c_s = concentration of hydrogen in the liquid-solid interface, mol/m^3
D_{eff} = effective diffusivity, m^2/s
d_{gm} = geometric mean particle diameter (number basis), m
E_a = activation energy, kJ/mol
E_D = activation energy of diffusion, kJ/mol
E = electrochemical potential, V
F = Faraday's constant, As/mol
He = Henry's constant, $bar{\cdot}m^3/mol$
i = current density, A/m^2
k_v = rate constant, $(s{\cdot}m^3 \text{ catalyst})^{-1}$
m = catalyst loading, m^3/m^3
N = rate of mass transfer, $mol/s{\cdot}m^2$
N_1, N_2 = number of logarithmic standard deviations from the mean corresponding to a lower and an upper particle size limit, respectively
RNH_2 = aminobenzoic acid
RNO_2 = nitrobenzoic acid
S = liquid-catalyst specific external surface area, m^2/m^3
α = charge transfer coefficient
η = effectiveness factor
θ_H = fractional coverage of hydrogen
θ_{RNO_2} = fractional coverage of nitrobenzoic acid and reaction intermediates of nitrobenzoic acid
σ_g = standard deviation of the log-normal particle size distribution
ϕ = Thiele modulus (Eqs. 10–13)
ϕ_{gm} = Thiele modulus corresponding to particle of size d_{gm}

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R&D NOTES

Laminar Free Convection with Suction or Blowing Along a Vertical Surface

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In the past, the effects of suction or blowing on laminar free convection flow over a vertical porous plate have been the subject of several investigations. Eichhorn (1960) investigated the particular distributions of surface temperature and transpiration rates which lead to similarity solutions of the laminar boundary-layer equations. Corresponding to a wall temperature with power law distribution, it was found that similarity solutions were possible only when the blowing velocity $V_w \sim X^{(n-1)/4}$. Sparrow and Cess (1961) had presented an approximate series solution for the case of uniform transpiration and wall temperature. These authors also provided a transformation to be used when both wall temperature and transpiration velocities vary with different powers of X. More recently, numerical solutions for the case of constant wall temperature and transpiration rate had been obtained by Merkin (1972), Clarke (1973), and Parikh et al (1974). Kao (1976) had solved the same problem using Sparrows' two-equation local non-similar method. The more general problem of laminar free convection with arbitrarily prescribed transpiration rate will be investigated here using the strained co-ordinates technique of Kao, Domoto and Elrod (1977).

ANALYSIS

As a starting point, the set of conservation equations governing laminar free convection adjacent to a vertical wall will be transformed into the following:

$$f''' + (3 - 2\tilde{\beta})ff'' - 2f^{12} + \theta = 4\xi\left[f'\frac{\partial f'}{\partial \xi} - f''\frac{\partial f}{\partial \xi}\right] \quad (1)$$

$$\frac{1}{\mathrm{Pr}}\theta'' + (3 - 2\tilde{\beta})f\theta' - 4\tilde{\beta}f\theta = 4\xi\left[f'\frac{\partial \theta}{\partial \xi} - \theta'\frac{\partial f}{\partial \xi}\right] \quad (2)$$

$$(3 - 2\tilde{\beta})f(\xi,0) + 4\xi\frac{\partial f}{\partial \xi}(\xi,0) = \gamma(x) = -\frac{V_w X}{\nu}\left[\frac{4}{Gr_x}\right]^{1/4}$$

$$f'(\xi,0) = 0, \qquad \theta(\xi,0) = 1 \quad (3)$$

$$f'(\xi,\infty) = 0 \qquad \theta(\xi,\infty) = 0 \quad (4)$$

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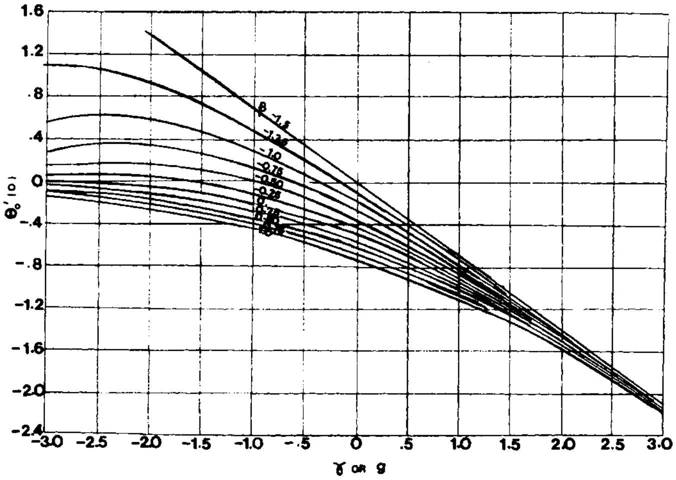

Figure 1. $\theta_0'(g,0)$.

Here primes denote partial derivatives with respect to η. V_w is the transpiration velocity at the wall and Gr_x is the the local Grashof number. The transformation used here are the same as given by Kao et al. (1977).

$$\xi = \int_0^x (T_w - T_\infty)dx \tag{5}$$

$$\eta = C_1(T_w - T_\infty)^{1/2}y/\xi^{1/4} \tag{6}$$

$$f(\xi,\eta) = (T_w - T_\infty)^{1/4}\psi/4C_1\nu\xi^{3/4} \tag{7}$$

$$\theta(\xi,\eta) = (T - T_\infty)/(T_w - T_\infty) \tag{8}$$

$$\tilde{\beta} = \frac{\int_0^x (T_w - T_\infty)dx}{(T_w - T_\infty)^2} \times \frac{d(T_w - T_\infty)}{dx} \tag{9}$$

$$C_1 = [\tilde{g}\tilde{\beta}/4\nu^2]^{1/4}$$

ψ is the stream function introduced to satisfy the continuity equation. Equation 9 defines $\tilde{\beta}$, the wall temperature similarity parameter. $\tilde{\beta}$ will be constant if the wall temperature distribution is of power law type. The prescribed transpiration velocity V_w, and therefore the transpiration parameter γ, is a function of the streamwise direction. Similarity solution can be obtained only when both $\tilde{\beta}$ and γ are constants. Local similarity solutions neglect the streamwise derivatives. Equations 1 to 4 are valid when both wall temperature and transpiration velocity are functions of X. In this note, we shall consider the case where $\tilde{\beta}$ is constant (i.e., power law type of wall temperature distribution), with arbitrarily prescribed transpiration rate.

Following the strained co-ordinate technique given by Kao et al. (1977), Eq. 1-4 can be rewritten as:

$$f''' + (3 - 2\tilde{\beta})ff'' - 2f'^2 + \theta = \epsilon(\gamma)\frac{dg}{d\gamma}\left[f'\frac{\partial f'}{\partial g} - f''\frac{\partial f}{\partial g}\right] \tag{10}$$

$$\frac{1}{\Pr}\theta'' + (3 - 2\tilde{\beta})f\theta' - 4\tilde{\beta}\theta f' = \epsilon(\gamma)\frac{dg}{d\gamma}\left[f'\frac{\partial\theta}{\partial g} - \theta'\frac{\partial f}{\partial g}\right] \tag{11}$$

with boundary conditions given by:

$$(3 - 2\tilde{\beta})f(g,0) + \epsilon(\gamma)\frac{dg}{d\gamma}\frac{\partial f(g,0)}{\partial g} = \gamma \tag{12}$$

$$f'(g,0) = 0 \qquad \theta(g,0) = 1 \tag{13}$$

$$f'(g,\infty) = 0 \qquad \theta(g,0) = 0 \tag{14}$$

where

$$\epsilon(\gamma) = 4\xi\frac{d\gamma}{d\xi} \tag{15}$$

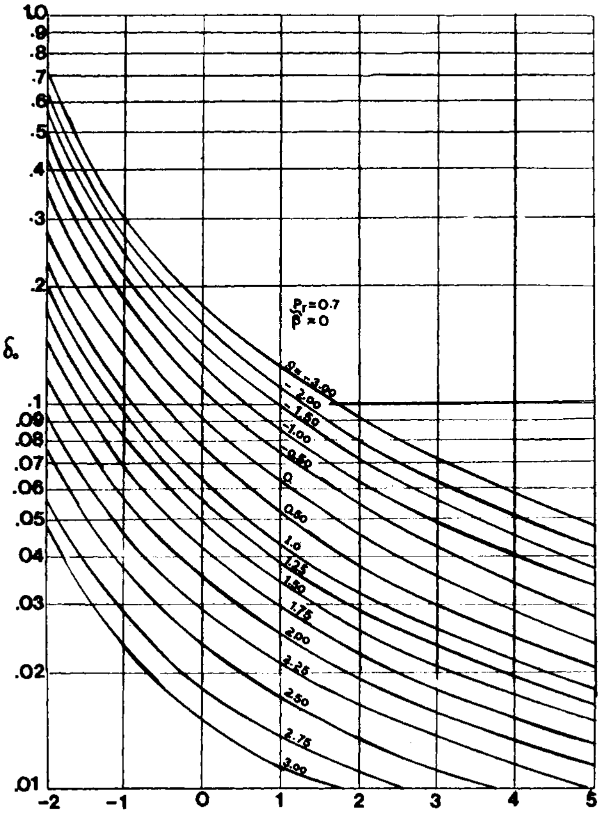

Figure 2. δ_0 for prescribed transpiration at the wall.

and g is a shifted value of γ given by the following equation:

$$\gamma = g + \epsilon(\gamma)\delta_0 + \epsilon^2\delta_1 + \ldots \tag{16}$$

Next we seek to expand f and θ in power series of $\epsilon(\gamma)$:

$$f = f_0(g,\eta) + \epsilon f_1(g,\eta) + \ldots \tag{17}$$

$$\theta = \theta_0(g,\eta) + \epsilon\theta_1(g,\eta) + \ldots \tag{18}$$

Here g is determined locally. the δ's are obtained by imposing the additional constraint that the zero order solution will provide an almost exact heat flux at the wall. Thus in order to find δ_o, we required that $\theta_1'(g,0) = 0$, for $\delta_1, \theta_2'(g,0)$ is set to zero, etc. Here we shall confine ourselves to the determination of δ_0 only.

Upon substituting the above expressions into Eqs. 10 to 14, and equating terms of like powers of ϵ, the first two sets of equations are:

ORDER UNITY

$$f_0''' + (3 - 2\tilde{\beta})f_0f_0'' - 2f_0'^2 + \theta_0 = 0 \tag{19}$$

$$\frac{1}{\Pr}\theta_0'' + (3 - 2\tilde{\beta})f_0\theta_0' - 4\tilde{\beta}f_0'\theta_0 = 0 \tag{20}$$

$$f_0(g,0) = \frac{g}{(3 - 2\tilde{\beta})} \tag{21}$$

$$f_0'(g,0) = 0 \qquad \theta_0(g,0) = 1 \tag{22}$$

$$f_0'(g,\infty) = 0 \qquad \theta_0(g,\infty) = 0 \tag{23}$$

Order ϵ:

$$f_1''' + (3 - 2\tilde{\beta} + \epsilon')f_0''f_1 + (4 + \epsilon')f_0'f_1' + (3 - 2\tilde{\beta})f_0f_1'' + \theta_1 = (1 - \epsilon'\delta_0)\left[f_0'\frac{\partial f_0'}{\partial g} - f_0''\frac{\partial f_0}{\partial g}\right] \tag{24}$$

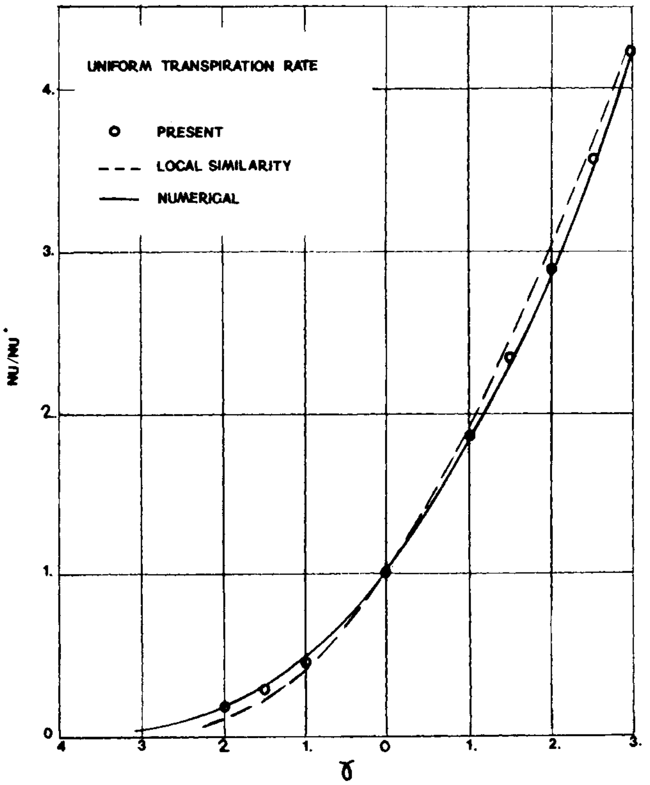

Figure 3. Comparison of Nu/Nu for free convection with constant transpiration at the wall.

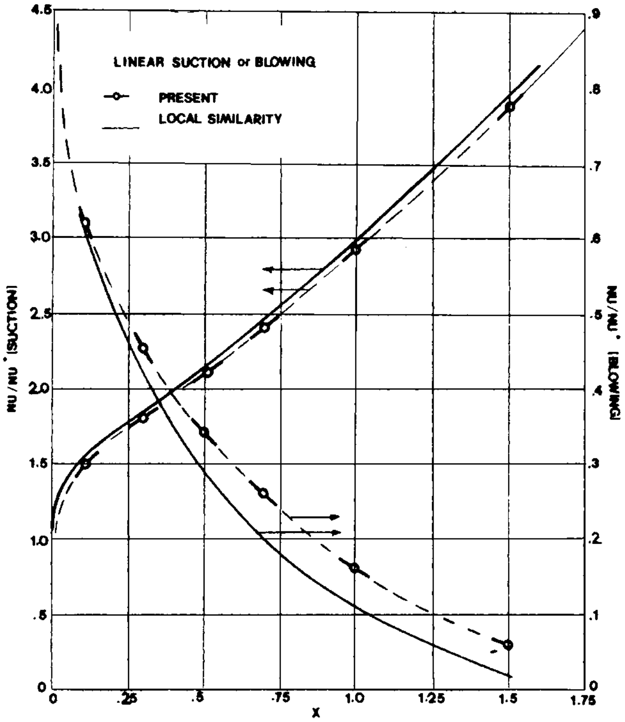

Figure 4. Comparison of Nu/Nu* for free convection with linear blowing or suction rate at the wall.

$$\frac{1}{\mathrm{Pr}}\theta_1'' + (3-2\tilde{\beta})f_0\theta_1' - (4\tilde{\beta}+\epsilon')f_0'\theta_1 = (1-\epsilon'\delta_0) \times \left[f_0'\frac{\partial\theta_0}{\partial g} - \theta_0'\frac{\partial f_0}{\partial g}\right] - (3-2\tilde{\beta}+\epsilon')\theta_0'f_1 + 4\tilde{\beta}\theta_0f_1' \quad (25)$$

$$(3-2\tilde{\beta})f_1(g,0) = \delta_0 - 1/(3-2\tilde{\beta}+\epsilon')$$

$$f_1'(g,0) = \theta_1'(g,0) = \theta_1(g,0) = 0 \quad (26)$$

$$f_1(g,\infty) = \theta_1(g,\infty) = 0$$

where $\epsilon' = \frac{d\epsilon}{d\gamma}$

The shooting technique of Nachtsheim and Swigert (1965) is used to solve for δ_0.

The solution for the case where Pr = 0.7 and $\tilde{\beta} = 0$ (i.e., constant wall temperature) has been obtained and the resultant δ_0 with g and ϵ' appearing as parameters is shown in Figures 1 and 2. At each streamwise location, γ, ϵ and ϵ' are known from the local transpiration rate. The following, iteration procedure can be used to solve for g using Figure 2 and Eq. 16.

a) Determine from data the local value of γ, ϵ and ϵ'.
b) Guess g.
c) Read δ_0 from Figure 2.
d) Get new value of g from Eq. 16.
e) Read a new value of δ_0 from Figure 2.
f) Average the new and previous δ_0s.
g) Get a new g from Eq. 16, etc.

Once g is found at the particular streamwise station under consideration, the corresponding zeroth order θ_0' can be obtained from Figure 1.

EXAMPLE

We shall consider two examples. The first example is that of free convection with uniform transpiration. In this example, quite a number of numerical solutions are available for comparison. In this case, $\epsilon = \gamma$. Thus $\epsilon' = 1.0$. The results for Nu/Nu* for the case of air is shown in Figure 3. Here Nu* is the Nusselt number for an impermeable wall. Comparisons with the numerical solution of Parikh et al. (1975), shows that the present solution is quite accurate.

In the second example, we consider the case of linearly varying blowing or suction.

$$V_w = \pm V_0(1 + x)$$

The transpiration parameter is given by:

$$\gamma = \frac{\pm 4V_0}{C_1(T_w - T_\infty)^{1/4}}(1 + x)x^{1/4}$$

Without loss of generality, we shall take $4V_0/C_1(T_w - T_\infty) = 1.0$. In Figure 4, we have plotted Nu/Nu* for both the local similarity solution and the strained co-ordinates solution. The discrepancy between the local similarity solution and the strained co-ordinate solution is rather small for the suction case. In the linear blowing case, we see that the discrepancy between the two solutions becomes large with increasing X. Published numerical solutions and experimental data seem to be lacking for the case under consideration. Thus further comparisons remain to be carried out in the future.

CONCLUSION

The problem of laminar free convection adjacent to a vertical wall with arbitrarily prescribed transpiration rate has been investigated using the method of strained coordinates. A set of universal functions have been obtained for air (Pr = 0.70). Two examples were considered. Comparisons with known numerical solution show that the present solution is quite accurate and warrants its use for most engineering purposes.

NOTATION

f = non-dimensional stream function
g = defined in Eq. 16

$\tilde{g}$ = gravitational acceleration
Gr_x = $\tilde{g}\bar{\beta}(T_w - T_\infty)X^3/\nu$
$\bar{h}$ = heat transfer coefficient
k = thermal conductivity
Nu_x = $\bar{h}x/k$
Pr = Prandtl number
T = temperature variable
u = velocity in the x-direction
v = velocity in the y-direction
x = coordinate along the plate
y = coordinate normal to the plate
α = thermal diffusivity
$\tilde{\beta}$ = wall temperature variation parameter as defined in Eq. 9
$\bar{\beta}$ = coefficient of volumetric expansion
$\epsilon(\gamma)$ = $4\xi \dfrac{d\gamma}{d\xi}$
ψ = stream function
ξ = transformed stream-wise coordinate
η = transformed normal coordinate
θ = $(T - T_\infty)/(T_w - T_\infty)$
ν = kinematic viscosity

Subscripts

w = surface condition
∞ = conditions in the ambient
0 = zero order solution
1 = first order solution

Superscript

= derivative with respect to the independent variable

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Correlation of Activity Coefficients of Hydrocarbons in Water at Infinite Dilution with Molecular Parameters

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Hydrocarbon solubilities in water are directly related to the prediction of activity coefficients at infinite dilution. Mackay and Shiu (1977) correlated the activity coefficients of polynuclear aromatic hydrocarbons in water at infinite dilution with the number of carbon atoms and Yalkowsky and Valvani (1979) related solubilities to molecular surface areas. These correlations, limited to a single hydrocarbon family and solvent, predict activity coefficients at infinite dilution where the generally accepted UNIQUAC and UNIFAC equations fail.

The present study correlates the activity coefficients at infinite dilution of aromatic and aliphatic hydrocarbons in water reported by Mackay and Shiu (1975, 1977) with physical properties of the hydrocarbon molecules, Table 1. A suitable physical property should reflect the size, shape and charge distribution of the molecule. A single parameter cannot fulfill all these characteristics and multiparametric correlations are necessary.

The data for the activity coefficients at infinite dilution of these hydrocarbons in water at 25°C, and the values of the parameters used are given in Tables 2, 3 and 4. The variations of the natural logarithm of the activity coefficient with the molecular connectivity of first order are represented in Figure 1. Similar linear trends would be obtained with the other selected physical parameters.

The multiple linear regression analysis, the calculation of the standard error of estimate (STD) and the multiple correlation coefficient (r) have been performed according to the method described by Cooley and Lohnes (1962) and Ostle (1954).

CORRELATIONS?

Aliphatic Hydrocarbons

The correlations of the natural logarithm of the activity coefficient at infinite dilution of aliphatic hydrocarbons with the molecular connectivity of first order, the acentric factor, and the number of carbon atoms, with the dipole moment as second parameter, are summarized in Table 5. The dipole moment has been selected since it accounts for the differences in molecular polarity. However, the corrective effect of the dipole moment is not sufficient to incorporate the cyclic hydrocarbons. The data for this

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