Diffusion of Gas into a Non-Newtonian Falling Film

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The effect of non-Newtonian behavior upon transfer of a gas to a falling liquid film is of potential importance in biomedical applications (for example, blood oxygenation), laboratory studies on diffusion in flowing non-Newtonian liquids, and in numerous industrial processes involving gas-liquid contacting. While the analogous problem for Newtonian liquids has received considerable attention, the effect of deviation from a parabolic velocity profile in the film (that is, Newtonian behavior) has apparently evoked little interest. Complete numerical solutions of the convective diffusion equation are of limited use since realistic rheological modeling of the liquid behavior introduces a number of fluid parameters, thus requiring many such calculations in order to treat a range of variation of these parameters. Inaccuracies involved in interpolation could conceivably be introduced if the number of such calculations was severely reduced. To account better for the variation of fluid (and system) parameters, a perturbation method seems promising.

The Ellis rheological model is chosen to describe fluid viscosity due to its realistic representation of transition from Newtonian to non-Newtonian behavior with increasing shear rate. Such transitions generally occur at rather low shear rates (for example, under 100 sec^{-1}) so this feature of the Ellis model is an important consideration for work with thin films. This model has previously been applied to several important engineering flows (Matsuhisa and Bird, 1965) and has the useful property of reducing to a powerlaw form. For the system shown in Figure 1 the Ellis equation for shear stress τ_{yx} is

$$-\eta_0 \frac{dv_x}{dy} = \tau_{yx}\left[1 + \left|\frac{\tau_{yx}}{\tau_{1/2}}\right|^{\alpha-1}\right] \tag{1}$$

where η_0, $\tau_{1/2}$, and α are constants characteristic of the liquid. For steady nonrippling flow of a film with constant thickness, the velocity profile is (Matsuhisa and Bird, 1965)

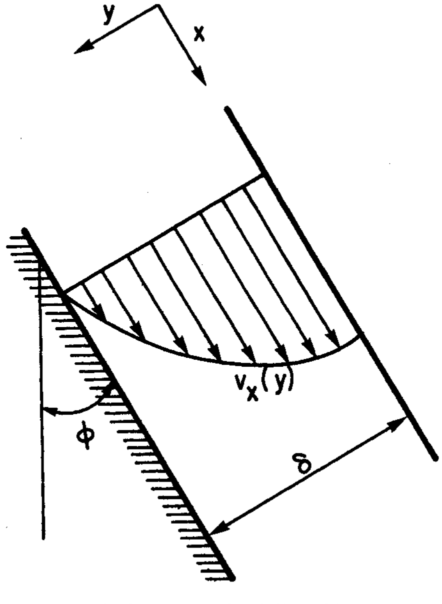

Fig. 1. Geometry of a falling film.

$$v_x = \frac{\rho g\delta^2\cos\phi}{2\eta_0}\left[1 - \left(\frac{y}{\delta}\right)^2 + \beta\left(1 - \frac{y^{\alpha+1}}{\delta^{\alpha+1}}\right)\right] \tag{2a}$$

where

$$\beta = \frac{2}{\alpha+1}(\rho g\delta\cos\phi/\tau_{1/2})^{\alpha-1} \tag{2b}$$

Upon the introduction of dimensionless variables

$$\zeta = y/\delta, \quad \xi = \frac{\mathcal{D}x}{\delta^2 v_{x,\max}}, \quad \theta = \frac{c - c_0}{c_s - c_0} \tag{3}$$

where c_0 and c_s are the inlet and surface concentrations of the diffusing component and $\mathcal{D}$ is its diffusivity, the convective diffusion equation (Bird, Stewart, Lightfoot, 1960) becomes

$$\left[1 - \frac{(\zeta^2 + \beta\zeta^{\alpha+1})}{1+\beta}\right]\frac{\partial\theta}{\partial\xi} = \frac{\partial^2\theta}{\partial\zeta^2} \tag{4a}$$

with boundary conditions

$$\begin{aligned} \theta(\zeta, 0) &= 0 \\ \theta(0, \xi) &= 1 \\ \left.\frac{\partial\theta}{\partial\zeta}\right|_{\zeta=1} &= 0 \end{aligned} \tag{4b}$$

The liquid surface is considered in equilibrium with the gas phase and longitudinal diffusion is neglected.

Equation (4a) contains two parameters α and β while the analogous equation for a Newtonian film contains no such parameters. As mentioned previously, the influence of α and β can be determined by exhaustive calculations over a range of values of each, but here we wish to investigate these influences more simply—by a perturbation analysis for both α and β. Consider

$$\alpha = \alpha_0 + \epsilon_\alpha$$

and (5a)

$$\beta = \beta_0 + \epsilon_\beta$$

where ϵ_α and ϵ_β are small perturbations about the typical values α_0 and β_0, and express θ as

$$\theta(\zeta, \xi) = \sum_{i=0}^{\infty}\sum_{j=0}^{\infty} \epsilon_\beta{}^i\epsilon_\alpha{}^j\theta_{i,j}(\zeta, \xi) \tag{5b}$$

Substitution of these expressions into Equation (4) and separation of terms of like order in ϵ_α and ϵ_β leads to a hierarchy of equations for the $\theta_{i,j}$'s, the first six of which are

$$\frac{\partial^2\theta_{0,0}}{\partial\zeta^2} - \left[1 - \frac{(\zeta^2 + \beta_0\zeta^{\alpha_0+1})}{1+\beta_0}\right]\frac{\partial\theta_{0,0}}{\partial\xi} = 0 \tag{6a}$$

$$\frac{\partial^2\theta_{0,1}}{\partial\zeta^2} - [\ldots]\frac{\partial\theta_{0,1}}{\partial\xi} = -\frac{\beta_0\zeta^{\alpha_0+1}\ln\zeta}{1+\beta_0}\frac{\partial\theta_{0,0}}{\partial\xi} \tag{6b}$$

$$\frac{\partial^2\theta_{1,0}}{\partial\zeta^2} - [\ldots]\frac{\partial\theta_{1,0}}{\partial\xi} = \frac{\zeta^2 - \zeta^{\alpha_0+1}}{(1+\beta_0)^2}\frac{\partial\theta_{0,0}}{\partial\xi} \tag{6c}$$

$$\frac{\partial^2\theta_{0,2}}{\partial\zeta^2} - [\ldots]\frac{\partial\theta_{0,2}}{\partial\xi} = -\frac{\beta_0\zeta^{\alpha_0+1}\ln\zeta}{1+\beta_0}\frac{\partial\theta_{0,1}}{\partial\xi} - \frac{\beta_0\zeta^{\alpha_0+1}(\ln\zeta^2)}{2(1+\beta_0)}\frac{\partial\theta_{0,0}}{\partial\xi} \tag{6d}$$

$$\frac{\partial^2\theta_{2,0}}{\partial\zeta^2} - [\ldots]\frac{\partial\theta_{2,0}}{\partial\xi} = \frac{\zeta^2 - \zeta^{\alpha_0+1}}{(1+\beta_0)^2}\frac{\partial\theta_{1,0}}{\partial\xi} - \frac{\zeta^2 - \zeta^{\alpha_0+1}}{(1+\beta_0)^3}\frac{\partial\theta_{0,0}}{\partial\xi} \tag{6e}$$

$$\frac{\partial^2\theta_{1,1}}{\partial\zeta^2} - [\ldots]\frac{\partial\theta_{1,1}}{\partial\xi} = -\frac{\beta_0\zeta^{\alpha_0+1}\ln\zeta}{1+\beta_0}\frac{\partial\theta_{1,0}}{\partial\xi} - \frac{\zeta^{\alpha_0+1} - \zeta^2}{(1+\beta_0)^2}\frac{\partial\theta_{0,1}}{\partial\xi} - \frac{\zeta^{\alpha_0+1}\ln\zeta}{(1+\beta_0)^2}\frac{\partial\theta_{0,0}}{\partial\xi} \tag{6f}$$

with boundary conditions

$$\theta_{k,l}(\zeta, 0) = 0 \quad k, l = 0, 1, 2, \ldots \tag{7a}$$

$$\theta_{k,l}(0, \xi) = 0 \quad k, l = 0, 1, 2, \ldots \tag{7b}$$

$$\text{except } \theta_{0,0}(0, \xi) = 1$$

$$\left.\frac{\partial\theta_{k,l}}{\partial\zeta}\right|_{\zeta=1} = 0 \quad k, l = 0, 1, 2, \ldots \tag{7c}$$

These coupled equations can be solved sequentially, utilizing the fact that the equation with $\theta_{k,l}$ on the left-hand side involves only $\theta_{i,j}$'s on the right hand side for which $i \leq k$ and $j \leq l$.

A Crank-Nicholson finite difference scheme (Forsythe and Wasow, 1960) was employed for the numerical solution of these parabolic equations. The result for each term contributing to the surface molar flux $J_y(x) = -\mathcal{D}\left.\frac{\partial c}{\partial y}\right|_{y=0}$ is presented in dimensionless form as the derivative $\frac{\partial\theta_{i,j}}{\partial\zeta}$ at the interface, as a function of ξ, in Figure 2. These derivatives are integrated along the surface, from 0 to ξ, to give terms contributing to the total mass transfer as a function of ξ in Figure 3. For these calculations, the values of α_0 and β_0 were taken to be 2.0 and 1.5 respectively. The value of α_0 is typical of many moderately dilute polymer solutions. Published values of Ellis model parameters (Bird, Stewart, Lightfoot, 1960) for a variety of non-Newtonian fluids suggest that $\beta_0 = 1.5$ is representative of a 1 mm thick vertical film of such a fluid.

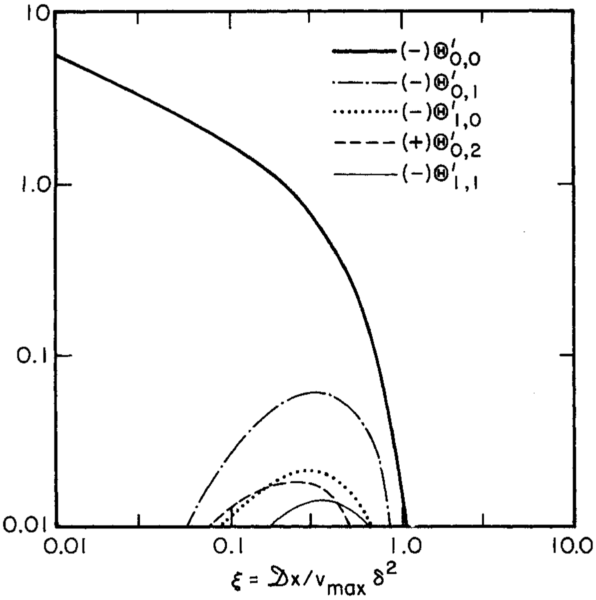

Fig. 2. Variation with film length of terms contributing to the power series (see Eq. 5b) for molar flux. Base values of rheological and geometric parameters are $\alpha_o = 2.0$, $\beta_o = 1.5$.

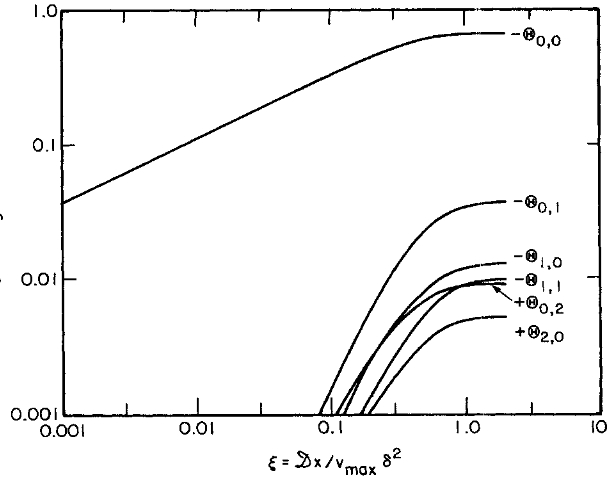

Fig. 3. Variation with film length of terms contributing to the power series for molar flow rate. $\alpha_o = 2.0$, $\beta_o = 1.5$.

As a test of the utility of this method, these perturbation results were compared to numerical solutions using exact α and β values with $1.4 \leq \alpha \leq 2.6$ and $1.0 \leq \beta \leq 2.0$ (or $|\epsilon_\alpha| \leq 0.6$ and $|\epsilon_\beta| \leq 0.5$). The solution algorithm was the same in each case, so that errors due to the approximate nature of the numerical method would be expected to play no role in the comparison. In all such comparisons, the total mass transfer results at $\xi = 0.85$ agreed to at least four significant figures when fifteen terms were included in this perturbation expansion—from zero to fourth order in ϵ_α and ϵ_β. At extreme values of ϵ_α and ϵ_β (-0.6 and -0.5 respectively), the total correction at $\xi = 0.85$ to the zeroth order approximation was just over 4%, while the 15-term approximation differed by less than 0.009%.

Although the perturbation scheme thus seems accurate within the range of fluid parameters commonly encountered, its use in falling film problems may not often be needed. Apparently, from Figure 3, the total mass transfer may be adequately represented up to $\xi \approx 0.1$ as being proportional to $\xi^{1/2}$, which can be predicted by Higbie's penetration theory (Bird, Stewart, Lightfoot, 1960) which assigns hydrodynamic importance only to the film surface velocity.

For a 1 mm thick film on a vertical wall, typical diffusion and viscosity data for dilute polymer solutions lead to the result that $\xi = 0.1$ is equivalent to a film length of several meters. This suggests that the much simpler penetration theory would be adequate for almost all systems of interest. Thus the coupling between non-Newtonian hydrodynamics and mass transfer occurs primarily through the independently calculated $v_{x,\max}$ used in the definition of ξ rather than through details of the velocity profile.

In the case of a nearly horizontal wall, complete analysis obviously becomes necessary. It may also be needed in certain other cases; for example, Wasan et al. (1972)

reported shear-dependent diffusion coefficients from falling film data wherein a power-law analysis was used, and our calculations can demonstrate that perhaps 30% of the shear dependence in $\mathcal{D}$ is removed when the more realistic Ellis model is employed.

The perturbation method proposed here is not limited to any particular rheological model or to the film problem. It should be useful in more complex flows and in those in which penetration theory is not appropriate. In general it would be expected that the number of dimensionless parameters appearing in the convective diffusion equation would be one less than the number of parameters in the model.

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Kinetics of Swelling of Dextran Gels in Aqueous Protein Solutions

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Sephadex, a cross-linked, spherical dextran gel that has been widely used in liquid chromatography, has been demonstrated to be effective in concentrating aqueous solutions of high molecular weight (MW) solutes. Upon contact with aqueous solutions, dry Sephadex imbibes relatively large quantities of solvent. Solutes which are too large to enter the gel are left behind in the external solution and are thereby concentrated. Low MW solutes, which can freely enter the gel, show essentially unchanged or only slightly higher external concentrations.

Some of the properties of Sephadex are given in Table 1. While both types listed exhibit relative rigidity in the swollen state, the G-25 gel is more extensively cross-linked (with epichlorohydrin) than the G-50 gel. The exclusion property of the Sephadex gels gives them many biological and biomedical applications.

Solutions containing macromolecules (for example, many biological fluids) can be quickly and efficiently concentrated two- or three-fold in a single step without changing *p*H or ionic strength (repeated separation of the supernatant and treatment with more dry gel can give greater and greater concentrating effects). The ability of dextran gels to concentrate sensitive biological fluids makes the gel hydration process an attractive alternative to methods such as evaporation, freeze drying, and ultrafiltration. No applied pressure is needed since the high internal osmotic pressure of the beads provides a strong solvent-uptake driving force, and extreme temperatures are unnecessary. Sephadex is convenient for fast concentration of moderately-sized dilute samples to quite small volumes for further use and/or analysis, for example, samples of biological fluids can be easily concentrated for subsequent separation in chromatographic columns. Gel hydration is especially useful when viscous solutions need to be concentrated, since the large specific surface area of the beads (for example, 10 cc of dry 200 micron beads has a total surface area of about 2000 cm^2) gives reasonable solvent removal rates even when solvent diffusivities are rather low.

Another application relates to treating the localized swelling (edema) of body tissues which occurs in various pathological conditions. Draining the excess fluid from the body alleviates the edema but causes a significant loss of protein. Sephadex could be used to recover these proteins via the concentration process, after which they could be reinfused.

Since Sephadex is sold commercially in the dry form and must be hydrated prior to use in aqueous systems, it is important to know the characteristics of the gel expansion. For example, packing a chromatographic column with Sephadex before complete swelling equilibrium has been achieved can result in either severe bed compaction or column rupture. It is clear that knowledge of the kinetics of gel hydration is crucial to all of the applications cited.

PREVIOUS WORK

Flodin et al. (1960) were the first to use the gel hydration method. Working with the G-25 type gel, it was found that 10 minutes were needed to obtain complete swelling of the gel in contact with solution, after which the material was centrifuged to effect separation. Recoveries of 90% at a 10- 20-fold concentration were common. The Sephadex was able to be effectively regenerated by washing with water, suspension in ethanol, and subsequent drying.

Vavruch (1965) later reported results of a detailed study of the swelling kinetics of Sephadex G-25, G-50, and G-75 in water. The volume change of the gel as a function of time was measured by an involved and delicate system of mercury displacement. Unfortunately, in Vavruch's apparatus uniform instantaneous wetting of the bed of dextran could not be achieved and the experimental results were found to be dependent on the size of the sample and the dimensions of the apparatus itself.