



Mathematical analysis of viscometric (polymer) flow fields in capillaries: Taylor dispersion revisited

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Abstract. A general formulation for capillary flow of two miscible fluids – one a dilute plug of polymer fluid inserted into a fully developed Poiseuille flow of the other, a Newtonian stream – is examined for its long time behavior. Phenomenologically, the system evolves from an initial state, that of a plug within the boundaries of sharp, well defined fronts inside a Newtonian stream, to a more homogenized state in the very long time scale. This problem was addressed by G.I. Taylor but with regard to a system of two Newtonian fluids, leading to the well-known results commonly described as ‘Taylor axial dispersion’. In this paper, a general and systematic perturbation analysis is presented from which Taylor’s result is recovered as a special case of a more general solution which applies to fluids incorporating elastic properties. In particular, the influence of viscoelasticity and (polymer) diffusivity on the observed pressure profile in the capillary conduit is examined. This effect is clearly separated out for small Peclet number flows using asymptotic and numerical analysis. The results identify the influence of fluid viscosity, elasticity, and diffusivity on the observed pressure profile and form the basis for the improved characterization of polymeric elasticity using capillaries – a finding that is of significant scientific and commercial interest. These results were obtained by the authors as a class of observations resulting from the perturbation analysis of forced-flow capillary devices in viscoelastic fluid property investigation.

Key words: capillary viscometers, differential capillary viscometer, forced flow viscometer, perturbation methods, Taylor dispersion.

1. Introduction

Taylor [1, 2] examined the behavior of two miscible (Newtonian) fluids of similar properties in a capillary flow. One liquid was inserted as a plug into the steady Poiseuille flow of the second liquid and the resulting concentration profiles were tracked over time. In particular, the balance of the competing effects of diffusion (especially radial diffusion) and of convection were examined. Taylor showed, through *ad hoc* analysis, and confirmed through experiment, that the radial diffusion works to offset axial convective transport so that the plug ‘sticks together’ longer/farther downstream. In fact, he found, that after enough time, an initial source could be found uniformly distributed (Gaussian distributed) about a point traveling at the mean velocity of the original Poiseuille flow, and of orders of magnitude larger amplitude than it would have been in purely convective flow. Taylor found that, even when axial diffusion is small, the combined effects of axial convection and radial diffusion work to give an axial diffusion equation governing the cross-section averaged concentration. Taylor’s results were later verified and extended by Aris [3] and Barton [4] using the method of moments, and by

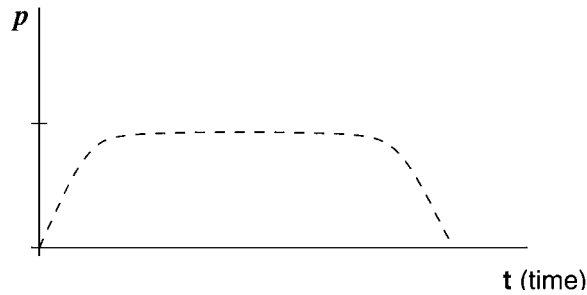


Figure 1. Plateau and transition fronts in the pressure profile.

Brenner [5, Chapter 3]. Using a centre-manifold approach, Mercer and Roberts [6] obtained higher-order approximations, including the case of channels of varying cross section, and Balakotaiah and Chang [7] included adsorption/desorption at walls, as well as bulk and surface reactions. Taylor's results were also systematized using similarity variables by Chatwin [8].

In recent work on polymer characterization [9] similar flow was examined, but with the additional complication that one fluid was a polymer mixture with behavior governed by the Upper Convected Maxwell Model (UCMM). The purpose of that work was to provide a framework for unambiguous polymer characterization using capillary viscometry. In that case, however, due to the non-Newtonian nature of the plug fluid (elasticity, higher viscosity and density), the system response and the governing equations are more complicated than those studied by Taylor. Thus, a clear formal perturbation process was needed in order to analyze the system of governing equations. In addition, the ensuing analysis provides the benefit of systematizing Taylor's procedure.

2. Background

In previous work [9, 10] two-component capillary flow was studied experimentally and analytically as a means for rapid characterization of polymers in industrial applications. In that work a dilute polymer plug (fluid b) was introduced into a constant volumetric flow-rate driven Poiseuille capillary flow of a Newtonian solvent (fluid a). The evolution of the polymer plug was tracked by observation of changes in the pressure drop at a point downstream of the injection port. While previous work had identified the pressure plateau (see Figure 1) with the intrinsic viscosity of the polymer, the goal of [9] was to relate the leading (trailing) edge behavior of the plug pressure profile to the polymer elasticity and diffusivity, thus giving additional information, namely on the molecular weight distribution.

This analysis is specifically for dilute polymer solutions, the goal being to minimize chain-chain interactions, thus simplifying the model needed and leaving molecular weight of the polymer, directly related to polymer chain length, as the primary material property, while simplifying the relationship between the molecular weight related parameters – intrinsic viscosity, elasticity and diffusion differential – and the experimentally measured quantity – the pressure drop. The goal of this analysis is to quantify the use of the flow referenced differential capillary rheometer to obtain real-time, at-line measurements of the polymer molecular weight in industrial processing conditions.

2.1. GOVERNING BOUNDARY-VALUE PROBLEM

The flow under consideration is assumed axisymmetric and the governing equations are nondimensionalized by the observation time and length scales as follows [9]:

Axial coordinate: $z = z'/\mathcal{L}$, where \mathcal{L} is an observation length (≈ 1 meter);

Radial coordinate: $r = r'/R$, where R is the capillary radius ($\approx 10^{-4}$ meters);

Axial velocity: $v = v'_z/V$, where $V = 2Q/(\pi R^2)$, and Q is the fixed volumetric flow rate;

Radial velocity: $w = (\mathcal{L} v'_r)/(RV)$;

Stress: $[\tau_{rr}, \tau_{\theta\theta}, \tau_{zz}, p] = 4/(G\mathcal{L})[\tau'_{rr}, \tau'_{\theta\theta}, \tau'_{zz}, p']$, where $G = 4\eta_a V/R^2 = 8\eta_a Q/(\pi R^4)$, and $\tau_{rz} = 4/(GR)\tau'_{rz}$;

Time: $t = (V/\mathcal{L})t'$.

The resulting equations involve the dimensionless parameters:

R/\mathcal{L} , the ratio of the capillary radius to the observation length;

$\text{Re} = \rho_a V R^2/(\eta_a \mathcal{L})$, the Reynolds number;

$\text{Sc}^r = (\rho_a D_{ab}^r/\eta_a)^{-1}$, the Schmidt number in the radial direction, where D_{ab}^r is the radial diffusion coefficient;

$\text{De} = \bar{\lambda} V/\mathcal{L}$, the Deborah number, where $\bar{\lambda}$ is the relaxation time of the plug;

$\Pi = \rho_b/(\rho_a - \rho_b)$, a measure of the density difference between the polymer solution and the solvent.

Finally, ϕ_a , ϕ_b are the volume fractions of species a and b , respectively, η_a is the solvent viscosity and ρ_a is the solvent density.

The flow is axisymmetric, and terms $O((R/\mathcal{L})^2) = O(10^{-8})$ or $O(\text{Re}) = O(10^{-6})$ to $O(10^{-3})$ (depending on how slow the flow is) are neglected. So, in cylindrical coordinates, using the UCMM, $\tau_{r\theta} = \tau_{\theta z} = 0$, and due to neglect of terms $O((R/\mathcal{L})^2)$, $\tau_{rr} = \tau_{\theta\theta} = 0$. Thus the governing equations valid for these scalings are [9]

$$\frac{1}{r}\partial_r(rw) + \partial_z v = -\{\partial_t \log|\phi_a + \Pi| + w\partial_r \log|\phi_a + \Pi| + v\partial_z \log|\phi_a + \Pi|\}, \quad (1)$$

$$\partial_r p = 0, \quad \partial_z p = \frac{1}{r}\partial_r(r\tau_{rz}) + \partial_z \tau_{zz}, \quad (2, 3)$$

$$\text{Re} \left\{ \partial_t \phi_a + \frac{1}{r}\partial_r(r\phi_a w) + \partial_z(\phi_a v) \right\} = \frac{\Pi}{r}\partial_r \left(\frac{r}{\text{Sc}^r} \partial_r \log|\phi_a + \Pi| \right), \quad (4)$$

with the constitutive relations

$$\frac{\lambda \text{De}}{\bar{\lambda}} \{\partial_t \tau_{rz} + w\partial_r \tau_{rz} + v\partial_z \tau_{rz} - \tau_{rz} \partial_r w - \tau_{zz} \partial_z w - \tau_{rz} \partial_z v\} + \tau_{rz} = \frac{\eta}{\eta_a} \partial_r v, \quad (5)$$

$$\frac{\lambda \text{De}}{\bar{\lambda}} \{\partial_t \tau_{zz} + w\partial_r \tau_{zz} + v\partial_z \tau_{zz} - 2\tau_{rz} \partial_r v - 2\tau_{zz} \partial_z v\} + \tau_{zz} = 0. \quad (6)$$

Note that $O(\text{Re})$ terms are kept in (4) since they are comparable to those $O(1/\text{Sc}^r)$, namely $\text{Re Sc}^r = \text{Pe} = (V R^2)/(\mathcal{L} D_{ab}^r) = O(1)$ or $O(10^{-1})$ [9]. The boundary conditions are those of no slip: $v(1, z, t) = w(1, z, t) = 0$; symmetry about $r = 0$: $v_r(0, z, t) = w(0, z, t) = 0$; and fixed volumetric flow rate: $\int_0^1 r \hat{v} dr = 1$, where \hat{v} is the volume averaged velocity related to v , the mass averaged velocity, by $\hat{v} = v + (1/\Pi)(v - v_a)\phi_a$; as well as boundary conditions on the concentrations, namely:

$$\phi_a|_{z=0} = 1, \quad \lim_{z \rightarrow \infty} \phi_a = 1, \tag{7}$$

$$\partial_r \phi_a|_{r=0} = 0, \quad \partial_r \phi_a|_{r=1} = 0. \tag{8}$$

2.2. EXPANSION IN TERMS OF THE DILUTION PARAMETER ϵ

The injected plug is dilute, where dilution is measured through the parameter ϵ :

$$\epsilon = (\text{moles of polymer in plug})/(\text{moles of solvent in the plug}).$$

In practice, for these problems, $\epsilon = O(10^{-2}, 10^{-1})$. The parameters of interest have the following expansions:

$$\eta = \eta_a(1 + \epsilon \alpha [\eta] \phi_b + \epsilon^2 K_H \alpha^2 [\eta]^2 \phi_b^2 + \dots),$$

$$(\text{Sc}^r)^{-1} = \mathcal{D}_0(1 + \epsilon K_D^r \alpha [\eta] \phi_{b,0} + \dots)$$

and

$$\Pi = \frac{\Pi_0}{\epsilon} + \dots, \quad \frac{\lambda \text{De}}{\lambda} = \epsilon \lambda_0 \phi_b + \dots.$$

Here $[\eta]$ is known as the intrinsic viscosity, K_H the Huggins constant, and K_D^r is the diffusion differential. Thus, when all the dependent variables above are expanded in terms of ϵ , $() = ()_0 + \epsilon ()_1 + \dots$, the governing equations show [9] to zeroth order in ϵ ($O(\epsilon^0)$)

$$v_0 = (1 - r^2), \tag{9}$$

$$\delta (\partial_t \phi_{a,0} + v_0 \partial_z \phi_{a,0}) = \frac{1}{r} \partial_r (r \partial_r \phi_{a,0}), \tag{10}$$

$$\tau_{zz}^{(0)} = 0, \quad \tau_{rz}^{(0)} = \partial_r v_0, \tag{11}$$

where $\delta = \text{Re}/\mathcal{D}_0$ is the Peclet number, and to first order in ϵ ($O(\epsilon^1)$),

$$\frac{1}{r} \partial_r (r w_1) + \partial_z v_1 = -\frac{1}{\delta} \frac{1}{\Pi_0} \frac{1}{r} \partial_r (r \partial_r \phi_{a,0}), \quad \partial_r p_1 = 0, \tag{12, 13}$$

$$\partial_z p_1 = \frac{1}{r} \partial_r (r \partial_r v_1 - 2 \alpha [\eta] r^2 \phi_{b,0}) + 8 \lambda_0 r^2 \partial_z \phi_{b,0}, \tag{14}$$

$$\delta \left\{ \partial_t \phi_{a,1} + v_0 \partial_z \phi_{a,1} + \partial_z (v_1 \phi_{a,0}) + \frac{1}{r} \partial_r (r w_1 \phi_{a,0}) \right\} = \frac{1}{r} \partial_r (r \partial_r \phi_{a,1})$$

$$+ K_D^r \alpha [\eta] \frac{1}{r} \partial_r (r \phi_{b,0} \partial_r \phi_{a,0}) - \frac{1}{\Pi_0} \frac{1}{r} \partial_r (r \phi_{a,0} \partial_r \phi_{a,0}). \tag{15}$$

We can rewrite Equation (15), using (12), as follows

$$\delta (\partial_t + v_0 \partial_z) \phi_{a,1} - \frac{1}{r} \partial_r (r \partial_r \phi_{a,1}) = -\delta \{ v_1 \partial_z \phi_{a,0} + w_1 \partial_r \phi_{a,0} \}$$

$$+ \alpha [\eta] K_D^r \frac{1}{r} \partial_r (r \phi_{b,0} \partial_r \phi_{a,0}) - \frac{1}{\Pi_0} (\partial_r \phi_{a,0})^2. \tag{16}$$

Following the mean flow, we introduce $\xi = z - t/2$ and change variables $(r, z, t) \rightarrow (r, \xi, t)$. Careful manipulation of (12)–(14) gives, with cross-sectional average represented as $\bar{f}(\xi, t) = 2 \int_0^1 r f(r, \xi, t) dr$,

$$v_1 = 2\alpha [\eta] \left\{ \int_0^r s \phi_{b,0}(s, \xi, t) ds - r^2 \overline{r^2 \phi_{b,0}} - \overline{\left(\frac{1}{2} - r^2\right) \phi_{b,0}} \right\} \quad (17)$$

$$- 4\lambda_0 \left\{ 2 \int_0^r s^3 \log(r/s) \partial_\xi \phi_{b,0} ds + (1 - r^2) \overline{r^2(1 - r^2) \partial_\xi \phi_{b,0}} + \overline{r^2 \log r \partial_\xi \phi_{b,0}} \right\},$$

$$w_1 = -\alpha [\eta] \left\{ \frac{1}{r} \int_0^r s(r^2 - s^2) \partial_\xi \phi_{b,0} ds - \frac{r^3}{2} \overline{r^2 \partial_\xi \phi_{b,0}} - r \overline{\left(\frac{1}{2} - r^2\right) \partial_\xi \phi_{b,0}} \right\}$$

$$+ \lambda_0 \left\{ 4r \int_0^r s^3 \left(\log \frac{r}{s} - \frac{1}{2} \right) \partial_\xi^2 \phi_{b,0} ds + \frac{2}{r} \int_0^r s^5 \partial_\xi^2 \phi_{b,0} ds \right. \quad (18)$$

$$\left. + r(2 - r^2) \overline{r^2(1 - r^2) \partial_\xi^2 \phi_{b,0}} + 2r \overline{r^2 \log r \partial_\xi^2 \phi_{b,0}} \right\} - \frac{1}{\delta \Pi_0} \partial_r \phi_{a,0}.$$

Note that \mathbf{v} is the mass-average velocity related to the volume-average velocity $\hat{\mathbf{v}}$ by $\hat{\mathbf{v}} = \mathbf{v} + (1/\Pi)(\mathbf{v} - \mathbf{v}_a)\phi_a$, where \mathbf{v}_a is the phase a velocity. The average of $\hat{\mathbf{v}}_1$ over a cross-section is zero, as this is a (constant) volumetric-flux-driven flow. Because this is a two-fluid mixture, and \mathbf{v} is the mass averaged velocity, the velocity is not, as might have been expected, unidirectional. To lowest order it is Poiseuille flow, but to $O(\epsilon)$ there is an axial perturbation to the Poiseuille profile as well as a radial velocity.

Boundary conditions for the expansion concentrations are [9]

$$\phi_{a,i} |_{z=0} = \lim_{z \rightarrow \infty} \phi_{a,i} = \begin{cases} 1 & \text{for } i = 0 \\ 0 & \text{for } i = 1, 2, 3, \dots \end{cases}, \quad \partial_r \phi_{a,i} |_{r=0} = \partial_r \phi_{a,i} |_{r=1} = 0.$$

Initial conditions are

$$\phi_{a,0}(r, z, 0) = 1 - \mathcal{H}(z + \ell) + \mathcal{H}(z - \ell), \quad (19)$$

$$\phi_{a,i}(r, z, 0) = 0 \quad \text{for } i = 1, 2, \dots,$$

where $\mathcal{H}(z)$ is the Heaviside function.

The specific interest in this application is in the influence of the intrinsic viscosity, elasticity and the diffusion differential K_D' on the flow or, conversely, on how variations in the flow profile can be used to determine those parameters, which in turn are linked to the molecular weight of the polymer [11, Chapter 9]. Note that the effects of elasticity (as measured by λ_0), polymer viscosity, differing densities of solutions, and diffusion differentials, do not appear until $O(\epsilon)$ as expected, because the solution is dilute. Thus, the $O(\epsilon^0)$ problem is identical with that investigated by Taylor (and others). The $O(\epsilon^1)$ problem introduces new effects.

The experimentally measured quantity is the pressure cross-sectional average, and careful manipulation of the above equations shows [9]

$$\begin{aligned} \partial_z \bar{p} = & -4 \left\{ 1 + 2\epsilon \left[\alpha [\eta] \overline{r^2 \phi_{b,0}} - 2\lambda_0 \overline{r^2(1-r^2)\partial_\xi \phi_{b,0}} \right] - \epsilon^2 \left[\alpha [\eta] \left(\overline{r \phi_{b,0} \partial_r v_1} \right. \right. \right. \\ & - 2r^2 \overline{(K_H \alpha [\eta] \phi_{b,0}^2 + \phi_{b,1})} \left. \left. \left. - \lambda_0 \left(\overline{r \phi_{b,0} \partial_C \partial_r v_1} - 2\alpha [\eta] \overline{r^2 \phi_{b,0} \partial_C \phi_{b,0}} \right. \right. \right. \right. \\ & + 2r^2 \overline{\phi_{b,0} \partial_\xi v_1} - 2r \overline{\phi_{b,0} w_1} + 6r^2 \overline{\phi_{b,0} \partial_r w_1} \\ & \left. \left. \left. - 2r(1-r^2)\partial_\xi A - 4r^2(1-r^2)\partial_\xi \phi_{b,1} \right) \right] + \dots \right\}, \end{aligned} \tag{20}$$

where

$$\partial_C = \partial_t + \left(\frac{1}{2} - r^2 \right) \partial_\xi, \quad A = 2(\alpha [\eta] r \phi_{b,0} - \partial_r v_1 - \lambda_0 r \partial_C \phi_{b,0}).$$

The case of ‘infinite dilution’ ($\epsilon \rightarrow 0$, a single species: Newtonian flow as used in Taylor’s analysis) is

$$\partial_z \bar{p} = -4 \quad (\text{Hagen-Poiseuille law}).$$

If the solute in the plug has no elasticity ($\lambda_0 = 0$), or if $\partial_\xi \phi_b = 0$ (a plateau region – see Figure 1), then

$$\partial_z \bar{p} = -4 \left\{ 1 + 2\epsilon \alpha [\eta] \overline{r^2 \phi_{b,0}} + \dots \right\}.$$

The $O(\epsilon^0)$ pressure is the standard Hagen-Poiseuille (Newtonian) result. The $O(\epsilon^1)$ pressure-drop term with $\alpha [\eta]$ is due to the polymer viscosity (related to the molecular weight of the polymer) and depends on $\phi_{b,0}$, whereas the elasticity terms (λ_0) are zero in a plateau region where $\partial_\xi \phi_b = 0$. The elasticity terms become important when ϕ_b changes with ξ , namely at fronts, while K_D^r , the diffusion differential, does not appear explicitly in the average pressure drop to this order, but rather appears there at $O(\epsilon^2)$ through $\phi_{b,1}$ (see (16)).

3. Perturbation expansion for small Peclet numbers δ

In order to gain more insight into the problem, the goal is to examine each of the $O(\epsilon^0)$ problem and the $O(\epsilon^1)$ problem for its solution for small Peclet number δ . This will clarify bounds for validity of the two-parameter expansion (ϵ, δ) as well as clarify the role of the parameters involved. In addition, analysis of these limits guided the numerics in [9]. To order ϵ^0 the governing equation is

$$\epsilon^0: \quad \delta \left(\partial_t + \left(\frac{1}{2} - r^2 \right) \partial_\xi \right) \phi_{a,0} - \frac{1}{r} \partial_r (r \partial_r \phi_{a,0}) = 0.$$

A straightforward perturbation expansion (regular or outer expansion)

$$\phi_{a,0} = \tilde{\phi}_{a,0}^{(0)} + \delta \tilde{\phi}_{a,0}^{(1)} + \dots$$

gives

$$\frac{1}{r} \partial_r \left(r \partial_r \tilde{\phi}_{a,0}^{(0)} \right) = 0, \tag{21}$$

$$\frac{1}{r} \partial_r \left(r \partial_r \tilde{\phi}_{a,0}^{(1)} \right) = \left(\partial_t + \left(\frac{1}{2} - r^2 \right) \partial_\xi \right) \tilde{\phi}_{a,0}^{(0)}, \quad (22)$$

etc. From (21) clearly $\tilde{\phi}_{a,0}^{(0)}$ is independent of r . Substitution in (22), followed by averaging over a cross section, gives

$$\tilde{\phi}_{a,0}^{(0)} = \tilde{\phi}_{a,0}^{(0)}(\xi).$$

Thus the partial differential equation is reduced to a hyperbolic (ordinary differential) equation. The solution to this order is the initial condition – there is no evolution. Continuing in this vein we'd find

$$\tilde{\phi}_{a,0}^{(1)}(r, \xi, t) = \frac{t}{192} \partial_\xi^2 \tilde{\phi}_{a,0}^{(0)} + \frac{1}{16} \left(r^2(2 - r^2) - \frac{2}{3} \right) \partial_\xi \tilde{\phi}_{a,0}^{(0)} + \tilde{d}_0^{(1)}(\xi).$$

Thus, the solution has a tendency to evolve in time, but the result of this outer expansion is that convective terms are not appropriately balanced. In particular, when $\delta \partial_\xi^2 \phi_{a,0}^{(0)} = O(1)$, the expansion is nonuniform. Later matching with the boundary-layer expansion for a front shows that $\tilde{\phi}_{a,0}^{(0)} = \mathcal{H}(\xi)$ and $\tilde{\phi}_{a,0}^{(1)} = 0$, hence the outer expansion for a step is trivial. For a plug, the outer expansion describes the plateau region. Motivated by this, we look more carefully at a boundary layer in ξ . The equation

$$\delta \{ \partial_t \phi_{a,0} + \left(\frac{1}{2} - r^2 \right) \partial_\xi \phi_{a,0} \} = \frac{1}{r} \partial_r (r \partial_r \phi_{a,0}) \quad (23)$$

clearly indicates that

$$\phi_{a,0}(r, \xi, t) = \phi_{a,0}^{(0)}(\xi, t) + O(\delta),$$

that is, any r dependence comes to higher order. From the above analysis clearly we must look at regions of rapid change in ξ (the fronts). So with

$$\zeta = \frac{\xi - \xi^*}{\mu(\delta)}, \quad \phi(r, \zeta, t) = \phi_0(\zeta, t) + \nu_1(\delta) \phi_1 + \dots,$$

where ξ^* indicates the location of the boundary layer, we obtain

$$\begin{aligned} \delta \{ \partial_t \phi_0 + \dots \} + \left(\frac{1}{2} - r^2 \right) \frac{\delta}{\mu} \partial_\zeta \phi_0 + \left(\frac{1}{2} - r^2 \right) \frac{\delta}{\mu} \nu_1 \partial_\zeta \phi_1 + \dots \\ = \nu_1 \frac{1}{r} \partial_r (r \partial_r \phi_{a,1}) + \nu_2 \frac{1}{r} \partial_r (r \partial_r \phi_{a,2}) + \dots \end{aligned}$$

The distinguished limit is

$$\frac{\delta}{\mu} = \nu_1$$

to balance the leading-order terms, and

$$\delta = \frac{\delta}{\mu} \nu_1 = \nu_2$$

to balance the next order terms, hence

$$\mu = \nu_1 = \sqrt{\delta} \quad \text{and} \quad \nu_2 = \delta.$$

This is the same stretching indicated by the non-uniformity in the outer expansion. With

$$\zeta = \frac{\xi - \xi_0}{\sqrt{\delta}}$$

where $\xi_0 = -\ell$ or, respectively, ℓ for the initial condition (19), and the commensurate expansion

$$\phi_{a,0}(r, \xi, t) = \phi_{a,0}^{(0)}(r, \zeta, t) + \sqrt{\delta} \phi_{a,0}^{(1)}(r, \zeta, t) + \dots,$$

we get, on substituting in (23) and equating corresponding powers of δ ,

$$\frac{1}{r} \partial_r \left(r \partial_r \phi_{a,0}^{(0)} \right) = 0, \tag{24}$$

$$\frac{1}{r} \partial_r \left(r \partial_r \phi_{a,0}^{(1)} \right) = \left(\frac{1}{2} - r^2 \right) \partial_\zeta \phi_{a,0}^{(0)}, \tag{25}$$

$$\frac{1}{r} \partial_r \left(r \partial_r \phi_{a,0}^{(2)} \right) = \left(\frac{1}{2} - r^2 \right) \partial_\zeta \phi_{a,0}^{(1)} + \partial_t \phi_{a,0}^{(0)}, \tag{26}$$

$$\frac{1}{r} \partial_r \left(r \partial_r \phi_{a,0}^{(3)} \right) = \left(\frac{1}{2} - r^2 \right) \partial_\zeta \phi_{a,0}^{(2)} + \partial_t \phi_{a,0}^{(1)}. \tag{27}$$

Note that, as in the outer expansion, and as assumed in the scaling, $\phi_{a,0}^{(0)}$ is independent of r , but the difference is that now it is no longer independent of t . The averaging of Equation (24) over a cross-section now just gives $0 = 0$. Integrating (25), we have

$$\phi_{a,0}^{(1)} = \frac{r^2}{16} (2 - r^2) \partial_\zeta \phi_{a,0}^{(0)} + c_0^{(1)}(\zeta, t)$$

and integrating (26), using the equation above, we have

$$\phi_{a,0}^{(2)} = \frac{r^4}{128} \left(\frac{1}{2} - \frac{5}{9} r^2 + \frac{r^4}{8} \right) \partial_\zeta^2 \phi_{a,0}^{(0)} + \frac{r^2}{16} (2 - r^2) \partial_\zeta c_0^{(1)}(\zeta, t) + \frac{r^2}{4} \partial_t \phi_{a,0}^{(0)} + c_0^{(2)}(\zeta, t).$$

Averaging the $O(\delta)$ Equation (26) over a cross-section now gives

$$\partial_t \phi_{a,0}^{(0)} = \frac{1}{192} \partial_\zeta^2 \phi_{a,0}^{(0)}. \tag{28}$$

Since we are particularly interested in the behavior at the front, we solve the problem with a step initial concentration. The superposition of the two front solutions, a step up at $\xi = -\ell$, down at $\xi = \ell$, gives the plug solution (see below). Thus, this diffusion Equation (28) for $\phi_{a,0}^{(0)}$ (the solution corresponding to a front) should be solved, for $\xi_0 = \ell$, with

$$\phi_{a,0}^{(0)}(\zeta, 0) = \mathcal{H}(\zeta)$$

and

$$\phi_{a,0}^{(0)}(\zeta, t) \rightarrow \begin{cases} 0, & \text{as } \zeta \rightarrow -\infty \\ 1, & \text{as } \zeta \rightarrow \infty. \end{cases}$$

This is precisely Taylor dispersion [12, pp. 82–96], namely

$$\partial_t \overline{\phi_{a,0}} = \frac{1}{192} \partial_\zeta^2 \overline{\phi_{a,0}} + O(\sqrt{\delta})$$

or, in dimensional terms,

$$\partial_t \overline{\phi_{a,0}} = D_{\text{eff}} \partial_{\xi^2} \overline{\phi_{a,0}} + \dots,$$

where

$$D_{\text{eff}} = \frac{1}{192} \frac{V^2 R^2}{D_0}.$$

The solution for the step initial concentration (front) is

$$\varphi_{a,0}^{(0)} = \frac{1}{2} \left\{ 1 + \operatorname{erf} \left(\frac{4\sqrt{3}\zeta}{\sqrt{t}} \right) \right\}. \quad (29)$$

By averaging the $O(\delta^{3/2})$ Equation (27) one finds that $c_0^{(1)}$ satisfies the nonhomogeneous diffusion equation

$$\partial_t c_0^{(1)} - \frac{1}{192} \partial_\zeta^2 c_0^{(1)} = -\frac{1}{120} \partial_t \partial_\zeta \phi_{a,0}^{(0)}$$

so that

$$c_0^{(1)} = \frac{4\sqrt{3}}{\sqrt{\pi t}} \int_{-\infty}^{\infty} c_0^{(1)}(y, 0) e^{-48(\zeta-y)^2/t} dy - \frac{\sqrt{3}}{30\sqrt{\pi}} \int_0^t \frac{d\tau}{\sqrt{t-\tau}} \int_{-\infty}^{\infty} e^{-48(\zeta-y)^2/(t-\tau)} \partial_\tau \partial_\zeta \phi_{a,0}^{(0)}(y, \tau) dy.$$

Since $\phi_{a,0}^{(1)}(r, \zeta, 0) = 0$, and $\phi_{a,0}^{(1)}(r, \zeta, t) = \frac{r^2}{16} (2 - r^2) \partial_\zeta \phi_{a,0}^{(0)} + c_0^{(1)}(\zeta, t)$, one finds for the front,

$$c_0^{(1)} = -\frac{\sqrt{3}}{20t\sqrt{\pi t}} (3t + 32\zeta^2) e^{-48\zeta^2/t}, \quad (30)$$

$$\phi_{a,0}^{(1)}(r, \zeta, t) = \frac{r^2}{16} (2 - r^2) \partial_\zeta \phi_{a,0}^{(0)} - \frac{\sqrt{3}}{20t\sqrt{\pi t}} (3t + 32\zeta^2) e^{-48\zeta^2/t}. \quad (31)$$

Note that the second term is a particular solution of the equation for $c_0^{(1)}$. The first term is a solution of the corresponding homogeneous equation. The reason for this particular value of the multiplicative constant will be described below.

At this point it is useful to rewrite $\phi_{a,0}^{(2)}$ substituting for $\partial_t \phi_{a,0}^{(0)}$ from (28) to obtain

$$\phi_{a,0}^{(2)} = \frac{r^2}{768} \left\{ \frac{3}{4} r^6 - \frac{10}{3} r^4 + 3r^2 + 1 \right\} \partial_\zeta^2 \phi_{a,0}^{(0)} + \frac{r^2}{16} (2 - r^2) \partial_\zeta c_0^{(1)} + c_0^{(2)}(\zeta, t).$$

Returning to the solution for a plug initially uniformly distributed across the capillary ($\phi_b(r, \xi, 0) = \mathcal{H}(\xi + \ell) - \mathcal{H}(\xi - \ell)$), note that we can add the boundary-layer solutions at $\xi = \ell$ and $\xi = -\ell$, subtracting the common part. Thus

$$\begin{aligned} \phi_{b,0}(r, \xi, t) = & \varphi_{b,0}^{(0)} \left(\frac{\xi + \ell}{\sqrt{\delta}}, t \right) + \sqrt{\delta} \varphi_{b,0}^{(1)} \left(\frac{\xi + \ell}{\sqrt{\delta}}, r, t \right) + \dots \\ & - \varphi_{b,0}^{(0)} \left(\frac{\xi - \ell}{\sqrt{\delta}}, t \right) - \sqrt{\delta} \varphi_{b,0}^{(1)} \left(\frac{\xi - \ell}{\sqrt{\delta}}, r, t \right) + \dots \end{aligned}$$

Mass must be conserved, thus

$$2\ell = \int_{-\infty}^{\infty} \overline{\phi_{b,0}}(r, \xi, t) d\xi = \int_{-\infty}^{\infty} \left[\varphi_{b,0}^{(0)}\left(\frac{\xi + \ell}{\sqrt{\delta}}, t\right) - \varphi_{b,0}^{(0)}\left(\frac{\xi - \ell}{\sqrt{\delta}}, t\right) \right] d\xi + \sqrt{\delta} \int_{-\infty}^{\infty} \left[\overline{\varphi_{b,0}^{(1)}}\left(\frac{\xi + \ell}{\sqrt{\delta}}, t\right) - \overline{\varphi_{b,0}^{(1)}}\left(\frac{\xi - \ell}{\sqrt{\delta}}, t\right) \right] d\xi + \dots,$$

so

$$\int_{-\infty}^{\infty} \left[\varphi_{b,0}^{(0)}\left(\frac{\xi + \ell}{\sqrt{\delta}}, t\right) - \varphi_{b,0}^{(0)}\left(\frac{\xi - \ell}{\sqrt{\delta}}, t\right) \right] d\xi = 2\ell$$

$$\int_{-\infty}^{\infty} \left[\overline{\varphi_{b,0}^{(1)}}\left(\frac{\xi + \ell}{\sqrt{\delta}}, t\right) - \overline{\varphi_{b,0}^{(1)}}\left(\frac{\xi - \ell}{\sqrt{\delta}}, t\right) \right] d\xi = 0,$$

etc. Also, calculation shows that $\int_{-\infty}^{\infty} \xi \overline{\phi_{b,0}}(\xi, t) d\xi = 0$ to this order, with the given choices of solutions of the homogeneous equations, e.g. in $\phi_{a,0}^{(1)}$. Without this choice the center of mass of the solute would be shifted.

Chatwin [8] found the analogous result for a source initial condition. Should his work be extended to the plug initial condition, he would find, in his notation, that his expansion would start with a T^0 instead of a T^{-1} term. In fact, he would get

$$C = C^{(0)}(X, R) + \frac{C^{(1)}(X, R)}{T} + \dots$$

where his variables X and T in terms of our ζ and t variables, thus at the step, are

$$X = \frac{\zeta\sqrt{96}}{\sqrt{t}}, \quad T = \frac{1}{4}\sqrt{\frac{t}{6\delta}}$$

with

$$C^{(0)} = f_0(X) = \frac{1}{2} \left(1 + \operatorname{erf} \frac{X}{\sqrt{2}} \right),$$

$$C^{(1)} = \sqrt{\frac{2}{\pi}} \left\{ \frac{1}{16} \left(R^2 - \frac{R^4}{2} - \frac{1}{3} \right) - \frac{X^2}{480} + \frac{1}{480} \right\} e^{-X^2/2}.$$

Changing variables to (ζ, t) , this agrees precisely with (29), (31). Taylor's correction to $C^{(0)}$ agreed with the first term in $C^{(1)}$ but, due to his solution form hypothesis, did not include the last two terms.

Now consider the $O(\epsilon^1)$ equation, with the boundary-layer expansion

$$\phi_{a,1}(r, \xi, t) = \phi_{a,1}^{(0)}(r, \zeta, t) + \sqrt{\delta} \phi_{a,1}^{(1)}(r, \zeta, t) + \dots$$

The expansions for w_1 and v_1 , from (17), (18) are

$$v_1 = \frac{1}{\sqrt{\delta}} v_1^{(-1)} + v_1^{(0)} + \sqrt{\delta} v_1^{(1)} + \dots, \quad w_1 = \frac{1}{\delta} w_1^{(-2)} + \frac{1}{\sqrt{\delta}} w_1^{(-1)} + w_1^{(0)} + \dots$$

where, expanding the explicit representations for v_1 and w_1 (17),(18), and using our knowledge of the $O(\epsilon^0)$ terms, we obtain

$$v_1 = -\frac{1}{\sqrt{\delta}} \frac{\lambda_0}{6} \partial_\zeta \phi_{b,0}^{(0)} (r^2 - 1)(3r^2 - 1) + \frac{\lambda_0}{16} (r^2 - 1) \left\{ \frac{r^6}{8} - \frac{23}{72} r^4 - \frac{23}{72} r^2 + \frac{53}{360} \right\} \partial_\zeta^2 \phi_{b,0}^{(0)} + \frac{\lambda_0}{6} (r^2 - 1)(3r^2 - 1) \partial_\zeta c_0^1 + O(\sqrt{\delta}), \quad (32)$$

$$w_1 = \frac{1}{\delta} \frac{\lambda_0}{12} r (r^2 - 1)^2 \partial_\zeta^2 \phi_{b,0}^{(0)} - \frac{1}{\sqrt{\delta}} \left\{ \frac{\lambda_0}{11520} \partial_\zeta^3 \phi_{b,0}^{(0)} r (r^2 - 1)^2 (9r^4 - 22r^2 - 53) + \frac{1}{\Pi_0} \partial_\zeta \phi_{a,0}^{(0)} \frac{r}{4} (1 - r^2) + \lambda_0 \partial_\zeta^2 c_0^{(1)} \frac{r}{12} (r^2 - 1)^2 \right\} + O(1). \quad (33)$$

Thus, from (16) in terms of δ

$$\delta \partial_t \phi_{a,1} + \sqrt{\delta} \left(\frac{1}{2} - r^2 \right) \partial_\zeta \phi_{a,1} - \frac{1}{r} \partial_r (r \partial_r \phi_{a,1}) = -\sqrt{\delta} v_1 \partial_\zeta \phi_{a,0} - \delta w_1 \partial_r \phi_{a,0} + \alpha[\eta] K_D^r \frac{1}{r} \partial_r (r \phi_{b,0} \partial_r \phi_{a,0}) - \frac{1}{\Pi_0} (\partial_r \phi_{a,0})^2,$$

and since $\partial_r \phi_{a,0}^{(0)} = 0$, one finds

$$\begin{aligned} \frac{1}{r} \partial_r (r \partial_r \phi_{a,1}^{(0)}) &= v_1^{(-1)} \partial_\zeta \phi_{a,0}^{(0)}, \\ \frac{1}{r} \partial_r (r \partial_r \phi_{a,1}^{(1)}) &= \left(\frac{1}{2} - r^2 \right) \partial_\zeta \phi_{a,1}^{(0)} + v_1^{(0)} \partial_\zeta \phi_{a,0}^{(0)} + v_1^{(-1)} \partial_\zeta \phi_{a,0}^{(1)} \\ &\quad + w_1^{(-2)} \partial_r \phi_{a,0}^{(1)} - \alpha[\eta] K_D^r \frac{1}{r} \partial_r (r \phi_{b,0}^{(0)} \partial_r \phi_{a,0}^{(1)}), \end{aligned}$$

and

$$\begin{aligned} \frac{1}{r} \partial_r (r \partial_r \phi_{a,1}^{(2)}) &= \partial_t \phi_{a,1}^{(0)} + \left(\frac{1}{2} - r^2 \right) \partial_\zeta \phi_{a,1}^{(1)} + v_1^{(1)} \partial_\zeta \phi_{a,0}^{(0)} + v_1^{(0)} \partial_\zeta \phi_{a,0}^{(1)} + v_1^{(-1)} \partial_\zeta \phi_{a,0}^{(2)} \\ &\quad + w_1^{(-1)} \partial_r \phi_{a,0}^{(1)} + w_1^{(-2)} \partial_r \phi_{a,0}^{(2)} - \alpha[\eta] K_D^r \frac{1}{r} \partial_r (r [\phi_{b,0}^{(0)} \partial_r \phi_{a,0}^{(2)} + \phi_{b,0}^{(1)} \partial_r \phi_{a,0}^{(1)}]) \\ &\quad + \frac{1}{\Pi_0} (\partial_r \phi_{a,0}^{(1)})^2. \end{aligned} \quad (34)$$

Solving gives

$$\phi_{a,1}^{(0)} = \frac{\lambda_0}{72} (\partial_\zeta (\phi_{a,0}^{(0)}))^2 r^2 (r^4 - 3r^2 + 3) + c_1^{(0)}(\zeta, t) \quad (35)$$

and

$$\begin{aligned} \phi_{a,1}^{(1)} &= -\frac{\lambda_0}{230400} r^2 \{53r^8 - 300r^6 + 500r^4 - 90r^2 - 265\} \partial_\zeta^2 (\partial_\zeta \phi_{a,0}^{(0)})^2 \\ &\quad + \frac{\lambda_0}{36} r^2 (r^4 - 3r^2 + 3) \partial_\zeta \phi_{a,0}^{(0)} \partial_\zeta c_0^{(1)} + \frac{r^2}{16} (2 - r^2) \partial_\zeta c_1^{(0)} \\ &\quad + \frac{r^2}{16} (2 - r^2) \alpha[\eta] K_D^r \partial_\zeta \phi_{a,0}^{(0)} (1 - \phi_{a,0}^{(0)}) + \alpha[\eta] K_D^r (1 - \phi_{a,0}^{(0)}) c_0^{(1)} + c_1^{(1)}. \end{aligned}$$

Averaging (34) gives the forced diffusion equation which then determines $\phi_{a,1}^{(0)}$ (via (35) and the solution to the following forced diffusion equation)

$$\begin{aligned} \partial_t c_1^{(0)} - \frac{1}{192} \partial_\zeta^2 c_1^{(0)} = & \frac{\lambda_0}{192} \left\{ \frac{4}{5} \partial_\zeta \left(\partial_\zeta \phi_{a,0}^{(0)} \partial_\zeta c_0^{(1)} \right) + \frac{67}{2016} \left(\partial_\zeta^2 \phi_{a,0}^{(0)} \right)^2 \right. \\ & \left. + \frac{25}{2016} \partial_\zeta \phi_{a,0}^{(0)} \partial_\zeta^3 \phi_{a,0}^{(0)} \right\} - \frac{1}{192} \alpha[\eta] K_D^r \partial_\zeta \left(\phi_{b,0}^{(0)} \partial_\zeta \phi_{a,0}^{(0)} \right). \end{aligned} \tag{36}$$

For the step initial condition, (35) and (36) give

$$\begin{aligned} \varphi_{b,1}^{(0)} = & \lambda_0 \left\{ \frac{2}{3\pi t} (r^6 - 3r^4 + 3r^2) e^{-96\zeta^2/t} + \frac{1}{2100t} \left[-3548 \frac{\zeta}{\sqrt{\pi t}} e^{-48\zeta^2/t} \operatorname{erf}(4\sqrt{3}\zeta/\sqrt{t}) \right. \right. \\ & \left. \left. - 331 e^{-96\zeta^2/t} + 32256 \frac{\zeta^2}{t} e^{-96\zeta^2/t} \right] \right\} + \frac{\alpha[\eta] K_D^r}{8} \left\{ \operatorname{erf}^2(4\sqrt{3}\zeta/\sqrt{t}) - 1 \right. \\ & \left. + \frac{2}{\sqrt{\pi}} e^{-48\zeta^2/t} \left[\frac{1}{\sqrt{\pi}} e^{-48\zeta^2/t} - 4\sqrt{3} \frac{\zeta}{\sqrt{t}} \left(1 - \operatorname{erf}(4\sqrt{3}\zeta/\sqrt{t}) \right) \right] \right\}, \end{aligned} \tag{37}$$

which is needed to determine the diffusion differential contribution to the pressure. Note the nonlinear interaction terms. For $\lambda_0 \neq 0$ the elasticity correction to the concentration is $O(\epsilon)$, as is the diffusion differential correction.

For the plug initial conditions,

$$\phi = \varphi_{b,1}^{(0)} \left(\frac{\xi + \ell}{\sqrt{\delta}}, t \right) - \varphi_{b,1}^{(0)} \left(\frac{\xi - \ell}{\sqrt{\delta}}, t \right).$$

This choice of solution assumes zero mass contribution to this order ($\int_{-\infty}^{\infty} \phi_{b,1}^{(0)} d\xi = 0$) and the center of mass remains fixed ($\int_{-\infty}^{\infty} \xi \phi_{b,1}^{(0)} d\xi = 0$).

4. Results

The goal of this work has been to clarify intrinsic viscosity, elasticity and diffusion differential effects on the capillary pressure profile in a capillary rheometer, thus allowing improved polymer characterization. The work deals with small Peclet number corrections to the original expansion in terms of the dilution parameter. The goal has been to clearly delineate each of these effects and, originally, to help guide the numerics for other Peclet-number domains. While the effects of intrinsic viscosity, elasticity and diffusion are clearly shown in the expansions (20), together with (32), (33) and (37), as well as the related nonlinear interactions, it is useful to have some pictures elucidating these effects.

In the figures which follow, results are graphed, for an initial concentration step. Unless otherwise noted, $t = \alpha[\eta] = 1$, $\xi_0 = 0.5$, $\epsilon = 0.1$ and $\delta = 0.5$.

In Figure 2, $\phi_{a,0}^{(0)}$ is graphed for $t = 1, 2, 3$. This is the equivalent, for a step function initial condition, of Taylor's result which was instead for a delta function initial condition. This is the Newtonian Taylor dispersion.

In Figure 3, the numerical solution $\bar{p}_1 = (\bar{p} - p_0)/\epsilon$ is graphed for $\lambda_0 = 1$ and $K_D^r = 1$, as is the perturbation solution $\bar{p}_1^{(0)}$, to order one in δ , in the boundary layer. Note that to this order the solutions agree well.

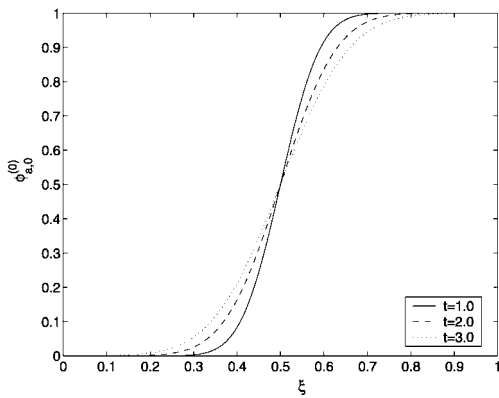


Figure 2. Volume fraction of species a : $\phi_{a,0}^{(0)}$.

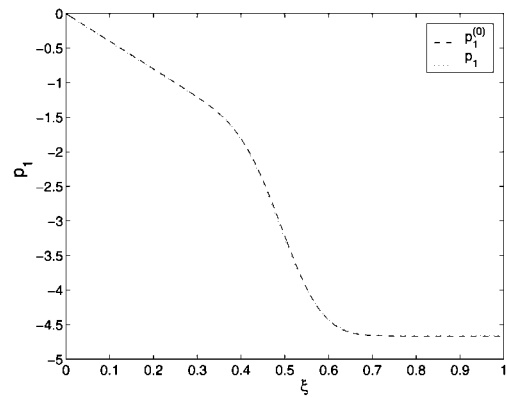


Figure 3. Cross-section-averaged pressure: \bar{p}_1 vs. $\bar{p}_1^{(0)}$, $\lambda_0 = K_D^r = 1$.

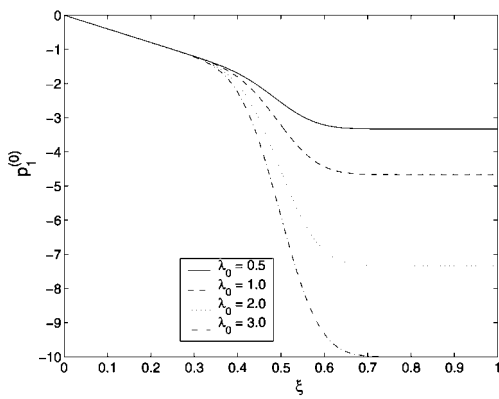


Figure 4. Effect of elasticity on cross-section-averaged pressure: $\bar{p}_1^{(0)}$.

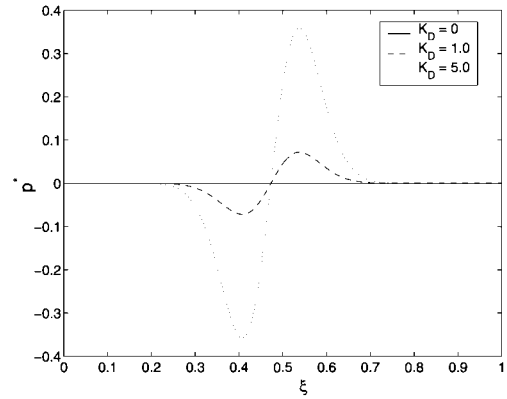


Figure 5. Effect of differential diffusion on cross-section-averaged pressure: p^* ; $\lambda_0 = 0$.

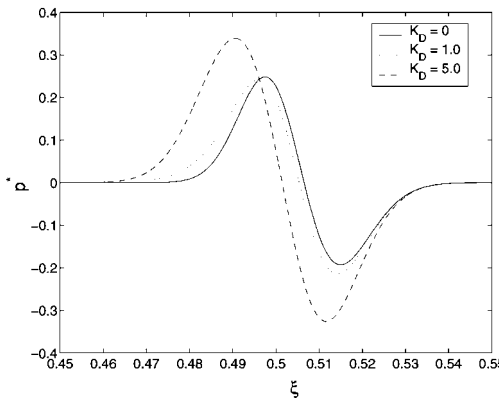


Figure 6. Effect of differential diffusion on cross-section-averaged pressure: p^* ; $\lambda_0 = 1$.

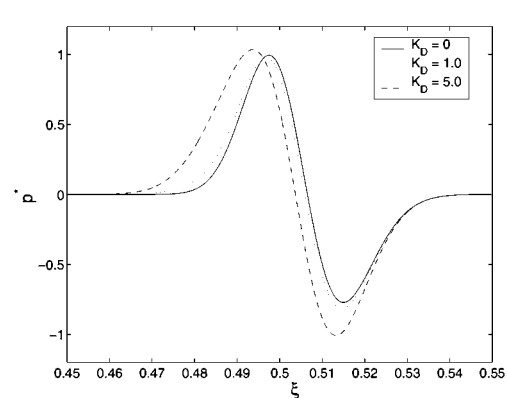


Figure 7. Effect of differential diffusion on cross-section-averaged pressure: p^* ; $\lambda_0 = 2$.

In Figure 4, the analytic pressure perturbation $\bar{p}_1^{(0)}$ is graphed as a function of ξ for $\lambda_0 = 0.5, 1, 2, 3$. Clearly, this shows the influence of elasticity. As the elasticity increases, the pressure drop increases as expected.

In Figures 5, 6 and 7 the analytic pressure perturbation due to the differential diffusivity is graphed for differential diffusivities $K_D = K_D^r = 0, 1, 5$ and for values of the elasticity parameter $\lambda_0 = 0, 1, 2$. There, p^* is the expansion of \mathcal{P} to first order in δ , where

$$\mathcal{P} = \frac{\bar{p} - p_0 - \epsilon \bar{p}_1 - \epsilon^2 \tilde{p}_2}{4 \epsilon^2 \alpha^2 [\eta]^2},$$

and \tilde{p}_2 is the value of \bar{p}_2 for $K_D^r = 0$. These figures summarize our goal, namely to isolate the effects of diffusivity differential and of elasticity on the pressure drop.

5. Conclusion

In this paper, the behavior of the solution to the equations governing the motion of a plug of dilute mixture of polymer fluid in a solvent, in a capillary tube, under constant volumetric flow conditions was examined for the dependence on the Peclet number δ . This clarified the mechanisms, at each order in the dilution parameter ϵ , for mixing and in particular isolated the effects of viscosity differential, diffusivity differential, density differential and elasticity on the plug profile. This information will, in turn, be used to characterize the polymer.

The asymptotic results, in δ , are more than just a guide for and check on the numerics [9], they isolate the effect of specific parameters, thus allowing one to identify $[\eta]$, λ_0 and K_D^r for particular processing events and hence identify the molecular properties of the batch.

In conclusion, this perturbation study has not only guided the numerics, but has also enabled isolating the role various parameters play. In particular, the density differential Π_0 did not enter the asymptotics to the order carried out. On the other hand, despite the weak elasticity in the problem, this dominated diffusion differential effects. Elasticity first entered in the boundary layer at $O(\epsilon)$ as did the intrinsic viscosity, the diffusion differential at $O(\epsilon^2/\sqrt{\delta})$.

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