Compressible laminar flow in a capillary

By H. R. VAN DEN BERG, C. A. TEN SELDAM
AND P. S. VAN DER GULIK

Van der Waals Laboratory, University of Amsterdam, Valckenierstraat 67,
1018 XE Amsterdam, The Netherlands

An equation based on the hydrodynamical equations of change is solved, analytically and numerically, for the calculation of the viscosity from the mass-flow rate of a steady, isothermal, compressible and laminar flow in a capillary. It is shown that by far the most dominant correction is that due to the compressibility of the fluid, computable from the equation of state. The combined correction for the acceleration of the fluid and the change of the velocity profile appears to be 1.5 times larger than the correction accepted to date.

1. Introduction

The study of a capillary flow was initiated 150 years ago by the French physician Poiseuille (1840) with his 'Recherches expérimentales sur le mouvement des liquides dans les tubes de très petits diamètres'. From this experimental work on distilled water he deduced the following proportion between the volume flow rate Q and the pressure difference Δp:

$$Q = k'' \frac{D^4 \Delta p}{L}.$$

(1)

L and D are the dimensions of the capillary, the length and the diameter. Poiseuille determined the proportion factor k'' from the experimental results on water and concluded that its value is constant for given temperature and pressure. The concept of the viscosity of the liquid was not mentioned at all at that time. When we now apply this value of k'' to calculate the viscosity η of water for the corresponding experimental circumstances, namely a temperature of 10 °C and a pressure of about 0.1 MPa, using $\eta = \pi/(128k'')$ we obtain a value which is, astoundingly, only 0.2% larger than the value calculated from the most recent formula for the viscosity of water given by Kestin et al. (1985). This very nice agreement is, of course, mainly due to the high accuracy of the experimental work of Poiseuille, but also to the fact that the experiment concerned a practically incompressible liquid flow, that is very well described by (1). However, van den Berg, ten Seldam & van der Gulik (1990) showed that, for instance, in the case of a gas flow, the compressibility of the fluid has to be taken into account, since this can cause a considerable reduction in the volume flow rate as calculated from (1). For a long period, incorporation of the correction for the compressibility has been based on heuristic arguments. It is the principal goal of the present paper to show that this correction originates from theoretical equations for a capillary flow and, moreover, that additional corrections are an order of magnitude lower. As a consequence, a sound basis for the accurate calculation of the viscosity measured with a capillary viscometer is established, even for experimental circumstances where a substantial correction for the compressibility of the fluid must be applied.

Section 2 contains the hydrodynamical conservation equations in their general form and the reduced version of the equation of motion in cylindrical coordinates corresponding with the simplifying conditions under which the problem of a *compressible capillary flow* will be solved. These conditions refer in particular to the laminar, axial and isothermal flow of a Newtonian fluid.

In §3 the solution of this flow problem is derived analytically from the equation of motion by means of a perturbation method, successively up to the second order, in terms of two dimensionless parameters, both of which are zero for an incompressible fluid. The main effect of the acceleration in a compressible flow is described by the key parameter C_1, whereas the second, less important, parameter C_3 accounts for the resulting effect of an extra viscous force. The zero-order calculation leads to the well-known parabolic velocity profile, while the viscosity is found to be the product of the Poiseuille expression, valid for an incompressible fluid, and a 'compression correction' factor equal to the ratio of a mean density in the capillary and the density at its beginning. In the first order, where C_1 is still small, a correction term is found which is of the same form as the previously calculated correction due to the acceleration of the fluid, but 1.5 times larger; the excess is because the velocity profile is no longer parabolic. For larger values of the parameter C_1, a method is described in §4 whereby the equation of motion with $C_3 = 0$ can be solved numerically and which also yields the development of various quantities such as pressure, density and velocity along the axis of the capillary.

2. Hydrodynamical equations and conditions

A compressible capillary flow, generated by a force due to a static pressure p in the fluid, is examined for a system without heat production from external sources. Therefore, the evolution of the density ρ, the velocity $\boldsymbol{u}$ and the internal energy $\hat{U}$ per unit mass in this system is described by the three hydrodynamical conservation equations:

continuity
$$\frac{\mathrm{D}\rho}{\mathrm{D}\tau} = -\rho(\boldsymbol{\nabla}\cdot\boldsymbol{u}), \tag{2}$$

motion
$$\rho\frac{\mathrm{D}\boldsymbol{u}}{\mathrm{D}\tau} = -\boldsymbol{\nabla}\cdot\boldsymbol{P}, \tag{3}$$

and energy
$$\rho\frac{\mathrm{D}\hat{U}}{\mathrm{D}\tau} = -(\boldsymbol{\nabla}\cdot\boldsymbol{q}+\boldsymbol{P}\!:\!(\boldsymbol{\nabla}\boldsymbol{u})), \tag{4}$$

where τ is the time and $\mathrm{D}/\mathrm{D}\tau$ is an abbreviation for $\partial/\partial\tau+\boldsymbol{u}\cdot\boldsymbol{\nabla}$, namely the 'derivative following the motion'; $\boldsymbol{P}$ is the pressure tensor and $\boldsymbol{q}$ is the heat-flow vector.

For our problem, namely compressible flow through a straight circular capillary, the various equations are not expressed in rectangular coordinates but rather in the more appropriate cylindrical coordinates (r, θ, z). The full hydrodynamical equations are rarely used to set up flow problems. Instead, restricted forms of these equations are usually adapted. All the conditions that underlie the solutions of the equations as deduced in this paper are summarized below.

(i) The fluid is Newtonian.

(ii) The radius R of the capillary is small compared to its length L; R/L is of the order 10^{-3}.

(iii) The flow is stationary, i.e. changes in time are sufficiently slow to allow terms with partial time derivatives to be discarded.

(iv) The radial and azimuthal flow velocity components, u_r and u_θ, can be discarded, i.e. the flow is strictly axial and laminar; the Reynolds number Re ($= 2R\rho\bar{u}/\eta$, with $\bar{u}$ the mean flow velocity) is less than about 2000.

(v) The pressure p is a function of z only.

(vi) There is axial symmetry, i.e. the axial flow velocity component u_z is not a function of θ, but only of r and z.

(vii) There is no Knudsen flow; the fluid is considered to be a continuum.

(viii) There is no slip flow at the wall; the fluid velocity along the wall is zero.

(ix) There are no gravity effects.

(x) An influx correction is not considered.

(xi) Both the shear and the bulk viscosity of the fluid are constant in the pressure range throughout the capillary.

(xii) The flow is isothermal.

Some additional comments should be made with respect to these conditions. Condition (i) means that the pressure tensor can be written as

$$\boldsymbol{P} = p\boldsymbol{I} - 2\eta\boldsymbol{S} - \kappa(\nabla \cdot \boldsymbol{u})\boldsymbol{I}, \tag{5}$$

where η is the coefficient of shear viscosity of the fluid and κ the coefficient of bulk viscosity, $\boldsymbol{I}$ the unit tensor and $\boldsymbol{S}$ the rate-of-shear tensor defined by

$$\boldsymbol{S} = \tfrac{1}{2}(\nabla\boldsymbol{u} + (\nabla\boldsymbol{u})^{\mathrm{T}}) - \tfrac{1}{3}(\nabla \cdot \boldsymbol{u})\boldsymbol{I}. \tag{6}$$

Condition (iv) seems reasonable in view of condition (ii). The problem of the additional pressure drop at the inlet of the capillary (condition x) has been tackled by many authors for an incompressible fluid. The corresponding relative correction on the volume flow rate can be written as $-\tfrac{1}{16}m(R/L)Re$, where the quantity m, i.e. the coefficient of the Hagenbeck–Couette correction, generally has a value of the order of unity, depending on the shape of the capillary entrance and exit. By a numerical computation for a capillary with square-cut ends Kestin, Sokolov & Wakeham (1973) found that m is not constant but varies in inverse proportion to the Reynolds number with a limiting value of 1.12 for $Re \gg 1$.

The important assumption that the flow is isothermal (condition xii) can only be partly justified, as shown in a separate paper by van den Berg, ten Seldam & van der Gulik (1993) in which the net thermal effect in a compressible viscous flow was calculated from the contributions for cooling and heating, due to expansion of the fluid and viscous dissipation respectively. In this calculation, the temperature of the wall of the capillary is assumed to be constant and equal to the ambient temperature T_0 over the whole length. The key parameter in the treatment is the dimensionless quantity $C = -(T_0/\rho)(\partial\rho/\partial T)_p$. A second parameter is the Péclet number $Pe = Re\,Pr$, where Pr is the Prandtl number. The authors also showed that the thermal effect evolves over a characteristic length, the so-called entry length ΔL_T, which for $Pe > 50$ is given by $\Delta L_T/L = 0.625(R/L)Pe$. It is concluded that, generally, the temperature changes in the flow are very small, namely a few mK, and that $\Delta L_T/L \ll 1$. However, for a very compressible fluid, e.g. in the vicinity of the gas–liquid critical point ($C \gg 1$, $Pe \gg 1$), the contribution of cooling is by far the most dominant, so that a substantial reduction of the temperature of the flowing fluid results and, moreover, a significant increase of the entry length. Consequently, for these special circumstances the premise of an isothermal flow must be abandoned.

Along with the equation of state

$$\rho = \rho(p, T), \tag{7}$$

and the boundary and initial conditions, (2)–(6) give a complete determination of the distributions of pressure, density, velocity components and viscosity in the flowing fluid at constant temperature T.

Under the above-mentioned simplifying conditions, the equation of continuity (2) reduces to

$$\frac{\partial(\rho u_z)}{\partial z} = 0, \tag{8}$$

and the equation of motion (3) for the radial and axial velocity components, respectively, to

$$\eta\left(\frac{1}{3} + \frac{\kappa}{\eta}\right)\frac{\partial^2 u_z}{\partial z\,\partial r} = \frac{\partial p}{\partial r} = 0 \tag{9}$$

and

$$\rho u_z \frac{\partial u_z}{\partial z} = -\frac{\mathrm{d}p}{\mathrm{d}z} + \eta\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u_z}{\partial r}\right) + \eta\left(\frac{4}{3} + \frac{\kappa}{\eta}\right)\frac{\partial^2 u_z}{\partial z^2}, \tag{10}$$

while the equation of energy becomes superfluous.

The equation of motion (10) can be solved using only the equation of continuity (8). Initially, (9) is omitted since the constraint it imposes on $u_z(r,z)$ shows that for a compressible fluid the conditions (iv) and (v), i.e. strictly axial flow in which the pressure is a function of z only, are in principle incompatible. However, at the end of the next section we will quantify the conditions under which the results may, nevertheless, be used. In that consideration the limitation on R/L as expressed by condition (ii) is crucial.

Because of conditions (v) and (xii), the density ρ of the fluid is also a function of z only. Integration of the equation of continuity (8) then implies

$$\rho(z)\,u_z(r,z) = f(r) \quad \text{or} \quad u_z(r,z) = u_{\mathrm{m}}(z)\,F(r). \tag{11}$$

From the point of view of symmetry it can be argued that the dimensionless velocity-profile function $F(r)$ has a maximum for $r = 0$ and hence, $\mathrm{d}F/\mathrm{d}r = 0$ for that value of r. The assumption that there is no slip at the wall (condition viii) yields $F(R) = 0$ and, by transfer of constant factors from $F(r)$ to $u_{\mathrm{m}}(z)$, $F(0)$ can be made equal to 1; $u_{\mathrm{m}}(z)$ is then identical to the maximum velocity $u_z(0,z)$. Expression (11) for $u_z(r,z)$ is inserted in the equation of motion (10); moreover, a reduced velocity-profile function $E(x)$ is defined by

$$E(x) = F(r) \quad \text{with} \quad x = r/R. \tag{12}$$

Equation (10) then becomes

$$\rho u_{\mathrm{m}}\frac{\mathrm{d}u_{\mathrm{m}}}{\mathrm{d}z}E^2(x) = -\frac{\mathrm{d}p}{\mathrm{d}z} + \frac{\eta u_{\mathrm{m}}}{R^2}\mathscr{T}E(x) + \eta\left(\frac{4}{3} + \frac{\kappa}{\eta}\right)\frac{\mathrm{d}^2 u_{\mathrm{m}}}{\mathrm{d}z^2}E(x), \tag{13}$$

where the operator

$$\mathscr{T} = \frac{1}{x}\frac{\partial}{\partial x}\left(x\frac{\partial}{\partial x}\right). \tag{14}$$

In (13), the centreline velocity $u_{\mathrm{m}}(z)$ is replaced by the density $\rho(z)$ by means of

$$u_{\mathrm{m}}(z) = W/\rho(z), \tag{15}$$

where the quantity W, in consequence of (11) and (12), is related to the mass-flow rate I, according to

$$I = \int_0^R 2\pi r \, dr \, \rho(z) \, u_z(r,z) = 2\pi R^2 W \int_0^1 E(x) \, x \, dx, \tag{16}$$

and thus W is a constant for the flow. The whole equation is then multiplied by $\rho(z)$ and a rearrangement of the terms leads to

$$-W^2 \frac{d \ln \rho}{dz} E^2(x) + \eta \left(\frac{4}{3} + \frac{\kappa}{\eta} \right) W \rho \frac{d}{dz} \left(\frac{1}{\rho^2} \frac{d\rho}{dz} \right) E(x) = -\rho \frac{dp}{dz} + \frac{\eta W}{R^2} \mathscr{T} E(x). \tag{17}$$

Before it is solved, (17) is transformed into a dimensionless form. Initially, this equation is further simplified by integrating it over the length of the capillary, where the axial coordinate z crosses the interval $[0, L]$, the pressure $p(z)$ decreases from $p_b = p(0)$ to $p_{ex} = p(L)$ and the density $\rho(z)$ from $\rho_b = \rho(0)$ to $\rho_{ex} = \rho(L)$. The result is

$$W^2 Y E^2(x) - \eta \left(\frac{4}{3} + \frac{\kappa}{\eta} \right) W Z E(x) = X + \frac{\eta W L}{R^2} \mathscr{T} E(x), \tag{18}$$

where the constants X, Y and Z are defined by

$$X = \int_{p_{ex}}^{p_b} \rho \, dp = \langle \rho(p) \rangle \Delta p, \quad Y = \ln \frac{\rho_b}{\rho_{ex}}, \quad Z = \int_{\rho_{exp}}^{\rho_b} \rho \, d \left(\frac{1}{\rho^2} \frac{d\rho}{dz} \right). \tag{19}$$

$\Delta p \, (= p_b - p_{ex})$ is the pressure difference over the capillary and $\langle \rho(p) \rangle$ a density defined as the average of $\rho(p)$ over the pressure interval $[p_{ex}, p_b]$. It should be noted that the evaluation of X and, thus, of this mean density can be carried out easily, since for that purpose only the equation of state of the fluid, $\rho = \rho(p)$, and the pressures at the capillary ends need to be known. Consequently, X and Y (but not Z) can be calculated without a knowledge of $\rho(z)$ and thus depend on the fluid and controllable external experimental conditions only and not on the flow. On the other hand, with $\rho(z)$ a different mean density $\langle \rho(z) \rangle$ can be defined as $(1/L) \int_0^L \rho(z) \, dz$, which is in general more difficult to compute. These two mean densities are numerically equal in the common case of a constant axial pressure gradient.

Finally, the introduction of the dimensionless constants C_1, C_2 and C_3 by

$$C_1 = W^2 \frac{Y}{X}, \quad C_2 = \eta W \frac{L}{R^2} \frac{1}{X}, \quad C_3 = \eta \left(\frac{4}{3} + \frac{\kappa}{\eta} \right) W \frac{Z}{X}, \tag{20}$$

offers the possibility of writing the equation governing the motion in a clear, dimensionless form:

$$C_1 E^2(x) - C_3 E(x) = 1 + C_2 \mathscr{T} E(x), \tag{21}$$

with the normalization and boundary conditions

$$E(0) = 1, \quad E(1) = 0, \quad \left(\frac{dE}{dx} \right)_{x=0} = 0. \tag{22}$$

For an incompressible fluid $\rho_b = \rho_{ex}$, so that the quantities Y and Z and, consequently, also the constants C_1 and C_3 are zero.

In the next section it will be shown that the present compressible flow problem can be treated by a perturbation method in terms of C_1 and C_3. It turns out that C_1 is the key parameter proportional to $(R/L) Re \, Y$, while the second, less important,

parameter C_3 is proportional to $((R/L) Y)^2$. Moreover, it should be emphasized that none of the perturbation parameters C_1, C_2 or C_3 are known in advance, but depend on the solution itself.

3. Perturbation solutions

3.1. *General formalism*

We now aim to solve (21) analytically for a compressible capillary flow. Since the left-hand side of this equation vanishes for an incompressible fluid, it may be presumed that, for a slightly compressible fluid, this left-hand side is small. Therefore, a perturbation method in terms of the parameters C_1 and C_3 is applied.

Firstly, the velocity-profile function $E(x)$ is developed in powers of C_1 and C_3:

$$E^{(n)}(x) = \sum_{\substack{i=0 \\ i+j \leqslant n}}^{n} \sum_{j=0}^{n} E_{i,j}(x)\, C_1^i C_3^j, \tag{23}$$

where the superscript (n) denotes the order n of the approximation. This power series implies

$$C_2^{(n)} = C_2^{(0)}\left[1 + \sum_{\substack{i=0 \\ 1 \leqslant i+j \leqslant n}}^{n} \sum_{j=0}^{n} \gamma_{i,j}\, C_1^i C_3^j\right]. \tag{24}$$

Subsequently, these two series expansions are substituted in (21). The solution of this equation is then derived in successive powers of $C_1^i C_3^j$ by equating the corresponding terms on both sides of the equation. This procedure is carried out in a purely formal way, which means that at present no attention is paid to the magnitude, in a physical sense, of the various terms. This leads to:

Zero order

$$i = 0, j = 0: \quad 0 = 1 + C_2^{(0)}\, \mathcal{T} E_{0,0}(x); \tag{25}$$

First order

$$i = 1, j = 0: \quad E_{0,0}^2(x) = C_2^{(0)}[\gamma_{1,0}\, \mathcal{T} E_{0,0}(x) + \mathcal{T} E_{1,0}(x)], \tag{26a}$$

$$i = 0, j = 1: \quad -E_{0,0}(x) = C_2^{(0)}[\gamma_{0,1}\, \mathcal{T} E_{0,0}(x) + \mathcal{T} E_{0,1}(x)]; \tag{26b}$$

Second order

$$i = 2, j = 0:$$

$$2E_{0,0}(x)\, E_{1,0}(x) = C_2^{(0)}[\gamma_{2,0}\, \mathcal{T} E_{0,0}(x) + \gamma_{1,0}\, \mathcal{T} E_{1,0}(x) + \mathcal{T} E_{2,0}(x)], \tag{27a}$$

$$i = 1, j = 1:$$

$$2E_{0,0}(x)\, E_{0,1}(x) - E_{1,0}(x)$$
$$= C_2^{(0)}[\gamma_{1,1}\, \mathcal{T} E_{0,0}(x) + \gamma_{0,1}\, \mathcal{T} E_{1,0}(x) + \gamma_{1,0}\, \mathcal{T} E_{0,1}(x) + \mathcal{T} E_{1,1}(x)], \tag{27b}$$

$$i = 0, j = 2:$$

$$-E_{0,1}(x) = C_2^{(0)}[\gamma_{0,2}\, \mathcal{T} E_{0,0}(x) + \gamma_{0,1}\, \mathcal{T} E_{0,1}(x) + \mathcal{T} E_{0,2}(x)], \tag{27c}$$

etc.

These sets of equations are solved at successive order, where the concept 'order' refers only to the total power of $C_1^i C_3^j$. The nth set consists of $n + 1$ equations. Each of these equations separately contains only one unknown function $E_{i,j}(x)$ and corresponding constant $\gamma_{i,j}$, with $i+j = n$, while the remaining functions and constants, for which $i+j < n$, have already been found from the foregoing sets of

equations. Thus, the functions $E_{i,j}(x)$ can easily be found, while the values of $\gamma_{i,j}$ and of the two integration constants are fixed by application of the normalization and boundary conditions (22):

$$
\left.
\begin{aligned}
E_{0,0}(0) &= 1, \quad \text{hence} \quad E_{i,j}(0) = 0 \quad \text{for} \quad i,j = 0,1,2,\ldots \quad \text{with} \quad i+j \geqslant 1, \\
E_{i,j}(1) &= 0, \quad \left(\frac{\mathrm{d}E_{i,j}(x)}{\mathrm{d}x}\right)_{x=0} = 0 \quad \text{for} \quad i,j = 0,1,2,\ldots.
\end{aligned}
\right\} \tag{28}
$$

To find the corresponding expression for the viscosity at the order (n), the nth-order velocity profile $E^{(n)}(x)$ is substituted in the integrand of (16). Using the fact that the mass-flow rate I is a constant for the flow, this leads, firstly, to an expression for the quantity $W^{(n)}$ in terms of the parameters C_1 and C_3, namely

$$
\frac{W^{(0)}}{W^{(n)}} = 1 + \sum_{\substack{i=0 \\ 1 \leqslant i+j \leqslant n}}^{n} \sum_{j=0}^{n} w_{i,j} C_1^i C_3^j, \tag{29}
$$

with

$$
w_{i,j} = \frac{\displaystyle\int_0^1 E_{i,j}(x)\, x\, \mathrm{d}x}{\displaystyle\int_0^1 E_{0,0}(x)\, x\, \mathrm{d}x}. \tag{30}
$$

Further, with (20) and (24) for C_2, the viscosity $\eta^{(n)}$ can then be written as

$$
\frac{\eta^{(n)}}{\eta^{(0)}} = \left[1 + \sum_{\substack{i=0 \\ 1 \leqslant i+j \leqslant n}}^{n} \sum_{j=0}^{n} \gamma_{i,j} C_1^i C_3^j\right]\left[1 + \sum_{\substack{i=0 \\ 1 \leqslant i+j \leqslant n}}^{n} \sum_{j=0}^{n} w_{i,j} C_1^i C_3^j\right], \tag{31}
$$

where, for consistency of the calculation, the final series expansion for $\eta^{(n)}$ in terms of $C_1^i C_3^j$ should be truncated to terms with $i+j \leqslant n$. For clarity, it should be noted that $\eta^{(n)}$ refers to the viscosity *calculated* at the nth order from experimental data. There is, therefore, no inconsistency at all with the assumption of a constant viscosity in the capillary (condition x).

The exact values of the parameters C_1 and C_3 can be calculated simultaneously from the respective expressions in (20), which are written for that purpose as

$$
C_1 = C_1^{(0)} \frac{1}{\left[1 + \displaystyle\sum_{\substack{i=0 \\ 1 \leqslant i+j}}^{\infty} \sum_{j=0}^{\infty} w_{i,j} C_1^i C_3^j\right]^2} \quad \text{and} \quad C_3 = C_3^{(0)}\left[1 + \sum_{\substack{i=0 \\ 1 \leqslant i+j}}^{\infty} \sum_{j=0}^{\infty} \gamma_{i,j} C_1^i C_3^j\right], \tag{32}
$$

with

$$
C_1^{(0)} = W^{(0)^2} \frac{Y}{X} \quad \text{and} \quad C_3^{(0)} = C_2^{(0)}\left(\frac{4}{3} + \frac{\kappa}{\eta}\right)\frac{R^2}{L} Z. \tag{33}
$$

The consistency of the perturbation calculation should be maintained throughout each order, also in the case of C_1 and C_3. In practice, this will be accomplished by developing C_1, like C_3, into a series of successive powers of $C_1^i C_3^j$ and, subsequently, by transformation of both series together into power series of the zero-order terms $C_1^{(0)^i} C_3^{(0)^j}$, and by restricting these series to that finite number of terms that does not exceed the order of the calculation.

3.2. *Zero-order solution*

From (25) follows that

$$
\mathscr{T} E_{0,0}(x) = -1/C_2^{(0)}. \tag{34}
$$

Integration of this second-order differential equation under the normalization and boundary conditions (28) then leads to

$$E_{0,0}(x) = 1 - x^2 \qquad (35)$$

and

$$C_2^{(0)} = \tfrac{1}{4}. \qquad (36)$$

$E_{0,0}(x)$ represents the well-known parabolic velocity profile. Substitution of this profile in (16) yields

$$\rho(z)\, u_m^{(0)}(z) = W^{(0)} = 2I/(\pi R^2). \qquad (37)$$

With these results for $C_2^{(0)}$ and $W^{(0)}$, the viscosity is calculated from (20) as

$$\eta^{(0)} = \frac{C_2^{(0)}}{W^{(0)}} \frac{R^2 X}{L} = \frac{\pi R^4}{8IL} X = \eta_p F_c, \qquad (38)$$

with

$$\eta_p = \frac{\pi R^4}{8IL} \rho_b \Delta p, \qquad (39)$$

and

$$F_c = \frac{\langle \rho(p) \rangle}{\rho_b}. \qquad (40)$$

Thus, as solution for $\eta^{(0)}$, the viscosity of a compressible fluid at zero order, we obtain the Poiseuille expression η_p for an incompressible fluid expressed in terms of the mass-flow rate, times the 'compression factor' F_c.

Parameters $C_1^{(0)}$ and $C_3^{(0)}$, given in (33), are expressed in terms of various experimentally obtainable quantities by substitution of the results (36) and (37) for $C_2^{(0)}$ and $W^{(0)}$. Namely,

$$C_1^{(0)} = \frac{I}{2\pi L} \frac{1}{\eta^{(0)}} Y, \qquad (41)$$

which, in order to elucidate the physical meaning of this parameter, can also be written in terms of the Reynolds number at zero-order $(Re^{(0)})$ and the isothermal compressibility κ_T as

$$C_1^{(0)} = \frac{1}{4}\frac{R}{L} Y Re^{(0)} \approx \frac{1}{4}\frac{R}{L}\kappa_T \Delta p\, Re^{(0)} \quad \text{with} \quad Re^{(0)} = \frac{2I}{\pi R \eta^{(0)}} = \frac{R^3 X}{4\eta^{(0)^2} L}, \qquad (42)$$

and furthermore

$$C_3^{(0)} = \frac{1}{4}\left(\frac{4}{3} + \frac{\kappa}{\eta}\right)\frac{R^2}{L} Z. \qquad (43)$$

For the calculation of the quantity Z from (19) the precise form of the function $\rho(z)$ is required. If we assume $Z = fY^2/L$, then

$$C_3^{(0)} = f^*\left(\frac{R}{L} Y\right)^2 \quad \text{with} \quad f^* = \frac{1}{3}\left(1 + \frac{3}{4}\frac{\kappa}{\eta}\right)f. \qquad (44)$$

Thus, $C_1^{(0)}$ and $C_3^{(0)}$ contain only (easily) measurable basic quantities, with the exception of f, since this quantity must be calculated from the axial dependence of the density in the capillary. In order to obtain a reasonable estimate of the quantity f, three particular cases are examined. Firstly, the usual linear dependence for $\rho(z)$, $\rho(z) = \rho_b - (\rho_b - \rho_{ex})z/L$, where f is calculated to be equal to about 2. Secondly, the exponential dependence, $\rho(z) = \rho_b \exp(-zY/L)$, in which case f equals 1, and, thirdly, the case of $\rho(z)$ as calculated by Prud'homme, Chapman & Bowen (1986) for

the compressible flow of an *ideal* gas. From their solution, expressed in somewhat different parameters, it can be derived that f equals about 3. From these examples we may conclude that f is most likely a number of the order of unity.

From (42) and (44) it can be seen that for $Re \approx 1$ one obtains $C_3 \approx C_1^2$. The only implication of this estimation is that the ordering with respect to magnitude does not coincide with the formal ordering in the expansion scheme of §3.1 and, consequently, that for a physical interpretation of the results, terms of different formal orders must be combined.

3.3. *First-order solution*

The first-order solutions $\gamma_{1,0}$ and $E_{1,0}(x)$ are computed from (26a) by substitution of the zero-order solutions (35) for $E_{0,0}(x)$ and (36) for $C_2^{(0)}$, followed by repeated integration with application of the boundary conditions (28). This results in

$$\gamma_{1,0} = -\tfrac{11}{18} \tag{45}$$

and

$$E_{1,0}(x) = \tfrac{1}{18}(1-x^2)\,x^2(7-2x^2), \tag{46}$$

and consequently

$$w_{1,0} = \frac{\displaystyle\int_0^1 E_{1,0}(x)\,x\,\mathrm{d}x}{\displaystyle\int_0^1 E_{0,0}(x)\,x\,\mathrm{d}x} = \tfrac{1}{9}. \tag{47}$$

Likewise, from (26b) follows

$$\gamma_{0,1} = \tfrac{3}{4}, \tag{48}$$

$$E_{0,1}(x) = -\tfrac{1}{4}(1-x^2)\,x^2, \tag{49}$$

$$w_{0,1} = -\tfrac{1}{12}. \tag{50}$$

Thus, according to (23), the velocity profile at first order is given by

$$E^{(1)}(x) = (1-x^2)\,[1 + \tfrac{1}{18}x^2(7-2x^2)\,C_1 - \tfrac{1}{4}x^2\,C_3], \tag{51}$$

and, according to (31), the corresponding perturbation solution for the viscosity $\eta^{(1)}$ by

$$\eta^{(1)} = \eta^{(0)}\,(1 - \tfrac{11}{18}C_1 + \tfrac{3}{4}C_3)\,(1 + \tfrac{1}{9}C_1 - \tfrac{1}{12}C_3), \tag{52}$$

which, for consistency of the calculation, must be truncated to

$$\eta^{(1)} = \eta^{(0)}\,(1 - \tfrac{1}{2}C_1 + \tfrac{2}{3}C_3). \tag{53}$$

By imposing corresponding consistency restrictions on (32), the values of the parameters C_1 and C_3 are found to be

$$C_1 = C_1^{(1)} = C_1^{(0)} \quad \text{and} \quad C_3 = C_3^{(1)} = C_3^{(0)}. \tag{54}$$

Therefore, after substitution of (42) and (44) for $C_1^{(0)}$ and $C_3^{(0)}$, the final form of the formal first-order solution for the viscosity reads

$$\eta^{(1)} = \frac{\pi R^4}{8IL}\rho_{\mathrm{b}}\,\Delta p\,\frac{\langle \rho(p)\rangle}{\rho_{\mathrm{b}}}\left[1 - \frac{1}{8}\left(\frac{R}{L}Y\right)Re^{(0)} + \tfrac{2}{3}f^*\left(\frac{R}{L}Y\right)^2\right]. \tag{55}$$

The third term in this expression originates from the $\partial^2 u_z/\partial z^2$ term in the equation of motion (10). As shown in (44), the accessory coefficient f^* contains the ratio κ/η of the bulk and shear viscosities. In experiments, Madigosky (1967) found values of up to 0.7 for this ratio in dense gaseous argon. From experimental data on water and

a number of organic liquids, Karim & Rosenhead (1952) deduced that the value of this viscosity ratio ranges from about 1 to 120. Consequently, we estimate that the corresponding relative correction to the calculated viscosity is smaller than 0.01 %, on condition that $R/L \leqslant 10^{-3}$, $Y \leqslant 1$ or $\rho_{ex} \geqslant 0.37\rho_b$, and $f \leqslant 3$.

It should be emphasized that the exact axial dependence of the density in the capillary, which is unknown in this calculation, has no quantitative effect on the outcome of the estimation for the third term in (55), because of the ample margin taken for the quantity f. Thus, for practical applications we can neglect this term which is, actually, of the second order with respect to magnitude as pointed out in §3.2. In that case, the real first-order solution for the viscosity can also be written as

$$\eta^{(1)} = \frac{\pi R^4}{8IL}\rho_b \Delta p \frac{\langle \rho(p) \rangle}{\rho_b} - \frac{I}{4\pi L}\ln\frac{\rho_b}{\rho_{ex}}, \tag{56}$$

which one could call the *modified Poiseuille formula* (MPF). It consists of the zero-order term $\eta^{(0)}$ and one correction term.

Erk (1929) found the same *form* for this correction term, with a difference only in the value of the numerical factor in the denominator, viz. 8 instead of 4. It was entitled 'acceleration correction', but it turns out that this name does not entirely fit the numerical factor in Erk's result. Its true value, the strict acceleration correction, can be obtained from (21) with $C_3 = 0$ by substitution of the zero-order parabolic velocity profile $E_{0,0}(x)$ in both sides of this equation and, subsequently, integration over the cross-section with the weight function x:

$$C_1 \int_0^1 (1-x^2)^2 \, x \, \mathrm{d}x = \int_0^1 [1 - 4C_2] \, x \, \mathrm{d}x, \tag{57}$$

$$4C_2 = 1 - \tfrac{1}{3}C_1.$$

The constant C_2 is expressed in terms of the coefficient of viscosity by using (24) with $C_2^{(0)} = \tfrac{1}{4}$ and (31) where all the coefficients $w_{i,j}$ are taken equal to zero (or $W = W^{(0)}$). This gives

$$C_2 = \tfrac{1}{4}\eta/\eta^{(0)}, \tag{58}$$

which leads to

$$\eta/\eta^{(0)} = 1 - \tfrac{1}{3}C_1, \tag{59}$$

or, substituting (41) for C_1, to

$$\eta = \eta^{(0)} - \frac{I}{6\pi L}\ln\frac{\rho_b}{\rho_{ex}}. \tag{60}$$

Thus, this approximation for the first-order solution takes the acceleration of the fluid into account, but retains the parabolic velocity profile (35) throughout. In comparison with the exact first-order solution (56), formula (60) shows that, due to the non-parabolicity of the velocity profile, an additional correction, $-I/(12\pi L)\ln(\rho_b/\rho_{ex})$, enters which is half the size of the strict acceleration correction. The left-hand side of (57) is actually a computation of the average of the squared velocity. Frequently in the past, e.g. Erk (1929), Kao, Ruska & Kobayashi (1968), and Kestin *et al.* (1973), instead of the term $\tfrac{1}{3}C_1$ in (59) the term $\tfrac{1}{4}C_1$ was found, deviating by a factor 2 instead of $\tfrac{3}{2}$ from the complete solution $\tfrac{1}{2}C_1$. This difference is because these authors approximated the acceleration correction on the basis of the square of the average velocity.

The derivation of the 'working equation for a capillary viscometer with non-steady compressible flow' by van den Berg *et al.* (1990) is based on the MPF, not

however in the form given in (56), but in a differential form. This form can be obtained from the basic equation (17), following the same procedure as used in the derivation of (56), but omitting the integration of (17) over the length of the capillary, i.e. over the axial coordinate z. This procedure implies that the differential MPF can also be obtained by a direct conversion of (56), replacing L by dz, Δp by dp, $\Delta(\ln \rho)$ by $d(\ln \rho)$ and $\langle \rho(p) \rangle$ by ρ, resulting in

$$\frac{I}{L}\,dz = \frac{\pi R^4}{8L}\frac{\rho}{\eta^{(1)}}\,dp - \frac{I^2}{4\pi L}\frac{1}{\eta^{(1)}}\,d(\ln \rho). \tag{61}$$

3.4. *Second-order solution*

The second-order solutions are computed from (27) following the same procedure as applied for the first-order solutions. The results of this straightforward calculation can be summarized as follows:

coefficients $\gamma_{i,j}$

$$\gamma_{2,0} = -\tfrac{2087}{32400}, \quad \gamma_{1,1} = \tfrac{3}{32}, \quad \gamma_{0,2} = -\tfrac{5}{144}; \tag{62}$$

velocity profile

$$\begin{aligned}
E^{(2)}(x) = (1-x^2)\,[&1 + \tfrac{1}{18}x^2(7-2x^2)\,C_1 - \tfrac{1}{4}x^2\,C_3 \\
&+ \tfrac{1}{10800}x^2(1871 + 671x^2 - 729x^4 + 96x^6)\,C_1^2 \\
&+ \tfrac{1}{288}x^2(-101 - 13x^2 + 11x^4)\,C_1 C_3 + \tfrac{1}{72}x^2(11+2x^2)\,C_3^2\,];
\end{aligned} \tag{63}$$

coefficients $w_{i,j}$

$$w_{2,0} = \tfrac{223}{3600}, \quad w_{1,1} = -\tfrac{521}{4320}, \quad w_{0,2} = \tfrac{1}{18}.$$

According to (31) the perturbation solution $\eta^{(2)}$ for the viscosity is then given by

$$\begin{aligned}
\eta^{(2)} = \eta^{(0)}(&1 - \tfrac{11}{18}C_1 + \tfrac{3}{4}C_3 - \tfrac{2087}{32400}C_1^2 + \tfrac{3}{32}C_1 C_3 - \tfrac{5}{144}C_3^2). \\
(&1 + \tfrac{1}{9}C_1 - \tfrac{1}{12}C_3 + \tfrac{223}{3600}C_1^2 - \tfrac{521}{4320}C_1 C_3 + \tfrac{1}{18}C_3^2),
\end{aligned}$$

or, consistent with the order of calculation, by

$$\eta^{(2)} = \eta^{(0)}\,(1 - \tfrac{1}{2}C_1 + \tfrac{2}{3}C_3 - \tfrac{19}{270}C_1^2 + \tfrac{29}{270}C_1 C_3 - \tfrac{1}{24}C_3^2). \tag{64}$$

The values of the parameters C_1 and C_3 to be substituted in the second-order results must also be calculated consistently. Therefore, C_1 is written as

$$C_1 = C_1^{(0)}\left[1 + \sum_{\substack{i=0 \\ 1 \leqslant i+j \leqslant 2}}^{2} \sum_{j=0}^{2} v_{i,j}\,C_1^i\,C_3^j\right]. \tag{65}$$

By using (32) for C_1, where the coefficients $w_{i,j}$ are known for $i,j = 0,1,2$, one obtains for the coefficients $v_{i,j}$

$$\left.\begin{aligned}
&v_{1,0} = -2w_{1,0} = -\tfrac{2}{9}, \quad v_{0,1} = -2w_{0,1} = \tfrac{1}{6}, \\
&v_{2,0} = 3w_{1,0}^2 - 2w_{2,0} = -\tfrac{469}{5400}, \quad v_{1,1} = 6w_{1,0}w_{0,1} - 2w_{1,1} = \tfrac{401}{2160}, \\
&v_{0,2} = 3w_{0,1}^2 - 2w_{0,2} = -\tfrac{13}{144}.
\end{aligned}\right\} \tag{66}$$

Eventually, (65) and (32) for C_1 and C_3 in terms of $C_1^i C_3^j$ are transformed into

$$\left.\begin{aligned}
C_1 &= C_1^{(0)}(1 - \tfrac{2}{9}C_1^{(0)} + \tfrac{1}{6}C_3^{(0)} - \tfrac{607}{16200}C_1^{(0)^2} + \tfrac{101}{2160}C_1^{(0)}C_3^{(0)} + \tfrac{5}{144}C_3^{(0)^2}), \\
C_3 &= C_3^{(0)}(1 - \tfrac{11}{18}C_1^{(0)} + \tfrac{3}{4}C_3^{(0)} + \tfrac{257}{3600}C_1^{(0)^2} - \tfrac{403}{864}C_1^{(0)}C_3^{(0)} + \tfrac{19}{36}C_3^{(0)^2}).
\end{aligned}\right\} \tag{67}$$

For the second-order calculation, only the first three terms of these expansions for C_1 and C_3 need be taken into account. Substitution of these terms in (64) leads to the final formal second-order perturbation solution for the viscosity

$$\eta^{(2)} = \eta^{(0)}(1 - \tfrac{1}{2}C_1^{(0)} + \tfrac{2}{3}C_3^{(0)} + \tfrac{11}{270}C_1^{(0)^2} - \tfrac{23}{60}C_1^{(0)}\,C_3^{(0)} + \tfrac{11}{24}C_3^{(0)^2}). \tag{68}$$

If an ordering with respect to magnitude is pursued, at second order the last two terms of (68) must be ignored.

3.5. *Correction due to non-zero radial pressure gradient*

For an incompressible fluid the following equivalence between the radial velocity component u_r and the radial pressure gradient holds:

$$u_r = 0 \Leftrightarrow \frac{\partial p}{\partial r} = 0. \tag{69}$$

However, for a compressible fluid this equivalence is no longer valid. In that case, assuming $u_r \equiv 0$,

$$\frac{\partial p}{\partial r} = \tfrac{1}{3}\eta\left(1 + 3\frac{\kappa}{\eta}\right)\frac{\partial^2 u_z}{\partial z\,\partial r}. \tag{70}$$

This equation is almost the same as (9), but without the equalization to zero which was based on the assumption $p = p(z)$. The incompatibility of these two assumptions (conditions iv and v in §2) has already been pointed out and, therefore, the axial part of the equation of motion (10) was solved without taking the radial part (9) into account. In this subsection it will be shown that the solution derived from (10) leads nevertheless to a correction for a non-zero radial pressure gradient by means of the parameter C_3.

In order to calculate the radial pressure gradient from (70), the axial velocity $u_z(r, z)$ is expressed in terms of the maximum centreline velocity $u_m(z)$ and the profile function $E(x)$ according to (11) and (12). With $x = r/R$ that gives

$$\frac{\partial p}{\partial x} = \tfrac{1}{3}\eta\left(1 + 3\frac{\kappa}{\eta}\right)\frac{\mathrm{d}u_m}{\mathrm{d}z}\frac{\mathrm{d}E}{\mathrm{d}x}. \tag{71}$$

Subsequently, (15) for $u_m(z)$ and (35) for $E(x)$, i.e. the zero-order (parabolic) velocity profile $E_{0,0}(x)$, are substituted and the average over the cross-section of the capillary is taken for both sides of the equation. This leads to

$$\left\langle\frac{\partial p}{\partial x}\right\rangle = 2\int_0^1 x\frac{\partial p}{\partial x}\,\mathrm{d}x = \tfrac{4}{9}\eta\left(1 + 3\frac{\kappa}{\eta}\right)W\frac{1}{\rho^2}\frac{\partial \rho}{\partial z}. \tag{72}$$

By applying the operator $\int_0^L \mathrm{d}z\,\rho\,\partial/\partial z\ldots$ on this equation and, furthermore, by using the expressions (19) and (20) for the quantity Z and the parameter C_3, the following relation between C_3 and the radial pressure gradient can be obtained:

$$C_3 = -\frac{3}{X}\frac{1 + \tfrac{3}{4}\kappa/\eta}{1 + 3\kappa/\eta}\int_0^L \rho\,\mathrm{d}z\,\frac{\partial}{\partial z}\left\langle\frac{\partial p}{\partial x}\right\rangle. \tag{73}$$

This relation proves that, from the assumption $\partial p/\partial r \equiv 0$, it follows that $C_3 \equiv 0$ or, vice versa, that the introduction of the parameter $C_3 \neq 0$ turns out to be equivalent to the tacit abandonment of the condition that p is a function of z only.

A simple expression for $\langle \partial p/\partial x \rangle$ can be found from (71) by substitution of the zero-order solutions for $E(x)$ and $u_m(z)$, which are given by (35) and by the combination of (37) and (38). With the dimensionless coordinate $\zeta = z/L$ that gives

$$\left\langle \frac{\partial p}{\partial x} \right\rangle = \frac{1}{9}\left(\frac{R}{L}\right)^2 \left(1 + 3\frac{\kappa}{\eta}\right)\frac{\partial^2 p}{\partial \zeta^2}. \tag{74}$$

Equations (73) and (74) show, once again, that C_3 is of second order in R/L and, consequently, is also the correction for the non-zero radial pressure gradient.

3.6. *Discussion*

Prins (1991) showed in a treatment of capillary flow in terms of the parameter R/L, that the ratio of the radial velocity u_r to the axial velocity u_z is of the order $(R/L)^3$. This means that for computations up to the second order the radial velocity component can be neglected, as assumed by condition (ii) of §2. However, from (74) can be concluded that the ratio of $\partial p/\partial r$ to $\partial p/\partial z$ is of the first order in R/L, a result which contradicts the intuitive feeling that the two ratios should be of the same order in R/L. A partial explanation of this apparent discrepancy can be given by the remark that in the z-direction a real flow of the fluid exists whereas in the radial direction there seems to be no net flow.

Equation (74) shows that, except for the case that p depends linearly on the axial coordinate, the solution of (10) contains a non-zero radial pressure gradient; thus, the conflict with condition (v) that p is a function of z only, remains. However, as shown by Prins (1991), if $p(r, z)$ is expanded in terms of R/L, the second-order term is found to be the first which depends on r also. Hence, the error made in imposing condition (v) is at most of the second order and is, moreover, partially accounted for by the introduction of the C_3 term.

We may conclude that, for small values of C_1 (10^{-3}–10^{-5}) describing normal experimental circumstances, the simple first-order perturbation solution of (21) is sufficiently accurate for the calculation of the viscosity (or flow rate) from experimental data. For larger values of C_1, (21) has been solved numerically as will be described in the next section.

Papers dealing with a basic calculation of a compressible capillary flow are very rare. The only possibility for an extensive comparison with the present results is the work of Prud'homme *et al.* (1986) who calculated the mass-flow rate through a long tube for an ideal gas. Their solution of (10), with the bulk viscosity $\kappa = 0$ (i.e. exact in the case of a monoatomic ideal gas), also uses a perturbation method but in terms of a different set of parameters. In (A 5) of the Appendix we have expressed their result in terms of the present parameters $C_1^{(0)}$ and $C_3^{(0)}$. Thence we may conclude that up to the second order of magnitude (i.e. the terms $C_1^{(0)}$, $C_3^{(0)}$ and $C_1^{(0)2}$), the transformed Prud'homme result and the present result (68) for $\eta^{(2)}$ are matched completely in the case of an ideal gas.

4. Numerical solution

4.1. *Method*

The perturbation solutions of (21) given in the previous section are applicable for *small* values of the parameter C_1. Moreover, in the analysis so far it has been tacitly assumed that C_1 (and hence C_2) is independent of z. Actually, this assumption arises from the fact that our derivation starts from the form of the equation of motion

given in (18), integrated over L, instead of from the unintegrated form (17). A consequence of this procedure is that no insight is revealed into the development of various quantities, such as pressure, density and velocity, along the capillary in the case of a compressible flow. To overcome both limitations, a *numerical* solution of (17) will be presented in this section. The second term on the left-hand side of the equation is neglected in this computation in view of the minor impact of this term, as concluded from the estimation made in §3.3.

In analogy with the dimensionless constants C_1 and C_2 introduced in (20) we define their z-dependent counterparts as

$$\tilde{C}_1 = u_{\mathrm{m}}^2 \left(\frac{\partial \rho}{\partial p} \right)_T \tag{75}$$

and

$$\tilde{C}_2 = -\frac{\eta u_{\mathrm{m}}}{R^2 (\mathrm{d}p/\mathrm{d}z)}, \tag{76}$$

so that (17) can again be written in the form given in (21) with $C_3 = 0$. By means of the transformation $q = x\Xi$ with $\Xi = \tilde{C}_2^{-\frac{1}{2}}$ and by defining $E(x) = E(q/\Xi) = D(q)$, (21) is then transformed into

$$\tilde{C}_1 D^2(q) = 1 + \frac{1}{q} \frac{\mathrm{d}}{\mathrm{d}q} \left(q \frac{\mathrm{d}D}{\mathrm{d}q} \right), \tag{77}$$

which, subsequently, is split up into

$$\mathrm{d}D/\mathrm{d}q = B(q) \tag{78}$$

and

$$\mathrm{d}(qB(q))/\mathrm{d}q = q[-1 + \tilde{C}_1 D^2(q)]. \tag{79}$$

For a given value of $\tilde{C}_1$, the profile function $D(q)$ and the function $qB(q)$ can be solved simultaneously from these two first-order differential equations by the Runge–Kutta method (Collatz 1960), starting from the initial conditions:

$$q = 0 \begin{cases} D(q) = 1, & \dfrac{\mathrm{d}D}{\mathrm{d}q} = 0 \\[2mm] qB(q) = 0, & \dfrac{\mathrm{d}(qB)}{\mathrm{d}q} = 0. \end{cases} \tag{80}$$

The calculation is carried out for various step sizes in q and, in each of these cases, is terminated when $D(q)$ becomes negative. The transformation factor $\Xi = \Xi(\tilde{C}_1)$ can then be obtained from the no-slip condition $E(1) = 0$ as that value of q for which $D(q) = 0$. The value of the constant $\tilde{C}_2(\tilde{C}_1)$ is then found to be

$$\tilde{C}_2(\tilde{C}_1) = 1/\Xi^2. \tag{81}$$

For practical applications it is appropriate to define a new parameter $\Lambda(\tilde{C}_1)$ by

$$\Lambda(\tilde{C}_1) = I/(WR^2), \tag{82}$$

which according to (16) corresponds to

$$\Lambda(\tilde{C}_1) = \frac{2\pi}{\Xi^2} \int_0^\Xi qD(q)\,\mathrm{d}q. \tag{83}$$

Integration of (78) and (79) was performed for 51 values of the compressibility parameter $\tilde{C}_1$ between 0 and 0.50 with an increment of 0.01; for each of these values
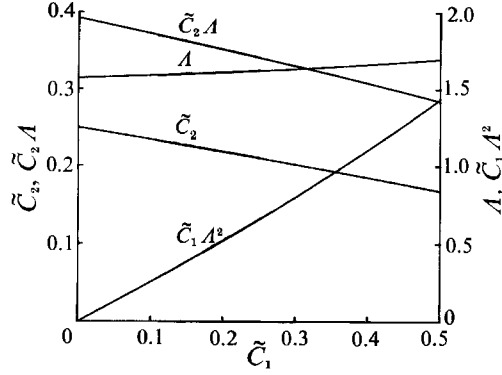
FIGURE 1. The dependence of the quantities $\tilde{C}_2$ and Λ and of the auxiliary quantities $\tilde{C}_1 \Lambda^2$ and $\tilde{C}_2 \Lambda$ on the parameter $\tilde{C}_1$, calculated numerically from the equation of motion.
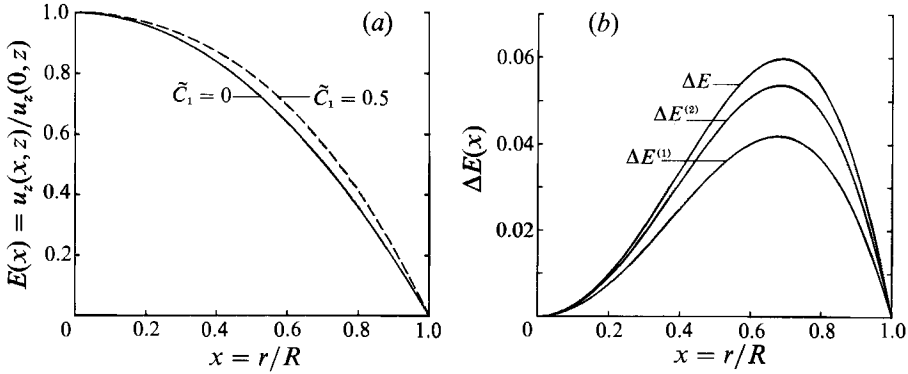

FIGURE 2. (*a*) The velocity profile $E(x)$ across the radius of the capillary for two values of the compressibility parameter $\tilde{C}_1$; $\tilde{C}_1 = 0$ represents the parabolic velocity profile for an incompressible fluid. (*b*) Deviations $\Delta E(x)$, where $\tilde{C}_1 = 0.5$, from the parabolic velocity profile for the numerically calculated profile $E(x)$, the first-order perturbation profile $E^{(1)}(x)$, and the second-order perturbation profile $E^{(2)}(x)$.

the corresponding values of both $\tilde{C}_2$ and Λ as well as those of the auxiliary quantities $\tilde{C}_1 \Lambda^2$ and $\tilde{C}_2 \Lambda$ are computed from $D(q)$. The latter two are introduced since they are convenient for practical purposes, being independent of W. The dependence on $\tilde{C}_1$ calculated for all four quantities is plotted in figure 1. By applying a step size in q as small as 0.005, the accuracy reached for Λ is 1×10^{-8}, and is even better for $\tilde{C}_2$. For $\tilde{C}_1 = 0$ (an incompressible fluid), analysis shows that $D(q) = 1 - \frac{1}{4}q^2$ so that $\bar{\Xi} = 2$, $\tilde{C}_2 = \frac{1}{4}$, and $\Lambda = \frac{1}{2}\pi$ and thus $\tilde{C}_1 \Lambda^2 = 0$ and $\tilde{C}_2 \Lambda = \frac{1}{8}\pi$.

Figure 1 shows that both $\tilde{C}_2(\tilde{C}_1)$ and $\Lambda(\tilde{C}_1)$ are monotonic functions, decreasing and increasing respectively. It turns out that the decrease of $\tilde{C}_2(\tilde{C}_1)$ is slightly steeper than that of the first- and second-order perturbation solutions $C_2^{(1)}(C_1)$ and $C_2^{(2)}(C_1)$; at $\tilde{C}_1 = 0.5$ the value of $\tilde{C}_2$ is 3.43 % lower than $C_2^{(1)}$ and 1.03 % lower than $C_2^{(2)}$.

The velocity profile $E(x)$ derived from the calculated function $D(q)$ is plotted in figure 2(*a*) for $\tilde{C}_1 = 0$ and $\tilde{C}_1 = 0.5$. The figure shows that, even for the very large value of $\tilde{C}_1 = 0.5$ (experimental values of $\tilde{C}_1$ are usually of the order 10^{-4}), only a slight deviation occurs from the parabolic profile that corresponds with $\tilde{C}_1 = 0$. The maximum absolute deviation is about 0.06 for $x = 0.69$ as can be read from figure

$a_0 =$	$3.9269904422 \times 10^{-1}$	$a_4 =$	$9.1193885456 \times 10^{-6}$
$a_1 =$	$-7.957480524 \times 10^{-2}$	$a_5 =$	$-1.3526212598 \times 10^{-6}$
$a_2 =$	$2.6279141191 \times 10^{-3}$	$a_6 =$	$-3.0505976722 \times 10^{-7}$
$a_3 =$	$2.385641376 \times 10^{-4}$	$a_7 =$	$6.3540042251 \times 10^{-9}$

TABLE 1. Polynomial coefficients for $\tilde{C}_2 \Lambda$ as a function of $\tilde{C}_1 \Lambda^2$

$2(b)$, where the deviations from the parabolic profile are plotted for the exact profile $E(x)$ and also for the first- and second-order perturbation profiles $E^{(1)}(x)$ and $E^{(2)}(x)$ as given in (51) and (63).

The calculation procedure for the viscosity, starting from the experimental data for the mass-flow rate I and the pressures p_b and p_{ex} at the ends of the capillary, is based on the quantities $\tilde{C}_2 \Lambda$ and $\tilde{C}_1 \Lambda^2$ which were determined in the foregoing numerical analysis. Firstly, $\tilde{C}_2 \Lambda$ was fitted by a least-squares method to a polynomial in $\tilde{C}_1 \Lambda^2$,

$$\tilde{C}_2 \Lambda = \sum_{i=0}^{7} a_i (\tilde{C}_1 \Lambda^2)^i. \tag{84}$$

The values of coefficients a_0–a_7 are given in table 1. The value of a_0 practically equals $\frac{1}{8}\pi$. The standard deviation of this fit is 9.3×10^{-11}.

By using definitions (15) and (82) for W and Λ we obtain

$$\tilde{C}_1 \Lambda^2 = \frac{I^2}{R^4 \rho^2} \frac{\partial \rho}{\partial p} \tag{85}$$

and

$$\tilde{C}_2 \Lambda = -\frac{I\eta}{R^4 \rho \, dp/dz} \tag{86}$$

The latter equation is rewritten as

$$\eta \, dz = -(R^4/I) \, (\tilde{C}_2 \Lambda) \, \rho \, dp, \tag{87}$$

and then integrated over L. This results in

$$\eta = \frac{R^4}{IL} \int_{p_{ex}}^{p_b} (\tilde{C}_2 \Lambda) \, \rho \, dp, \tag{88}$$

or

$$\eta = \eta^{(0)}(1+\Delta) \quad \text{with} \quad \Delta = \frac{1}{X} \int_{p_{ex}}^{p_b} \left[\frac{8}{\pi} (\tilde{C}_2 \Lambda) - 1 \right] \rho \, dp. \tag{89}$$

The interval $[p_{ex}, p_b]$ is divided into a sufficiently large number, $2n$, of equal intervals. For each intermediate pressure

$$p_i = p_b - \frac{i}{2n} (p_b - p_{ex}), \quad i = 1, 2, \ldots, 2n-1,$$

the density $\rho = \rho(p)$ and the derivative $\partial \rho / \partial p$ are calculated from the equation of state (7). Then, for the series of pressure values p_i, the quantity $\tilde{C}_1 \Lambda^2$ is computed using (85) and, next, the corresponding values of $\tilde{C}_2 \Lambda$ are calculated, using the polynomial fit (84). Finally, the integrals appearing in (19) for X and in (89) for Δ are computed using the well-known Simpson method. For the particular case of an incompressible fluid ($\tilde{C}_2 \Lambda = \frac{1}{8}\pi$), the correction Δ equals zero, as required.

If the common assumption is made that parameter $\tilde{C}_1$ (and hence $\tilde{C}_2$ and Λ) has a constant value in the pressure range over the capillary, then

$$\Delta = (8/\pi)(C_2\Lambda) - 1, \tag{90}$$

and

$$C_1\Lambda^2 = I^2 Y/(R^4 X). \tag{91}$$

With (38) and (42) this expression for $C_1\Lambda^2$ is written as

$$C_1\Lambda^2 = (\tfrac{1}{2}\pi)^2 C_1^{(0)}, \tag{92}$$

and substituted in the polynomial (84). Using also the values of the coefficients a_i given in table 1, this yields

$$\Delta = \frac{8}{\pi}\sum_{i=1}^{7}(\tfrac{1}{2}\pi)^{2i}\, a_i\, C_1^{(0)^i}, \; = -0.500\,000\, C_1^{(0)} + \frac{11.0000}{270} C_1^{(0)^2} + \dots. \tag{93}$$

Thus, from this result for Δ, we may conclude that the numerical calculation for a constant C_1 leads to the same coefficients for the linear and quadratic term in $C_1^{(0)}$ as found in the second-order perturbation solution (68).

Calculation of the correction Δ on the viscosity according to (89) for a non-constant $\tilde{C}_1$ and according to (90) for a constant C_1 shows that, for practical purposes, the two (small) values of Δ do not differ significantly. Therefore, there is no necessity to apply the more elaborate non-constant $\tilde{C}_1$ differential method for calculation of the viscosity. On the other hand, this method is very well suited for obtaining insight into the dependence on the axial coordinate for various quantities.

4.2. *Application*

The main goal of this paper is to provide a soundly based formalism for the evaluation of the coefficient of viscosity from experimental data measured with a capillary viscometer. We have applied (van den Berg *et al.* 1990) this formalism to our experimental data for ethylene, obtained by means of a viscometer with a capillary with radius $R = 3.87 \times 10^{-5}$ m and length $L = 0.8162$ m. This application showed in particular the significance of the compression factor F_c (equation (40)) with respect to the calculated viscosity values. Moreover, as will be reported in a future paper, it turned out that these values agree very well with those obtained by other authors from various experimental techniques. This agreement yields an independent argument for the validity of the formalism for a compressible capillary flow as presented here.

To give an example of the actual numerical computation of the dependence on z for various functions, we have selected one of our data points on ethylene. The point chosen is in the critical region (temperature 1.3 K above the critical temperature $T_c = 282.35$ K) in order to emphasize the impact of a large compressibility κ_T of the fluid on the z-dependence of the quantities involved. This point is characterized by a mass-flow rate $I = 4.555 \times 10^{-7}$ kg/s, pressure $p_b = 5.197\,00$ MPa and $p_{ex} = 5.160\,94$ MPa and thus a pressure difference $\Delta p = 3.606 \times 10^{-2}$ MPa, and density $\rho_b = 8.264$ mol/l and $\rho_{ex} = 6.355$ mol/l. We have calculated a mean density $\langle\rho(p)\rangle = 7.182$ mol/l, compression factor $\langle\rho(p)\rangle/\rho_b = 0.8691$, a Reynolds number $Re^{(0)} = 435$, acceleration/profile correction $\Delta = 0.00068$, viscosity $\eta_p = 19.81$, $\eta^{(0)} = 17.22$ and $\eta = 17.21$ µPa s. The equation of state developed by IUPAC (Jacobsen *et al.* 1988) has been used.

The profiles of the functions $p(z)$, $\rho(z)$ and $u_m(z)$, $\tilde{C}_1(z)$ and $\kappa_T(z)$ versus the reduced axial coordinate z/L are displayed respectively in figures 3(a), 3(b) and 3(c). In
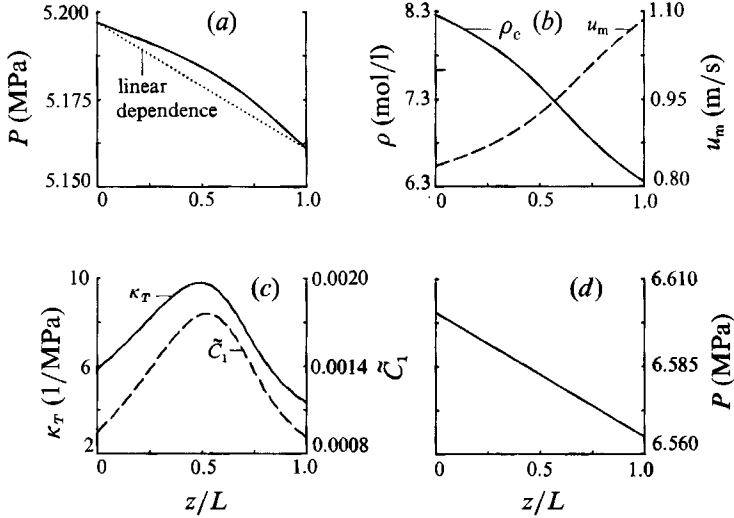
FIGURE 3. The dependence of various quantities on the axial coordinate in a capillary (radius 0.0387 mm, length 816.2 mm) for a flow of ethylene: (a–c) refer to a data point close to the critical point and (d) to a point far away from it. (a) and (d) the dependence of the pressure: (b) the dependence of the density and the velocity, ρ_c is the critical density; (c) the dependence of the isothermal compressibility and the compressibility parameter.

figure 3(a), the deviation of $p(z)$ from the frequently used approximation of a linear pressure dependence is striking. The determination of $p(z)$ is based on (86). For the series of equidistant pressures p_i, the values of dp/dz are calculated with this equation at given η from the known $\tilde{C}_2\Lambda$-values. Subsequently, successive Simpson integrations over n sets of three dz/dp-values lead to the values $z_{2i} = z(p_{2i})$ for $i = 1$, $2, \ldots, n$ starting from $z(p_b) = 0$, and thus lead to $p(z)$. In figure 3(b), the decreasing S-curve for the density $\rho(z)$, crossing the critical density ρ_c, is shown, together with the (30%) increasing velocity $u_m(z)$. The density is found directly from $p(z)$ by means of the equation of state. From $\rho(z)$ the other mean density $\langle\rho(z)\rangle$, defined in the paragraph following (19), has been calculated as 7.316 mol/l, which is 1.9% larger than $\langle\rho(p)\rangle$. For the quantity Z (equation (19)), written as $fY^2/L, f = 1.49$ is found. The velocity is calculated from (75) using the $\tilde{C}_1$-values found from the set of $\tilde{C}_2\Lambda$-values by means of the polynomial fit

$$\tilde{C}_1 = \sum_{i=1}^{4} b_i \left(1 - \frac{8}{\pi}\tilde{C}_2\Lambda\right)^i. \tag{94}$$

This polynomial is determined by a least-squares method applied to the 51 pairs of $(\tilde{C}_1, \tilde{C}_2\Lambda)$-values for $\tilde{C}_1 = 0$, 0.01, 0.02,..., 0.5 which were introduced earlier and which correspond with $1 - (8/\pi)\tilde{C}_2\Lambda = 0$, ≈ 0.005, $\approx 0.010, \ldots, \approx 0.275$. The values of the coefficients b_1–b_4 are: $b_1 = 2.0000179$; $b_2 = -0.56375100$; $b_3 = -0.32775611$; $b_4 = -0.21998542$. The standard deviation of this fit is 1.7×10^{-7}.

From figure 3(c) it can be seen that, due to the maximum in the compressibility κ_T, $\tilde{C}_1$ also has a maximum nearly halfway along the capillary and that, in spite of the large κ_T, the values of $\tilde{C}_1$ remain small with an average of 1.4×10^{-3}.

The computation of $z(p)$ and $u_m(z)$ can easily be checked since $z(p_{ex})$ must be equal to L and the product $\rho(z)u_m(z)$ is equal to the quantity W, which must be constant, i.e. independent of z.

For comparison, the function $p(z)$ is shown in figure 3(d) for a similar data point, but at a temperature much farther (16 K) above the critical temperature. The pressure dependence is linear in this case, where $\kappa_T \approx 0.54 \text{ MPa}^{-1}, \tilde{C}_1 \approx 8.10^{-5}$, $\langle\rho(p)\rangle = 6.475$ mol/l, $\langle\rho(p)\rangle/\rho_b = 0.9902$, $\langle\rho(z)\rangle = 6.477$ mol/l and $u_m(z)$ shows a slight (2%) linear increase with z.

Appendix

The corrected† result of Prud'homme *et al.* (1986) for the mass flow of an ideal gas through a long tube can be written as

$$I = \frac{\pi R^4}{8\eta L}\rho_b h(\epsilon)\,\Delta p\,[1 - \tfrac{1}{32}\kappa^*\epsilon\beta(1-\epsilon)\,(h(\epsilon))^{-2}$$
$$+ \tfrac{2}{3}(\epsilon\beta)^2\,(h(\epsilon))^{-1} + \tfrac{73}{34560}(\kappa^*\epsilon\beta)^2\,(h(\epsilon))^{-3} + \ldots\,], \quad \text{(A 1)}$$

with

$$\epsilon = \frac{\rho_b - \rho_{ex}}{\rho_b}, \quad h(\epsilon) = 1 - \tfrac{1}{2}\epsilon, \quad \kappa^* = \frac{R^3\rho_b\,\Delta p}{\eta^2 L}h(\epsilon), \quad \beta = \frac{R}{L}. \quad \text{(A 2)}$$

Furthermore, since the gas is ideal, the mean density is $\langle\rho(p)\rangle = \tfrac{1}{2}(\rho_b + \rho_{ex}) = h(\epsilon)\rho_b$. In order to make a comparison between (A 1) and the present second-order perturbation solution (68), the quantities $\kappa^*\epsilon\beta$ and $(\epsilon\beta)^2$ must be expressed in the parameters $C_1^{(0)}$ and $C_3^{(0)}$ as given in (42) and (44) with $f^* = 1$ (so $f = 3$). Therefore, we substitute

$$\kappa^* = \frac{R^3 X}{\eta^2 L} = 4Re^{(0)}\left(\frac{\eta^{(0)}}{\eta}\right)^2 \quad \text{and} \quad \epsilon = 1 - \mathrm{e}^{-Y} = Y(1 - \tfrac{1}{2}Y + \ldots). \quad \text{(A 3)}$$

Using (68) for $\eta/\eta^{(0)}$ and omitting those terms which exceed the second order of magnitude, one finds

$$\kappa^*\epsilon\beta = 16C_1^{(0)}(1 + C_1^{(0)}), \quad (\kappa^*\epsilon\beta)^2 = 256C_1^{(0)^2}, \quad (\epsilon\beta)^2 = C_3^{(0)}. \quad \text{(A 4)}$$

Substitution in Prud'homme's formula (A 1) yields

$$\eta = \eta^{(0)}[1 - \tfrac{1}{2}C_1^{(0)} - \tfrac{1}{2}C_1^{(0)^2} + \tfrac{2}{3}C_3^{(0)} + \tfrac{146}{270}C_1^{(0)^2}]$$
$$= \eta^{(0)}[1 - \tfrac{1}{2}C_1^{(0)} + \tfrac{2}{3}C_3^{(0)} + \tfrac{11}{270}C_1^{(0)^2}]. \quad \text{(A 5)}$$

REFERENCES

BERG, H. R. VAN DEN, SELDAM, C. A. TEN & GULIK, P. S. VAN DER 1990 *Physica* A **167**, 457.
BERG, H. R. VAN DEN, SELDAM, C. A. TEN & GULIK, P. S. VAN DER 1993 *Intl J. Thermophys.* (in press).

† Prud'homme *et al.* (1986) erroneously calculated the coefficient of $\kappa^*\epsilon\beta$ as 0.0291854 instead of $\tfrac{1}{32} = 0.03125$ and the coefficient of $(\kappa^*\epsilon\beta)^2$ as 0.0022685 instead of $73/34560 = 0.0021122685$.

BIRD, R. B., STEWART, W. E. & LIGHTFOOT, E. N. 1960 *Transport Phenomena*. John Wiley & Sons.

COLLATZ, L. 1960 *The Numerical Treatment of Differential Equations*. Springer.

ERK, S. 1929 *Z. Techn. Phys.* **10**, 452.

JACOBSEN, R. T., JAHANGIRI, M., STEWART, R. B., McCARTY, R. D., LEVELT SENGERS, J. M. H., WHITE, H. J., SENGERS, J. V. & OLCHOWY, G. A. 1988 *Ethylene (Ethene), International Thermodynamic Tables of the Fluid State*, Vol. 10. Blackwell Scientific.

KAO, J. T. F., RUSKA, W. & KOBAYASHI, R. 1968 *Rev. Sci. Instrum.* **39**, 824.

KARIM, S. M. & ROSENHEAD, L. 1952 *Rev. Mod. Phys.* **24**, 108.

KESTIN, J., IMAISHI, N., NOTT, S. H., NIEUWOUDT, J. C. & SENGERS, J. V. 1985 *Physica* A **134**, 38.

KESTIN, J., SOKOLOV, M. & WAKEHAM, W. 1973 *Appl. Sci. Res.* **27**, 241.

MADIGOSKY, W. M. 1967 *J. Chem. Phys.* **46**, 4441.

POISEUILLE, J. L. 1840 *C.R. Hebd. Sean. Acad. Sci.* **11**, 961; 1041.

PRINS, H. J. 1991 The optimal model for a non-Newtonian compressible gass. *Rep. Fac. of Techn. Math. & Informatics, Delft Univ. of Technol.*

PRUD'HOMME, R. K., CHAPMAN, T. W. & BOWEN, J. R. 1986 *Appl. Sci. Res.* **43**, 67.