partial y} = \frac{\partial^2 \theta}{\partial y^2} \tag{57b}$$

$$\frac{\partial \psi}{\partial y}\frac{\partial \phi}{\partial x} - \frac{\partial \psi}{\partial x}\frac{\partial \phi}{\partial y} = \frac{1}{Le}\frac{\partial^2 \theta}{\partial y^2} \tag{57c}$$

$$\psi = 0 \ , \ \frac{\partial \theta}{\partial y} = -\delta \varphi_w \exp\left(\frac{\theta_w}{1+\varepsilon \theta_w}\right) , \ \frac{\partial \varphi}{\partial y} = \lambda \delta \varphi_w \exp\left(\frac{\theta_w}{1+\varepsilon \theta_w}\right) , \ \text{on } y = 0, \ x \geq 0 \tag{58a}$$

$$\frac{\partial \psi}{\partial y} \to 0 \ , \ \theta \to 0 \ , \ \varphi \to 1 \ , \text{as } y \to \infty \ , \ x \geq 0 \tag{58b}$$

Looking for similarity solutions, we introduce the following quantities

$$\psi = xf(y) \ , \ \theta = x^{n-1} g(y) \ , \ \varphi = x^{n-1} h(y) \tag{59}$$

that render the problem (57-58) in the form

$$\left(f'\right)^n = g \tag{60a}$$

$$g'' + fg' - (n-1)f'g = 0 \tag{60b}$$

$$\frac{1}{Le} h'' + fh' - (n-1)f'h = 0 \tag{60c}$$

$$f(0) = 0 \ , \ g'(0) = -\lambda h_w \exp\left(\frac{x^{n-1} g_w}{1+\varepsilon x^{n-1} g_w}\right) , \ h'(0) = \lambda \delta h_w \exp\left(\frac{x^{n-1} g_w}{1+\varepsilon x^{n-1} g_w}\right) \tag{61a}$$

$$g \to 0 \ , \ h \to 1 \ , \text{as } y \to \infty \tag{61b}$$

Using the transformations $f = g_w^{1/2} F(Y)$, $g = g_w^n G(Y)$, $h = 1 - (1-h_w)H(Y)$, $Y = g_w^{1/2} y$, Eqs (60-61) become

$$\left(F'\right)^n = G \tag{62a}$$

$$G'' + FG' - (n-1)F'G = 0 \tag{62b}$$

$$\frac{1}{Le} H'' + FH' - (n-1)\left[1-(1-h_w)H\right]F' = 0 \tag{62c}$$

$$F(0) = 0 \ , \ G(0) = 1 \ , \ H(0) = 1 \tag{63a}$$

$$G(\infty) = 0 \ , \ H(\infty) = 0 \tag{63b}$$

where now primes denote differentiation with respect to Y. It is worth to remark that the problems in (F, G) and in H are now no more coupled. The last two boundary conditions from (63a) become

$$g_w^{n+1/2}\left(\frac{dG}{dY}\right)_{Y=0} = -\lambda h_w \exp\left(\frac{x^{n-1} g_w}{1+\varepsilon x^{n-1} g_w}\right) \tag{64a}$$

$$-\left(1-h_w\right)g_w^{1/2}\left(\frac{dH}{dY}\right)_{Y=0}=\lambda\delta h_w\exp\left(\frac{x^{n-1}g_w}{1+\varepsilon x^{n-1}g_w}\right)\tag{64b}$$

i.e. two equations in the unknowns g_w and h_w. Eliminating h_w between (64) gives

$$\lambda=g_w^{1/2}\exp\left(-\frac{x^{n-1}g_w}{1+\varepsilon x^{n-1}g_w}\right)\Big/\left[\frac{\delta}{C_1}+\frac{\left(g_w\right)^{-n}}{C_0}\right]\tag{65}$$

where $C_0=-\left(dG/dY\right)_{Y=0}$ and $C_1=\left(dH/dY\right)_{Y=0}$. We remark that C_0 depends only on n, while C_1 depends on n, Le, ε, δ and h_w.

a.   Case of no reactant consumption

In this case, $\delta=\gamma=0$ and $h_w\equiv1$ so that Eq. (65) simplifies to

$$\lambda=C_0g_w^{n+1/2}\exp\left(-\frac{x^{n-1}g_w}{1+\varepsilon x^{n-1}g_w}\right)\tag{66}$$

The critical points on the graphs g_w vs. λ are obtained from the condition: $d\lambda/dg_w=0$ and are given by

$$g_w^{(1,2)}=\frac{1-\left(2n+1\right)\varepsilon\pm\sqrt{1-2\left(2n+1\right)\varepsilon}}{\left(2n+1\right)\varepsilon^2x^{n-1}}\tag{67}$$

The following conclusions can be obtained from (67)

*   For $0<\varepsilon<0.5/\left(2n+1\right)$, there are two critical points $\lambda_1=\lambda\left(g_w^{(1)}\right)$ and $\lambda_2=\lambda\left(g_w^{(2)}\right)$.

*   At $\varepsilon=0.5/\left(2n+1\right)$, there is a hysteresis bifurcation, where the slope becomes vertical.

*   For $\varepsilon>0.5/\left(2n+1\right)$, g_w increases with λ

*   In the case $\varepsilon\ll1$, one obtains using (67),

$$g_w^{(1)}\sim\frac{2n+1}{2}\left[1+\left(2n+1\right)\varepsilon+...\right]x^{1-n},\ g_w^{(2)}\sim\frac{2-\left(2n+1\right)\varepsilon-\frac{1}{2}\left(2n+1\right)^2\varepsilon^2+...}{\left(2n+1\right)\varepsilon^2}x^{1-n}\tag{68}$$

so that

$$g_w^{(1)}\to\frac{2n+1}{2}x^{1-n}\ \text{and}\ g_w^{(2)}\to\infty\ \text{as}\ \varepsilon\to0\tag{69}$$

Some curves g_w vs. λ are represented in Fig. 13, for no reactant consumption, when ε = 0 and δ = 0.5.

b.   General case, reactant consumption

In this case, we have to cope with equation (65). Looking again for the critical points, the condition $d\lambda/dg_w=0$ gives

$$\left(\frac{\delta^2}{C_1} + \frac{g_w^{-n}}{C_0}\right)\left[\frac{1}{2}g_w^{-1/2} - \frac{x^{n-1}g_w^{1/2}}{\left(1 + \varepsilon x^{n-1}g_w\right)^2}\right] + \frac{n\delta^2 C_0 C_2}{C_1^3}g_w^{-n-1/2} + \frac{n}{C_0}g_w^{-n-1/2} = 0 \qquad (70)$$

In deriving this equation, it was necessary to compute dC_1/dg_w, which is obtained after some algebra as

$$\frac{dC_1}{dg_w} = \frac{n\delta C_0 C_2}{C_1}g_w^{n-1} \qquad (71a)$$

$$C_2 = \frac{dC_1}{dh_w} = \left(\frac{dS}{dY}\right)_{Y=0} \qquad (71b)$$

In order to find the hysteresis bifurcation curve in the (ε, γ) space, with (n, x, δ) as remainder parameters, it is needed to solve equation (70) together with its derivative with respect to g_w. The following values of the index parameter have been considered: $n = 0.25, 0.5, 0.75, 1.5$ and 2.0. In each case, parameters ε, δ and Le have been varied as follows: $\varepsilon = (0, 0.05, 0.1$ and 0.15), $\delta = (0.5$ and 1.0), Le $= (1, 10$ and 100), while x was taken as 0.1, 0.5 and 1.0. We found that the basic shape of the bifurcation diagram does not depend basically on x, once the other parameters are held at fixed values.

Let us proceed firstly with the case $n = 0.25$. Fig. 14 shows a typical plot g_w as a function of γ for $\varepsilon = 0$, $\delta = 0.5$ and Le $= 1$. Basically, this types of variation, known also for Newtonian fluids, is found for any combination of $(\varepsilon, \delta, \text{Le})$ and they do not lead to hystheresis.

The case $n = 0.5$ presents many interesting features. Figs. 15 and 16 show two cases when the vertical slope becomes infinite for $x = 0.1$, but not for $x = 0.5$ and 1.0. We found that this characteristic for any case associated with Le $= 1$. But for Le $= 10$ and several cases associated with Le $= 100$ the vertical slope becomes infinite for any x, see Fig. 17 and 18.
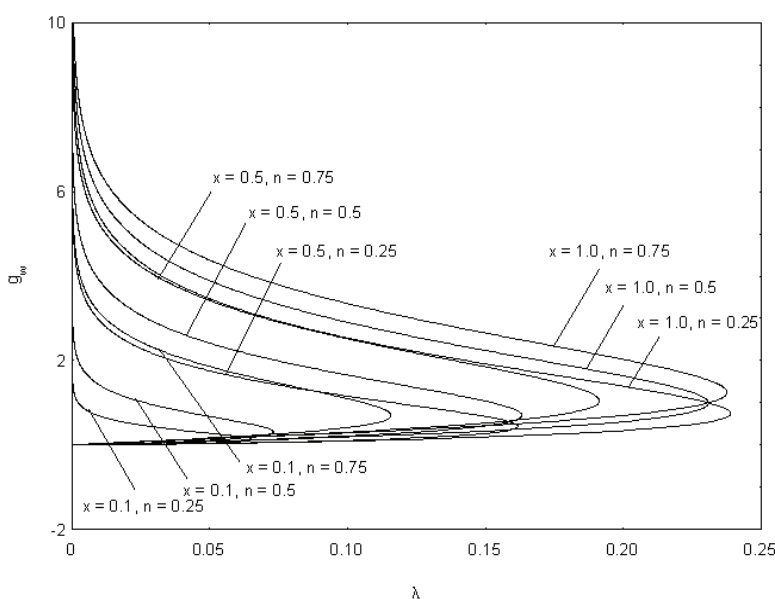

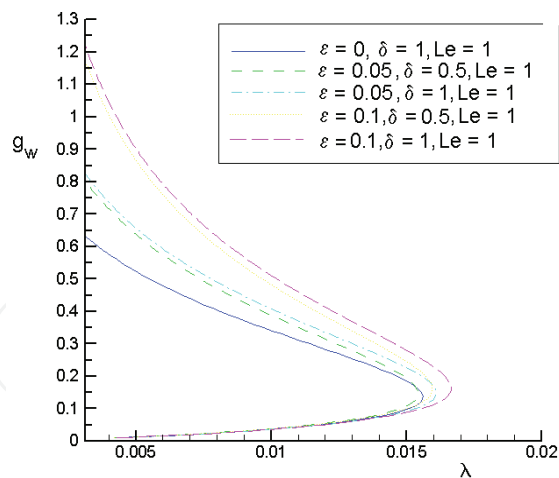Fig. 13. Curves g_w vs. λ: no reactant consumption, $\varepsilon = 0$, $\delta = 0.5$

Fig. 14. Bifurcation diagrams for the case of reactant consumption $n = 0.25$, $x = 0.1$
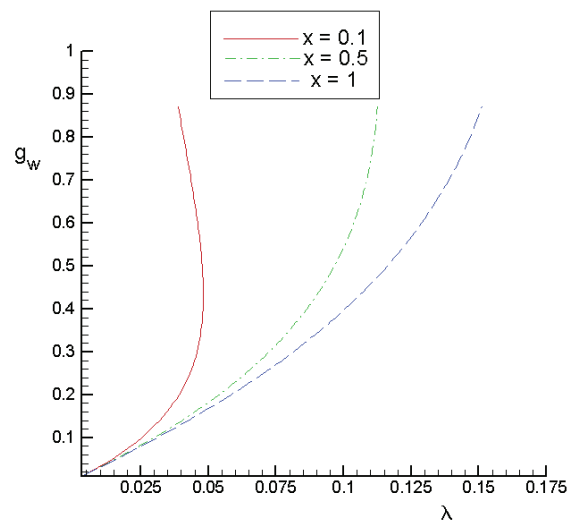

Fig. 15. Bifurcation diagrams for the case of reactant consumption $n = 0.5$, $\varepsilon = 0.1$, $\delta = 1.0$ and Le = 1
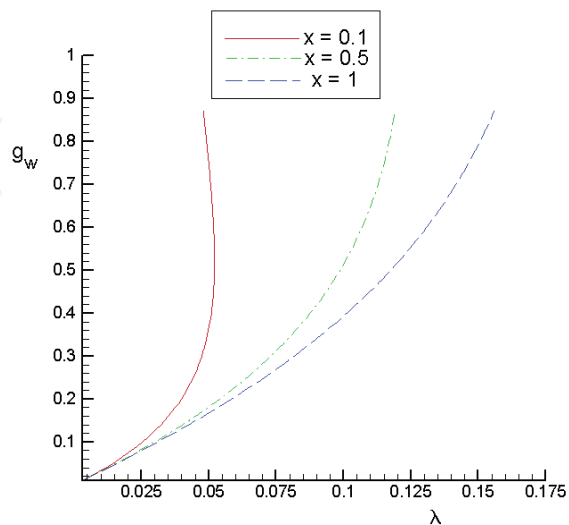

Fig. 16. Bifurcation diagrams for the case of reactant consumption $n = 0.5$, $\varepsilon = 0.15$, $\delta = 1.0$ and Le = 1
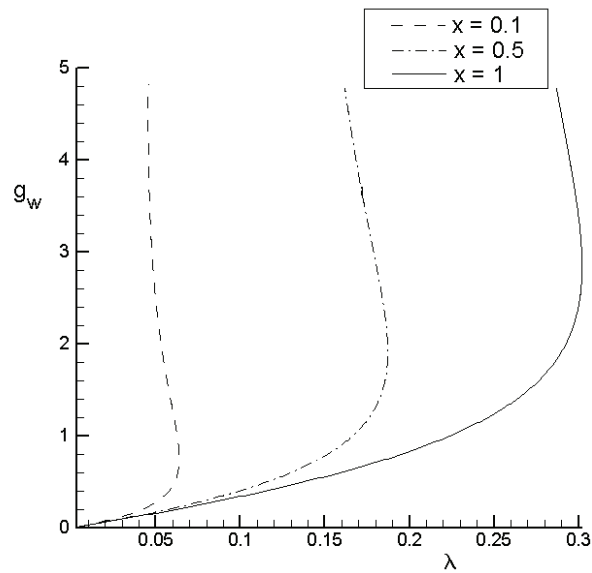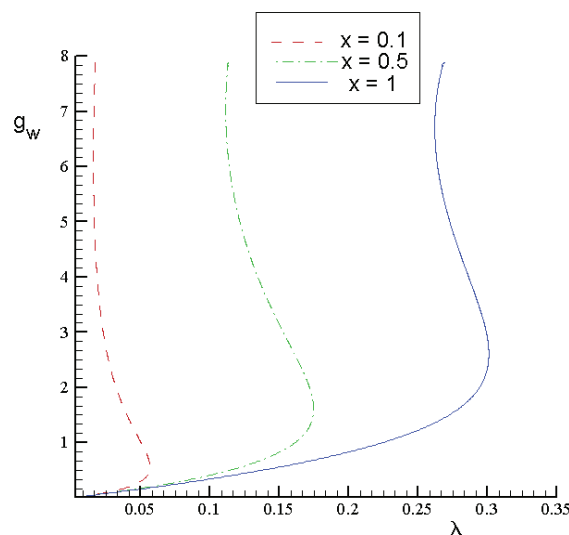
Fig. 17. Bifurcation diagrams for the case of reactant consumption $n = 0.5$, $\varepsilon = 0.15$, $\delta = 1.0$, $Le = 10$

Fig. 18. Bifurcation diagrams for the case of reactant consumption $n = 0.5$, $\varepsilon = 0.1$, $\delta = 1.0$, $Le = 100$

One kind of behaviour in the case $n = 1.5$ is shown in Fig. 19 specific for $Le = 1$. A thorough investigation, peformed also for $Le = 10$ and 100 leads to the conclusion is that there are not chances to obtain hystheresis conditions for $n = 1.5$ irrespective of ε, δ and Le.

Finally the bifurcation diagrams in the case $n = 2.0$ look like in Fig. 20. These shapes are similar to those obtained in the $n = 1.5$ case, for $Le = 10$ and 100 but this time they are obtained for any Lewis number. We conclude that no hysteresis conditions can be obtained in the case $n = 2$.

In conclusion, we proved that in the case of no reactant consumption it is possible to proceed entirely analytically, and the hysteresis bifurcation was found at a certain value of the activation parameter ε, similarly as in the Newtonian fluids. But in the case of reactant consumption, it is no more possible to use analytical means of analysis. Our numerical runs

revealed that the most prolific case in bifurcation diagrams shapes is when the index parameter $n = 0.5$. Cases leading to hysteresis were found to be $n = 0.5$ and $n = 0.75$. Finding hysteresis bifurcation curves is more difficult due to the increased number of parameters as compared to the Newtonian case.
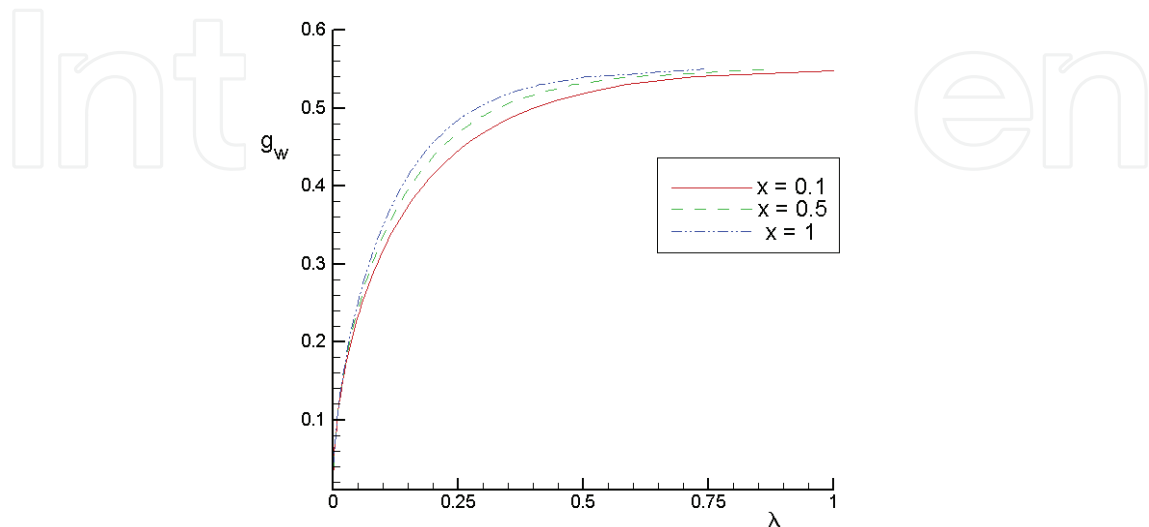

Fig. 19. Bifurcation diagrams for the case of reactant consumption $n = 1.5$, $\varepsilon = 0.05$, $\delta = 1$, $Le = 1$

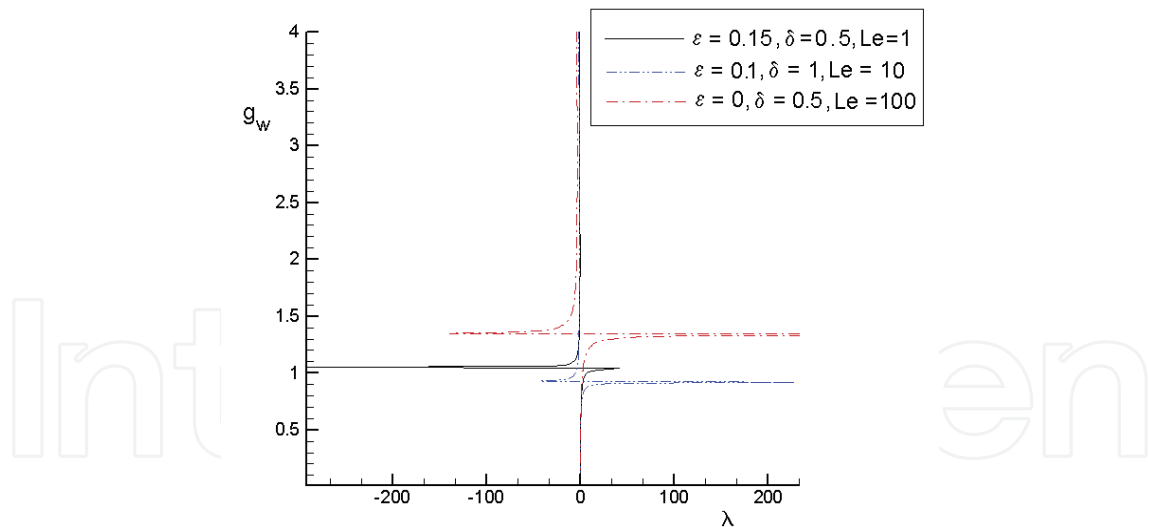Fig. 20. Bifurcation diagrams for the case of reactant consumption $n = 2.0$, $x = 0.1$

4.2 Onset of convection in a horizontal porous layer driven by catalytic surface reaction on the lower wall

We consider in this subsection the situation when the convective flow in a horizontal porous layer is driven by an exothermic catalytic reaction taking place on the lower surface whereby a reactive species A reacts to form an inert product B. The upper wall is subjected to uniform temperature and concentration, while on the lower wall there is an exothermic

surface reaction, whereby reactant *P* is converted to an inert product *B*, via the first-order Arrhenius kinetics non-isothermal reaction (54). The surface reaction releases heat, which produces a convective flow close to the surface and, in turn, fresh reactant will replace that used up in the reaction. In this way, an interaction will occur between the convective flow, heat transfer and mass transport of the reactant.

Using usual notations, the governing equations which describe the problem at hand are mass conservation, Darcy's law, equation of energy and that of concentration

$$\frac{\partial \bar{u}}{\partial \bar{x}} + \frac{\partial \bar{v}}{\partial \bar{y}} = 0 \tag{72}$$

$$\bar{u} = -\frac{K}{\mu}\frac{\partial \bar{p}}{\partial \bar{x}} \;,\; \bar{v} = -\frac{K}{\mu}\frac{\partial \bar{p}}{\partial \bar{y}} + \frac{\rho g \beta K}{\mu}(T - T_r) \tag{73}$$

$$\frac{\partial T}{\partial \bar{t}} + \bar{u}\frac{\partial T}{\partial \bar{x}} + \bar{v}\frac{\partial T}{\partial \bar{y}} = \alpha_m\left(\frac{\partial^2 T}{\partial \bar{x}^2} + \frac{\partial^2 T}{\partial \bar{y}^2}\right) \tag{74}$$

$$\frac{\partial C}{\partial \bar{t}} + \bar{u}\frac{\partial C}{\partial \bar{x}} + \bar{v}\frac{\partial C}{\partial \bar{y}} = D_m\left(\frac{\partial^2 C}{\partial \bar{x}^2} + \frac{\partial^2 C}{\partial \bar{y}^2}\right) \tag{75}$$

where T_r is a reference temperature and over-bars refer to dimensional quantities. The $\bar{x}$ and $\bar{y}$ axes are taken along the porous layer and normal to it respectively, and the lower wall is located at $\bar{y} = 0$. We point out that in writing equations (73), the Boussinesq approximation was invoked and differences in reactant concentration (which may induce buoyancy forces) are assumed to be small. The Darcy model is justifiable when the heat of reaction is small or moderate. Otherwise, when the heat of reaction is large, non-Darcy models must be used.

The thermal boundary conditions on the lower wall are

$$k_T\frac{\partial T}{\partial \bar{y}} = -Qk_0 C\exp\left(-\frac{E}{RT}\right) \;,\; D\frac{\partial C}{\partial \bar{y}} = k_0 C\exp\left(-\frac{E}{RT}\right) \tag{76}$$

where k_T is the thermal conductivity of the surface, Q is the heat of reaction, which is taken as positive, meaning that heat is taken from the surface into the surrounding fluid-porous medium by conduction. Eliminating the pressure, using the streamfunction ψ and introducing dimensionless quantities, Eqs. (72-75) become

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = Ra\frac{\partial \theta}{\partial x} \tag{77}$$

$$\frac{\partial \theta}{\partial t} + u\frac{\partial \theta}{\partial x} + v\frac{\partial \theta}{\partial y} = \frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} \tag{78}$$

$$\frac{\partial \varphi}{\partial t} + u\frac{\partial \varphi}{\partial x} + v\frac{\partial \varphi}{\partial y} = \frac{1}{Le}\left(\frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2}\right) \tag{79}$$

see (Postelnicu, 2009b), where $Ra = \dfrac{\rho g \beta K h}{\mu \kappa} \cdot \dfrac{RT_r^2}{E}$ is the Rayleigh number. The boundary conditions in the final model are

$$\psi = 0 \text{, on both } y = 0 \text{ and } y = 1 \tag{80a}$$

$$\frac{\partial \theta}{\partial y} = -A\varphi \exp\left(\frac{\theta}{1+\varepsilon\theta}\right), \ \frac{\partial \varphi}{\partial y} = B\varphi \exp\left(\frac{\theta}{1+\varepsilon\theta}\right), \text{ on } y = 0 \tag{80b}$$

$$\theta = 0 \text{ , } \varphi = 1 \text{, on } y = 1 \tag{80c}$$

where

$$A = \left(Qk_0 C_0 h / k\right) \cdot \left(E / RT_r^2\right), \ B = k_0 h / D$$

are dimensionless parameters, while $\varepsilon = RT_r / E$ is the activation energy parameter.
The basic state is motionless $u_b = v_b = \psi_b = 0$ and is characterized by the linear temperature and concentrations profiles

$$\theta_b = ay + b \text{ , } \varphi_b = cy + d \text{ ,}$$

where the constants a, b, c, and d are obtained by enforcing the boundary conditions (80). The following transcendental equation is obtained for a

$$a + \left(A + Ba\right)\exp\left(-\frac{a}{1-\varepsilon a}\right) = 0 \tag{81}$$

where three parameters are involved: A, B and ε. For b, c and d see (Postelnicu , 2009b).
For the stability analysis, one expresses

$$\psi = \Psi \text{ , } \theta = \theta_b + \Theta = ay + b + \Theta \text{ , } \varphi = \varphi_b + \Phi = cy + d + \Phi \tag{82}$$

where ψ, Θ and Φ are perturbed quantities, $|\Psi| \ll 1$, $|\Theta| \ll 1$ and $|\Phi| \ll 1$, and looking for the solutions in the form

$$\Psi = e^{\lambda t} f(y)\sin kx \text{ , } \Theta = e^{\lambda t} g(y)\cos kx \text{ , } \Phi = e^{\lambda t} h(y)\cos kx \tag{83}$$

the linearised stability problem is governed by the equations

$$f'' - k^2 f + kRg = 0 \tag{84a}$$

$$g'' - \left(k^2 + \lambda\right)g + akf = 0 \tag{84b}$$

$$h'' - \left(k^2 + \lambda\right)h + ckf = 0 \tag{84c}$$

$$f(0) = 0 , \ g'(0) = -Ah(0) , \ h'(0) = Bh(0) \tag{85a}$$

$$f(1) = 0 , \ g(1) = 0 , \ h(1) = 0 \tag{85b}$$

The eigenvalue problem formulated in (84)-(85) must be solved for the Rayleigh number. It can be shown that the principle of exchange of stability holds, so we can take $\lambda = 0$ in the previous equations. We mention that a problem where the frequency (λ in our case) is real, so that the marginal stability occurs when $\lambda = 0$, is said to obey the principle of exchange of stability. Since there are no analytical solutions of this eigenvalue problem, it will be solved numerically, by minimizing the Rayleigh number over the wave number. The corresponding values of the wavenumber and Rayleigh number are termed critical.

In Fig. 21 there is depicted the variation of the critical wave number with B, for $A = 0.5$ and $\varepsilon = 0.5$. It is seen that, at given Lewis number, the critical wave-number increases with B, while increase of the Lewis number leads to an increase of k_c. Critical Rayleigh number vs B is shown in Fig. 22, when $A = 0.5$ and $\varepsilon = 0.5$. The critical Rayleigh number increases with B, almost linearly for small Lewis number. On the other hand, we remark the usual increase of R_c with Le, a value near 240 being reached by the critical Rayleigh number for $B = 1$, when Le = 100.
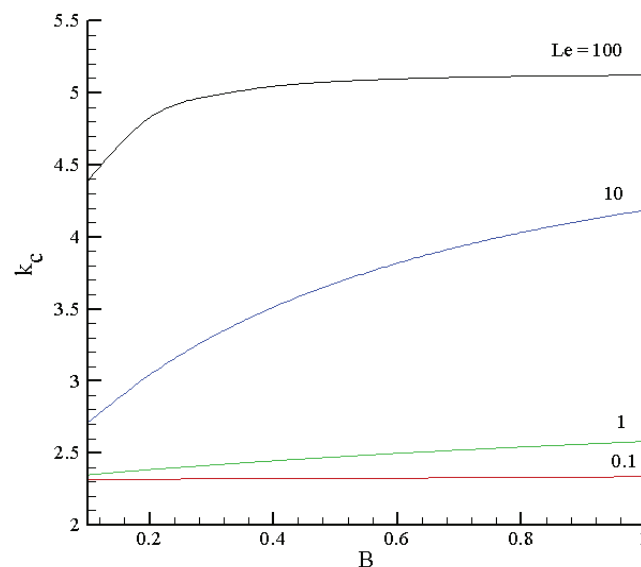

Fig. 21. Variation of the critical wave number with B, for $A = 0.5$ and $\varepsilon = 0.5$
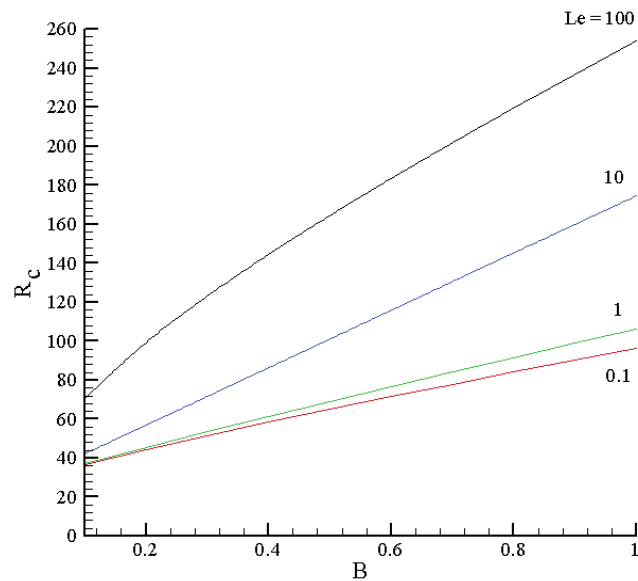
Fig. 22. Critical Rayleigh number vs B, when $A = 0.5$ and $\varepsilon = 0.5$

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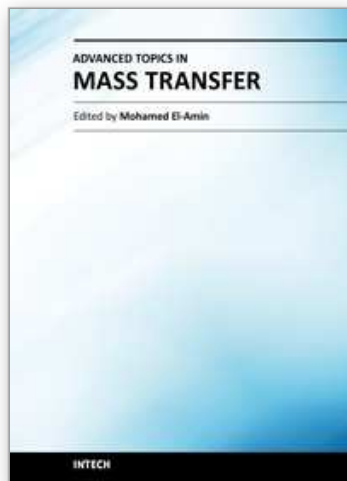
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