Investigating enhanced mass flow rates in pressure-driven liquid flows in nanotubes

Alexandros Stamatiou ©, S Kokou Dadzie © and M H Lakshminarayana Reddy ©
School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, Scotland, United Kingdom
E-mail: alexandros.stamatiou@hw.ac.uk
Keywords: micro- and nanofluidics, continuum models, Navier–Stokes equations, mass/volume diffusion

Abstract
Over the past two decades, several researchers have presented experimental data from pressure-driven liquid flows through nanotubes. They quote flow velocities which are four to five orders of magnitude higher than those predicted by the classical theory. Thus far, attempts to explain these enhanced mass flow rates at the nanoscale have focused mainly on introducing wall-slip boundary conditions on the fluid mass velocity. In this paper, we present a different theory. A change of variable on the velocity field within the classical Navier–Stokes equations is adopted to transform the equations into physically different equations. The resulting equations, termed re-casted Navier–Stokes equations, contain additional diffusion terms whose expressions depend upon the driving mechanism. The new equations are then solved for the pressure driven flow in a long nano-channel. Analogous to previous studies of gas flows in micro- and nano-channels, a perturbation expansion in the aspect ratio allows for the construction of a 2D analytical solution. In contrast to slip-flow models, this solution is specified by a no-slip boundary condition at the channel walls. The mass flow rate can be calculated explicitly and compared to available data. We conclude that the new re-casting methodology may provide an alternative theoretical physical explanation of the enhanced mass flow phenomena.

1. Introduction

Advances in technology have highlighted the importance of understanding and modelling fluids in micro- and nano-structures found in many mechanical and bio-mechanical devices. An important example of these structures are micro- and nano-electro-mechanical systems (MEMS/NEMS) devices such as micromotors, comb microdrives, blood flow analysers and particle separators [1, 2]. Other areas of interest include transport in aquaporin water channels in biological cell membranes [3] and gas flow through shale rock formations [4]. A key feature of fluid flow in these confined spaces is a significant departure from predictions of the classical Navier–Stokes equations. Experimental evidence on both gases and liquids points towards enhanced mass flow rates in micro- and nano-sized ducts when compared to the classical no-slip Hagen–Poiseuille flow law. This was first observed by Knudsen [5] while investigating the flow of rarefied gases in narrow tubes. His findings were later confirmed and extended for gases in various states of rarefaction [6, 7]. The extent to which a gas is rarefied is conveniently expressed by the dimensionless Knudsen number \( Kn = \lambda/h \), where \( \lambda \) is the mean free path of a gas molecule and \( h \) the height/diameter of the confining duct. An extensive experimental data-set covering the widest range of Knudsen number (0.01 < \( Kn < 100 \)) to date is given by Ewart et al [8] for the flow of helium in long rectangular micro-channels of 9.38 \( \mu \)m height and the reported data clearly capture the famous Knudsen minimum at \( Kn \approx 0.8 \). In stark contrast to Navier–Stokes based predictions, the mass flow rate increases further as the gas becomes more rarefied.

While enhanced flow rates of rarefied gases have been known since Knudsen’s original findings, the phenomenon of enhanced liquid flows in micro- and nano-channels is a more recent discovery. Early indications of this were given by Pfahler et al, who found \( n \)-propanol flow rates to be three times higher than expected in rectangular channels of 800 nm long [9]. At much smaller scales, both Majumder et al [10, 11] and
Du et al. reported very large enhancement factors of order $10^6-10^7$ for flow of different liquids in carbon nanotubes (CNTs) of 5–7 nm diameter. Concentrating on water flow through CNTs of diameter < 2 nm, Holt et al. found enhancement factors of order $10^5–10^6$, while Qin et al. found enhancement factors of order less than $10^5$. With the aim of expanding this data-set, Whitby et al. investigated liquid flow through channels of 46 nm diameter, calculating a factor 20–37 enhancement over no-slip Hagen-Poiseuille flow. In addition to these experiments, several researchers have performed molecular dynamics (MD) simulations [16, 17], although computational costs put a limit on the diameter and length of simulated channels.

With regard to the theoretical explanation of anomalous flow phenomena such as enhanced mass flow rates, it can be concluded that the Navier–Stokes equations fall short. One major analytical approach is to extend their applicability by replacing the classical wall-adherence (no-slip) condition with a wall–slip condition. This idea can be traced back to the work of Maxwell [18], who introduced the tangential momentum accommodation coefficient (TMAC) as the ratio of molecules which are specularly (keeping their momentum) and diffusively (giving up their momentum) deflected after a collision with the wall. For the analysis of rarefied gas flow, the TMAC has been used in first order [6] and in second order [7] Navier–Stokes based slip-flow models to obtain agreement with experimental data up to $Kn \approx 0.3$. This was further improved by Arlemark et al. [19] through the introduction of a geometry-dependent, effective mean free path of gas molecules confined to small ducts. However, for $Kn > 0.5$, even this modified slip model starts to deviate clearly from the experimental data [8], suggesting that slip models cannot fully account for the observed mass flow rates. What is more, the TMAC is strictly an empirical parameter and cannot be used in a predictive manner. Further doubts on the slip flow approach in rarefied gas flow have been cast by Veltzke and Thöming [20]. In fact, they highlighted several contradictory experimental measurements of the TMAC and point towards the apparent inconsistency of combining the Navier–Stokes equations (first order in $Kn$) with higher order boundary conditions.

A second major analytical approach focuses on the inclusion of mass diffusion as an additional transport mechanism. In [20], the authors proposed to model the mass flow rate expression as a simple superposition of the no-slip Hagen–Poiseuille flow law with a Fickian diffusive term. Replacing the slip-flow condition by mass diffusion allowed them to successfully predict a range of experimental data.

The contemplation of a mass diffusive term stems from the idea that the Navier–Stokes equations are incomplete, in the sense that they break down under certain extreme conditions such as large density or temperature gradients or indeed for flow at the micro- and nanoscale. Several researches have suggested that the constitutive assumptions of the Navier–Stokes–Fourier formalism must be extended (e.g. [21, 22]). A variety of such extended hydrodynamic equations have been suggested. Among them are the Quasihydrodynamic/Quasigasdynamic (QHD/QGD) equations [23, 24], Brenner’s Volume Diffusion/Bi-velocity model [25], the Extended Navier–Stokes equations by Chakraborty and Durst [26] and, more recently, a new Eulerian model for compressible flow by Svärd [27]. A common feature of all these fluid models is the appearance somehow of an additional mass diffusive term in the system of equations. Dadzie and Brenner applied the Volume Diffusion/Bi-velocity model to gaseous flow in microchannels [28]. In combination with a first-order slip condition, they found agreement with the experimental data in [8] up to a Knudsen number of 5. Taking into account a corrected mean-free path for flow in confined spaces, Lv et al. were able to improve this agreement up to a Knudsen number of 50. More recently, Christou and Dadzie achieved a match over the entire range of Knudsen number in another numerical simulation based on the Bi-velocity model [30].

Motivated by the success of mass diffusive models in the analysis of rarefied gas flow, the present paper explores the possibility of applying the idea to liquid flows. We propose a unifying re-casting methodology by which a new class of continuum models, termed re-casted Navier–Stokes equations (RNS), can be directly derived from the original Navier–Stokes equations [31, 32]. The idea is based on transforming the velocity vector field within the classical equations depending on the driving mechanism of the flow. This theory is described in detail in section 2 for the case of isothermal, pressure-driven liquid flow. In section 3, a rigorous perturbation analysis of the new set of equations is carried out to derive a simpler set of equations governing the flow in channels of small aspect ratio. The latter are solved analytically in section 4 to yield an expression for the mass flow rate through the tube. Finally, in section 5, the theoretical mass flow rate is compared with the available experimental data. Our aim is to show that the RNS model can provide an alternative explanation for enhanced liquid flow rates observed in nano-channels.

2. Re-casted Navier–Stokes equations for isothermal pressure-driven flow

For flow under isothermal conditions, we can restrict attention to the transport of mass and momentum only. In the classical Navier–Stokes formalism, these are governed by the following balance laws:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{U}_m) = 0, \quad (1)
\]
\begin{equation}
\frac{\partial (\rho U_m)}{\partial t} + \nabla \cdot (\rho U_m \otimes U_m) + \nabla \cdot [p I + \Pi^{(NS)}] = 0.
\end{equation}

Here, \( \rho = \rho(x, t) \) is the fluid density, \( p = p(x, t) \) is the pressure and \( \Pi^{(NS)} \) is the Newtonian stress tensor which is given in terms of the fluid’s dynamic viscosity \( (\mu) \) as:

\begin{equation}
\Pi^{(NS)} = -2\mu \left[ \frac{1}{2}(\nabla U_m + (\nabla U_m)^T) - \frac{1}{3} I (\nabla \cdot U_m) \right] = -2\mu \frac{\rho}{p} \nabla U_m.
\end{equation}

The unknown velocity field \( U_m = U_m(x, t) \) is that of the conventional mean mass velocity. In our new theory, an externally applied pressure gradient is the principal driving mechanism of the flow; hence we assume that the classical mass velocity can be written in terms of a new pressure diffusion velocity \( U_p \) as:

\begin{equation}
U_m = U_p - \kappa_p \nabla \ln p = U_p - \frac{\kappa_p}{\rho} \frac{\nabla p}{p}.
\end{equation}

The second term on the right hand side represents a mass diffusion mechanism driven by the pressure gradient. This distinction between \( U_m \) and \( U_p \) is analogous to the idea of a volume velocity in gas [22, 25, 28]. The precise functional form of the molecular pressure diffusion coefficient \( \kappa_p \) is not yet understood. For simplicity, it is assumed to be constant in the following derivations.

Substituting equation (4) into the Navier–Stokes equations (1)–(2) and later re-arranging terms leads to the re-casted Navier–Stokes (RNS) equations for mass and momentum:

\begin{equation}
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho U_p) = \nabla \cdot (\kappa_p \rho \nabla \ln p),
\end{equation}

\begin{equation}
\frac{\partial (\rho U_p)}{\partial t} - \kappa_p \rho \nabla \ln p + \nabla \cdot (\rho U_p \otimes U_p) + \nabla \cdot [p I + \Pi^{(RNS)}] = 0.
\end{equation}

The last term on the left-hand side of equation (6) contains the new stress tensor:

\begin{equation}
\Pi^{(RNS)} = \Pi_p - \rho \kappa_p (U_p \otimes \nabla \ln p + \nabla \ln p \otimes U_p) + \rho \kappa_p \nabla \nabla \ln p \otimes \nabla \ln p,
\end{equation}

where \( \Pi_p \) denotes the transformed Newtonian stress tensor,

\begin{equation}
\Pi^{(NS)} \longrightarrow \Pi_p = -2\mu \nabla U_p + 2\mu \kappa_p \nabla \nabla \ln p + \frac{2}{3} \mu \kappa_p (\nabla^2 \ln p) I.
\end{equation}

We can also write the new momentum equation (6) in the following form:

\begin{equation}
\frac{\partial (\rho U_p - \kappa_p \rho \nabla \ln p)}{\partial t} + \nabla \cdot (\rho U_p \otimes U_p) = \nabla \cdot T^{(RNS)},
\end{equation}

with the tensor \( T^{(RNS)} \) on the right-hand side of this equation given by,

\begin{equation}
T^{(RNS)} = \left( -p - \frac{2}{3} \frac{\mu \kappa_p}{\rho^2} \| \nabla p \|^2 + \frac{2}{3} \frac{\mu \kappa_p}{\rho} \nabla^2 p \right) I
\end{equation}

\begin{equation}
+ \frac{1}{p^2} (2\mu \kappa_p - \rho \kappa_p^2) \nabla \nabla \nabla \rho \otimes \nabla \rho + 2\mu D(U_p) - \frac{2}{3} \mu \nabla \nabla \nabla U_p) I
\end{equation}

\begin{equation}
- 2\frac{\mu \kappa_p}{p} \nabla \nabla \rho + \frac{\rho \kappa_p}{p} U_p \otimes \nabla p + \frac{\rho \kappa_p}{p} \nabla p \otimes U_p.
\end{equation}

Here, \( D(U_p) \) denotes the symmetric part of the velocity gradient. A parallel can be drawn from the structure of tensor \( T^{(RNS)} \) and Korteweg’s stress tensor \( T^{33} \). Korteweg augmented the Newtonian stress tensor with the dyadic product \( \nabla \rho \otimes \nabla \rho \) to represent forces experienced by fluids during phase transitions. His complete tensor may be written as [34]:

\begin{equation}
T = (-p + \alpha_0 \| \nabla p \|^2 + \alpha_1 \nabla^2 p) I + \beta \nabla \rho \otimes \nabla \rho + 2\mu D(v) - \lambda (\nabla \cdot v) I,
\end{equation}

where the material coefficients \( \alpha_0, \alpha_1, \beta, \mu, \lambda \) may depend on \( \rho \) as well. On comparing equation (11) with (10), we note that all terms involved in the structure of the Korteweg stress tensor are found in the re-casted Navier–Stokes tensor, but written with \( p \) rather than \( \rho \).

3. Model equations for flows in micro- and nanotubes

In the experiment described by Majumder et al [11], different liquids were forced to flow through carbon nanotube (CNT) membranes by means of a constant externally applied pressure gradient of 1 bar. The cross-sectional area of CNT membrane exposed to the flow was 0.785 cm², with a length \( L \) of only 126 µm. The millions of fluid-carrying pores were envisaged as aligned cylindrical tubes of diameter \( d \) and length \( L \), where \( d \) was determined to be about 7 nm. The volume of fluid exiting the membrane was collected over a period of time.
Table 1. Summary of experimental data available in the literature and corresponding $\alpha^*$ values as predicted by the new equation (66).

**Experimental data for 2 nm CNTs; Holt et al (2006)**

| Liquid          | Pore diameter $d$ (nm) | Membrane thickness $L$ (μm) | Pressure difference $\Delta P$ (bar) | Enhancement factor $\gamma$ | Pressure diffusivity $K_p$ ($\times 10^{-7}$ m$^2$/s) | Dimensionless parameter $\alpha^*$ |
|-----------------|------------------------|-----------------------------|-------------------------------------|----------------------------|---------------------------------------------------|----------------------------------|
| water (DWNT 1)  | 2                      | 2                           | 1                                   | 1500–8400                  | 0.27–1.5                                          | 0.027–0.15                       |
| water (DWNT 2)  | 2                      | 3                           | 1                                   | 680–3800                   | 0.12–0.69                                         | 0.012–0.069                      |
| water (DWNT 3)  | 2                      | 2.8                         | 1                                   | 560–3100                   | 0.1–0.56                                          | 0.01–0.056                       |

**Experimental data for 7 nm CNT membranes; Majumder et al (2005)**

| Liquid | Pore diameter $d$ (nm) | Membrane thickness $L$ (μm) | Viscosity $\mu$ (cP) | Density $\rho$ (kg/m$^3$) | Pressure difference $\Delta P$ (bar) | Hagen-Poiseuille velocity (cm/s) | Measured velocity (cm/s) | Enhancement factor $\gamma$ | Pressure diffusivity $K_p$ ($\times 10^{-21}$ m$^3$/s) | Dimensionless parameter $\alpha^*$ |
|--------|------------------------|-----------------------------|----------------------|--------------------------|-------------------------------------|--------------------------------|----------------------------|--------------------------|---------------------------------------------------|----------------------------------|
| hexane | 7                      | 126                         | 0.3                  | 635                      | 1                                   | $4.1 \times 10^{-4}$          | 5.6                        | 1.1 $\times 10^4$           | 80                                                | 17.45                             |
| decane | 7                      | 126                         | 0.9                  | 730                      | 1                                   | $1.4 \times 10^{-4}$          | 0.67                       | 3.9 $\times 10^3$           | 9.6                                               | 0.78                              |
| water (1) | 7                   | 34                           | 1                    | 1000                     | 1                                   | $1.2 \times 10^{-4}$          | 26.1                       | 1.7 $\times 10^5$           | 370                                               | 37.24                             |
| water (2) | 7                   | 34                           | 1                    | 1000                     | 1                                   | $1.2 \times 10^{-4}$          | 43.90                      | 2.8 $\times 10^5$           | 630                                               | 62.64                             |
| water (3) | 7                   | 126                          | 1                    | 1000                     | 1                                   | $1.2 \times 10^{-4}$          | 9.50                       | 6.1 $\times 10^4$           | 140                                               | 13.56                             |
| EtOH    | 7                      | 126                         | 1.1                  | 789                      | 1                                   | $1.1 \times 10^{-4}$          | 4.5                        | 3.2 $\times 10^3$           | 64                                                | 4.61                              |
| IPA     | 7                      | 126                         | 2                    | 786                      | 1                                   | $0.61 \times 10^{-4}$         | 1.12                       | $1.4 \times 10^3$          | 16                                                | 0.63                              |

**Experimental data for 44 nm CNT membranes; Whitby et al (2008)**

| Liquid | Pore diameter $d$ (nm) | Membrane thickness $L$ (μm) | Pressure difference $\Delta P$ (bar) | Hagen-Poiseuille flow rate ($\times 10^{-21}$ m$^3$/s) | Measured velocity flow rate ($\times 10^{-21}$ m$^3$/s) | Enhancement factor $\gamma$ | Pressure diffusivity $K_p$ ($\times 10^{-7}$ m$^3$/s) | Dimensionless parameter $\alpha^*$ |
|--------|------------------------|-----------------------------|-------------------------------------|----------------------------------------------------------|--------------------------------------------------------|--------------------------|---------------------------------------------------|----------------------------------|
| decane | 44                     | 78                          | 0.071                               | 8.7                                                      | 190–410                                               | 22–47                    | 1.4–3.1                                           | 0.11–0.24                       |
| ethanol | 44                     | 78                          | 0.071                               | 7.8                                                      | 120–210                                               | 15–27                    | 8.8–1.6                                           | 0.07–0.12                       |
| water  | 44                     | 78                          | 0.071                               | 8.4                                                      | 170–310                                               | 20–37                    | 1.2–2.3                                           | 0.13–0.23                       |
Taking into account the membrane’s porosity, it was then possible to establish the volumetric flow rate through a single nanotube, which was compared with the theoretical flow rates predicted by the classical (no-slip) Hagen-Poiseuille flow law (see table 1 in section 5). Figure 1 shows a schematic of a CNT membrane (not to scale) with an individual nanopore enlarged to highlight its cylindrical geometry. A similar experimental set-up was adopted by other researchers [12–15].

3.1. Governing equations

For an analytical treatment of the flow configuration described in figure 1 using the re-casted Navier–Stokes equations (5)–(8), we can make several simplifications based on geometrical considerations. Firstly, we assume that the liquid density $\rho$ and viscosity $\mu$ are constant. Furthermore, the maintenance of a constant pressure difference and the length of the tube imply that the flow can be considered steady, with minimal entrance/exit losses. Thus, the unknown fields $U_p$ and $p$ are functions of position $x = (x, y, z)$ only. With these assumptions in place, equations (5)–(8) can be simplified and re-written as follows:

$$\nabla \cdot U_p = \kappa_p \nabla^2 \ln p,$$

$$\rho U_p \cdot \nabla U_p - \rho \kappa_p \nabla \ln p \cdot \nabla U_p - \rho \kappa_p U_p \cdot \nabla (\nabla \ln p) + \rho \kappa_p \nabla \ln p \cdot \nabla (\nabla \ln p) = - \nabla p + \mu \nabla^2 U_p - \kappa_p \mu \nabla^2 (\nabla \ln p).$$

For the nanotube geometry shown in figure 1, it is most convenient to transform these equations into cylindrical polar coordinates $(r, \theta, z)$. The radial symmetry implies that the flow fields are independent of the swirl angle $\theta$. Moreover, we can assume that the $\theta$-component of the velocity is zero, so:

$$U_p = U_p(r, z) = U_p^r(r, z) \hat{r} + U_p^\theta(r, z) \hat{\theta} + U_p^z(r, z) \hat{z}, \quad p = p(r, z).$$

Then, using the transformed expression for the gradient operator in cylindrical polar coordinates, equations (12)–(13) can be written in component form as follows:

**mass balance:**

$$\frac{\partial U_p^r}{\partial r} - \kappa_p \frac{\partial^2 \ln p}{\partial r^2} + \frac{U_p^r}{r} - \kappa_p \frac{\partial \ln p}{\partial r} + \frac{\partial U_p^z}{\partial z} - \kappa_p \frac{\partial^2 \ln p}{\partial z^2} = 0,$$

**$r$-momentum balance:**

$$\rho U_p^r \frac{\partial U_p^r}{\partial r} - \rho \kappa_p \frac{\partial \ln p}{\partial r} \frac{\partial U_p^r}{\partial r} - \rho U_p^r \kappa_p \frac{\partial^2 \ln p}{\partial r^2} - \rho \kappa_p \frac{\partial \ln p}{\partial z} \frac{\partial U_p^r}{\partial z} + \rho \kappa_p^2 \frac{\partial \ln p}{\partial z} \frac{\partial^2 \ln p}{\partial z^2} + \rho U_p^r \frac{\partial U_p^z}{\partial z}$$

$$= - \rho \kappa_p \frac{\partial \ln p}{\partial z} \frac{\partial U_p^r}{\partial z} - \rho U_p^r \kappa_p \frac{\partial^2 \ln p}{\partial z^2} - \rho \kappa_p^2 \frac{\partial \ln p}{\partial z} \frac{\partial^2 \ln p}{\partial z^2} = - \frac{\partial p}{\partial r} + \mu \frac{\partial^2 U_p^r}{\partial r^2}.$$

Then, using the expression for the gradient operator in cylindrical polar coordinates, equations (12)–(13) can be written in component form as follows:
z-momentum balance:
\[
\rho U_p \frac{\partial U_{p,r}}{\partial r} - \rho \kappa_p \frac{\partial \ln p}{\partial r} \frac{\partial U_{p,r}}{\partial r} - \rho \kappa_p U_p \frac{\partial^2 \ln p}{\partial r^2} + \rho \kappa_p \frac{\partial \ln p}{\partial r} \frac{\partial^2 U_{p,r}}{\partial r \partial z} + \rho U_{p,\nu} \frac{\partial U_{p,r}}{\partial z} - \rho \kappa_p \frac{\partial \ln p}{\partial z} \frac{\partial U_{p,r}}{\partial z} - \rho \kappa_p \frac{\partial \ln p}{\partial r} \frac{\partial U_{p,\nu}}{\partial z} + \rho \kappa_p \frac{\partial \ln p}{\partial z} \frac{\partial U_{p,\nu}}{\partial z} - \rho \kappa_p \frac{\partial \ln p}{\partial r} \frac{\partial^2 U_{p,\nu}}{\partial r \partial z} + \rho \kappa_p \frac{\partial \ln p}{\partial z} \frac{\partial^2 U_{p,\nu}}{\partial z^2} = 0.
\]

In order to solve equations (15)–(17), we must stipulate appropriate boundary conditions on the velocity field \(U_p(r, z)\) and the pressure distribution \(p(r, z)\). The radial component of the pressure diffusion velocity, \(U_{p,r}\), is chosen in such a way that no mass passes through the confining walls. This amounts to setting:
\[
U_{m,r}(R, z) = U_{p,r}(R, z) - \kappa_p \frac{\partial \ln p}{\partial r} \bigg|_{(R,z)} = 0, \quad 0 \leq z \leq L.
\]

Furthermore, we will adopt a no-slip condition on the tangential component of the pressure diffusion velocity:
\[
U_{p,\nu}(R, z) = 0, \quad 0 \leq z \leq L.
\]

Finally, we set inlet/outlet values on the pressure field as usual:
\[
p(r, 0) = P_{in}, \quad p(r, L) = P_{out}, \quad 0 \leq r \leq R.
\]

Note that imposing the no-slip condition (19) leads to the following expression for the tangential component of the mass velocity at the wall:
\[
U_{m,\nu}(R, z) = -\kappa_p \frac{\partial \ln p}{\partial z} \bigg|_{(R,z)} = 0, \quad 0 \leq z \leq L.
\]

Equation (21) highlights that, by imposing a no-slip condition on the pressure diffusion velocity, the mass transfer along the wall becomes a purely diffusive process driven by the pressure gradient. We believe this boundary condition to be physically more sound than that used in [28]. There, the authors imposed the conventional Maxwell slip expression on the volume velocity. On the other hand, using the condition expressed in equation (19), a form of wall-slip arises naturally from the new equations while retaining the traditional wall-adherence in connection with the advective transport of mass. No additional constitutive relation is imposed on the form of the velocity slip.

To proceed with our analysis we introduce the following dimensionless variables:
\[
\tilde{r} = \frac{r}{d}, \quad \tilde{z} = \frac{z}{L}, \quad \tilde{U}_p = \frac{U_p}{U_p}, \quad \tilde{U}_{p,\nu} = \frac{U_{p,\nu}}{U_p}, \quad \tilde{p} = \frac{p d}{U_p \mu}, \quad \epsilon = \frac{d}{L}.
\]

Here, \(U_p\) is a typical value of the pressure diffusion velocity and \(p\) has been normalized based on reasoning provided in [24]. In addition to these variables, we define the Reynold’s number by,
\[
\text{Re}_p = \frac{\rho U_p d}{\mu}.
\]

Finally, we turn to the pressure diffusion coefficient, \(\kappa_p\). As stated earlier the precise nature of this coefficient is not yet known. However, in previous investigations on rarefied gas flows [30], it was assumed that
\[
\kappa_p = \alpha^* \frac{\mu}{\rho},
\]
where \(\alpha^*\) is a dimensionless number. This form of \(\kappa_p\) is reminiscent of the kinematic viscosity \(\nu = \mu/\rho\) and it is useful for the dimensional analysis carried out in this section. Indeed, making use of (22)–(24), equations (15)–(17) become:

mass balance:
\[
\frac{\partial \tilde{U}_{p,r}}{\partial \tilde{r}} - \frac{\alpha^*}{\text{Re}_p} \frac{\partial^2 \ln \tilde{p}}{\partial \tilde{r}^2} + \frac{\tilde{U}_{p,\nu}}{\tilde{r}} = -\frac{\alpha^*}{\text{Re}_p} \frac{1}{\tilde{r}} \frac{\partial \ln \tilde{p}}{\partial \tilde{r}} + \epsilon \frac{\partial \tilde{U}_{p,\nu}}{\partial \tilde{z}} - \frac{\alpha^*}{\text{Re}_p} \frac{\partial^2 \ln \tilde{p}}{\partial \tilde{z}^2} = 0,
\]
3.2. Regular perturbation solutions

As the aspect ratio \( \varepsilon \) of the nanotubes used in flow experiments cited earlier is typically very small, it is reasonable to seek regular perturbation expansions in \( \varepsilon \) for the pressure and velocity fields. That is, we are looking for solutions to equations (25)–(27) of the form:

\[
\tilde{\rho} = \tilde{\rho}_0 + \varepsilon \tilde{\rho}_1 + \varepsilon^2 \tilde{\rho}_2 + \cdots , \\
\tilde{U}_0 = \tilde{U}_{0,0} + \varepsilon \tilde{U}_{0,1} + \varepsilon^2 \tilde{U}_{0,2} + \cdots , \\
\tilde{U}_p = \tilde{U}_{p,0} + \varepsilon \tilde{U}_{p,1} + \varepsilon^2 \tilde{U}_{p,2} + \cdots .
\]  

(28)

(29)

(30)

To determine the coefficient functions in the above expansions, the derivatives involving \( \ln \tilde{\rho} \) in equations (25)–(27) need to be fully expanded. Regularized equations are then obtained by multiplying both sides with appropriate powers of \( \tilde{\rho} \). Substituting the expansions (28)–(30) into these regularized equations and collecting terms involving the same powers of \( \varepsilon \) leads to a set of equations from which the coefficients can be determined.

Clearly, for this approach to work we need to know the magnitude of the dimensionless numbers \( \text{Re}_p, \alpha^* \) in relation to the aspect ratio \( \varepsilon \). Frequently (see e.g. [6, 24]), for the analysis of gas flows in micro-channels, the assumption is made that \( \text{Re}_p = O(\varepsilon) \). Further, supposing that \( \alpha^* = O(1) \), the regularized mass and \( r \)-momentum equations yield the following two \( O(1/\varepsilon) \)-relations, rewritten in terms of \( \ln \tilde{\rho}_0 \):

\[
\text{mass balance, } O(1/\varepsilon): \quad \tilde{\rho}_0 \frac{\partial^2 \tilde{\rho}_0}{\partial \tilde{r} \partial \tilde{t}} - \left( \frac{\partial \tilde{\rho}_0}{\partial \tilde{r}} \right)^2 + \tilde{\rho}_0 \frac{\partial \tilde{\rho}_0}{\tilde{r} \partial \tilde{t}} = 0,
\]

\[
\Rightarrow \tilde{\rho}_0 \left( \frac{\partial^2 \ln \tilde{\rho}_0}{\partial \tilde{r} \partial \tilde{t}} + \frac{1}{\tilde{r}} \frac{\partial \ln \tilde{\rho}_0}{\partial \tilde{t}} \right) = \tilde{\rho}_0 \frac{\partial}{\tilde{r} \partial \tilde{t}} \left( \frac{\partial \ln \tilde{\rho}_0}{\partial \tilde{r}} \right) = 0.
\]

(31)

(32)

Integrating equation (31) twice with respect to \( \tilde{r} \), we obtain the general solution for the pressure to zeroth-order in \( \varepsilon \) as:

\[
\tilde{\rho}_0 (\tilde{r}, 2) = \tilde{r} ^{g(\tilde{r})} \cdot e^{f(\tilde{r})},
\]

(33)

where \( f(\tilde{r}) \) and \( g(\tilde{r}) \) are arbitrary functions resulting from the integration steps. Now, to prevent the pressure from tending to zero or infinity as we approach the central axis of the tube (\( \tilde{r} = 0 \)), it must be that \( g(\tilde{r}) \equiv 0 \) and hence:

\[
\frac{\partial \tilde{\rho}_0}{\partial \tilde{r}} = 0.
\]

(34)
This result can be used to obtain the following $O(1)$-equations:

\begin{align}
\text{mass balance, } O(1): & \\
\dot{\tilde{p}}_0 \frac{\partial \tilde{U}_{b,0}}{\partial \tilde{r}} + \tilde{p}_0 \frac{\partial^2 \tilde{U}_{b,0}}{\partial \tilde{z}^2} = \frac{\alpha^\varepsilon}{\text{Re}_p} \frac{\partial^2 \tilde{p}_1}{\partial \tilde{r}^2} - \frac{\alpha^\varepsilon}{\text{Re}_p} \frac{\partial \tilde{p}_1}{\partial \tilde{r}} = 0, \\
\text{r-momentum balance, } O(1): & \\
0 = -\dot{\tilde{p}}_0 \frac{\partial \tilde{U}_{p,0}}{\partial \tilde{r}} + \tilde{p}_0 \frac{\partial^2 \tilde{U}_{p,0}}{\partial \tilde{z}^2} - \frac{\alpha^\varepsilon}{\text{Re}_p} \frac{\partial^2 \tilde{p}_1}{\partial \tilde{r}^2} - \frac{\alpha^\varepsilon}{\text{Re}_p} \frac{\partial \tilde{p}_1}{\partial \tilde{r}}.
\end{align}

Differentiating equation (35) with respect to $\tilde{r}$, multiplying by $\dot{\tilde{p}}_0$ and subtracting from equation (36), we obtain,

\begin{align}
\frac{\partial \tilde{p}_1}{\partial \tilde{r}} = 0.
\end{align}

Putting this back in equation (35) and simplifying then yields:

\begin{align}
\dot{\tilde{p}}_0 \frac{\partial}{\partial \tilde{r}} (\tilde{U}_{b,0}) = 0.
\end{align}

Hence, the general solution for the zeroth order term of the radial velocity is,

\begin{align}
\tilde{U}_{b,0}(\tilde{r}, \tilde{z}) = \frac{h(\tilde{z})}{\tilde{r}},
\end{align}

where $h(\tilde{z})$ is an arbitrary function. As with the pressure before, the radial velocity should not become infinite at $\tilde{r} = 0$, so that we must have $h(\tilde{z}) \equiv 0$ and therefore $\tilde{U}_{b,0} \equiv 0$. It follows that all terms in equations (35) and (36) vanish and the perturbation expansions take the form:

\begin{align}
\tilde{p}(\tilde{r}, \tilde{z}) &= \tilde{p}_0(\tilde{z}) + \varepsilon \tilde{p}_1(\tilde{r}, \tilde{z}) + \varepsilon^2 \tilde{p}_2(\tilde{r}, \tilde{z}) + \cdots, \\
\tilde{u}_r(\tilde{r}, \tilde{z}) &= \varepsilon \tilde{U}_{b,1}(\tilde{r}, \tilde{z}) + \varepsilon^2 \tilde{U}_{b,2}(\tilde{r}, \tilde{z}) + \cdots, \\
\tilde{u}_z(\tilde{r}, \tilde{z}) &= \tilde{U}_{p,0}(\tilde{r}, \tilde{z}) + \varepsilon \tilde{U}_{p,1}(\tilde{r}, \tilde{z}) + \varepsilon^2 \tilde{U}_{p,2}(\tilde{r}, \tilde{z}) + \cdots.
\end{align}

Finally, the four coefficient functions $\tilde{p}_0(\tilde{z}), \tilde{p}_1(\tilde{r}, \tilde{z}), \tilde{U}_{b,1}(\tilde{r}, \tilde{z})$ and $\tilde{U}_{p,0}(\tilde{r}, \tilde{z})$ can be shown to satisfy the following set of equations, which are found from the regularized equations of mass and momentum balance upon substitution of the above perturbation expansions:

\begin{align}
\text{mass balance, } O(\varepsilon): & \\
\frac{\partial \tilde{U}_{b,1}}{\partial \tilde{r}} + \frac{\tilde{U}_{b,1}}{\tilde{r}} + \frac{\partial \tilde{U}_{p,0}}{\partial \tilde{z}} = \frac{\alpha^\varepsilon}{\text{Re}_p} \left( \frac{d^2 \ln \tilde{p}_0}{d \tilde{z}^2} + \frac{1}{\tilde{r}} \frac{\partial \tilde{p}_1}{\partial \tilde{r}} + \frac{1}{\tilde{r}} \frac{\partial^2 \tilde{p}_2}{\partial \tilde{r}^2} \right), \\
\text{r-momentum balance, } O(\varepsilon): & \\
0 = -\frac{\partial \tilde{p}_1}{\partial \tilde{r}} + \frac{\partial^2 \tilde{U}_{b,1}}{\partial \tilde{z}^2} + \frac{1}{\tilde{r}} \frac{\partial \tilde{U}_{b,0}}{\partial \tilde{r}} - \frac{\alpha^\varepsilon}{\text{Re}_p} \left( \frac{\partial^2 \tilde{p}_1}{\partial \tilde{r}^2} + \frac{1}{\tilde{r}^2} \frac{\partial \tilde{p}_2}{\partial \tilde{r}} \right), \\
\text{z-momentum balance, } O(1): & \\
0 = \frac{\partial \tilde{p}_0}{\partial \tilde{z}} + \frac{\partial^2 \tilde{U}_{p,0}}{\partial \tilde{r}^2} + \frac{1}{\tilde{r}} \frac{\partial \tilde{U}_{p,0}}{\partial \tilde{r}} = 0.
\end{align}

4. Analytical solution

Equations (43)–(45) may be solved analytically to obtain the stream-wise pressure and velocity variation along the nano-tube to zeroth order in $\varepsilon$.

4.1. Velocity and pressure profiles

Making use of the perturbation expansions (40)–(41), the $O(\varepsilon)$ dimensionless no-penetration condition on the mass velocity (equation (18)) reads:

\begin{align}
\tilde{p}_0 C_m,0 \left( \frac{1}{2}, \frac{1}{2} \right) = \tilde{p}_0 C_{p,1} \left( \frac{1}{2}, \frac{1}{2} \right) - \frac{\alpha^\varepsilon}{\text{Re}_p} \frac{\partial \tilde{p}_2}{\partial \tilde{r}} \bigg|_{(1/2, z)} = 0, \ 0 \leq z \leq 1.
\end{align}
Similarly, equations (19)–(20) yield:

\[
\tilde{U}_{p,0} \left( \frac{1}{2}, \tilde{z} \right) = 0, \quad 0 \leq \tilde{z} \leq 1
\]  

(47)

\[
\tilde{P}_0(0) = \tilde{P}_{in}, \quad \tilde{P}_0(1) = \tilde{P}_{out}.
\]  

(48)

Subject to these conditions, equation (45) yields the well-known parabolic profile for the zeroth-order streamwise velocity component:

\[
\tilde{U}_{p,0}(\tilde{r}, \tilde{z}) = \frac{1}{4} \left( \tilde{r}^2 - \frac{1}{4} \right) \frac{d\tilde{P}_0}{d\tilde{z}}.
\]  

(49)

Substituting this into the mass balance equation (43), we obtain,

\[
\frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} (\tilde{r} \tilde{U}_{p,1}) + \left( \tilde{r}^2 - \frac{r^2}{16} \right) \frac{d^2\tilde{P}_0}{d\tilde{z}^2} = \frac{\alpha^* e}{Re_p} \frac{d^2 \ln \tilde{P}_0}{d\tilde{z}^2} + \frac{1}{\tilde{P}} \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial \tilde{P}_0}{\partial \tilde{r}} \right).
\]  

(50)

Integrating with respect to \( \tilde{r} \) and re-arranging, we find an expression for the radial velocity component:

\[
\tilde{U}_{p,1}(\tilde{r}, \tilde{z}) = \left( \tilde{r} - \frac{r^3}{32} \right) \frac{d^2\tilde{P}_0}{d\tilde{z}^2} + \tilde{r} \frac{\alpha^* e}{2 Re_p} \frac{d\ln \tilde{P}_0}{d\tilde{z}} + \frac{1}{\tilde{P}} \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial \tilde{P}_0}{\partial \tilde{r}} \right) + C(\tilde{z}).
\]  

(51)

The arbitrary function \( C(\tilde{z}) \) appearing here is found upon application of the boundary condition given in equation (46) and it yields,

\[
C(\tilde{z}) = -\frac{1}{256} \frac{d^2 \tilde{P}_0}{d\tilde{z}^2} - \frac{1}{8 \Re_p} \frac{d^2 \ln \tilde{P}_0}{d\tilde{z}^2}.
\]  

(52)

Looking at equation (51), we see that \( \tilde{U}_{p,1} \) blows up at \( \tilde{r} = 0 \) unless \( C(\tilde{z}) = 0 \). This solubility condition then defines the zeroth-order pressure distribution as:

\[
\frac{d^2\tilde{P}_0}{d\tilde{z}^2} + \frac{32 \alpha^* e}{Re_p} \frac{d\ln \tilde{P}_0}{d\tilde{z}} = 0.
\]  

(53)

Integrating twice with respect to \( \tilde{z} \) yields the pressure \( \tilde{P}_0(\tilde{z}) \) implicitly:

\[
\tilde{P}_0(\tilde{z}) + \frac{32 \alpha^* e}{Re_p}, \ln \tilde{P}_0(\tilde{z}) = A\tilde{z} + B,
\]  

(54)

where \( A \) and \( B \) are the integration constants which are determined from the dimensionless inlet/outlet pressures \( \tilde{P}_{in}, \tilde{P}_{out} \) as,

\[
A = -\Delta \tilde{P} - \frac{32 \alpha^* e}{Re_p} \ln \mathcal{P}, \quad B = \tilde{P}_{in} + \frac{32 \alpha^* e}{Re_p} \ln \tilde{P}_{in},
\]  

(55)

with \( \Delta \tilde{P} = \tilde{P}_{in} - \tilde{P}_{out} \) is the dimensionless inlet/outlet pressure difference and \( \mathcal{P} = \tilde{P}_{in}/\tilde{P}_{out} = P_{in}/P_{out} \) the inlet/outlet pressure ratio. For completeness, we note that the radial velocity component \( \tilde{U}_{p,1}(\tilde{r}, \tilde{z}) \) in equation (51) can now be calculated by determining \( \frac{\partial \tilde{P}_0}{\partial \tilde{r}} \). Eliminating terms between equations (43) and (44), we find that:

\[
\frac{\partial \tilde{P}_2}{\partial \tilde{r}} = \frac{\partial \tilde{U}_{p,0}}{\partial \tilde{r} \tilde{z}} = \frac{1}{2} \frac{d\tilde{P}_0}{d\tilde{z}}.
\]  

(56)

Expressing equations (49) and (54) in dimensional form using the tube radius \( R = d/2 \), we obtain a parabolic velocity profile,

\[
u_{p,0}(r, z) = \frac{r^2 - R^2}{4\mu} \frac{d\tilde{P}_0}{d\tilde{z}},
\]  

(57)

as well as a non-linear pressure distribution,

\[
\tilde{P}_0(z) + \frac{8\mu \ln \tilde{P}_0}{R^2} \ln \left( \frac{\tilde{P}_0(z)}{\tilde{P}_{in}} \right) = \tilde{P}_{in} - \left( \frac{\Delta \tilde{P}}{L} + \frac{8\mu \ln \tilde{P}_0}{R^2L} \ln (\mathcal{P}) \right) z.
\]  

(58)

Figure 2 shows profiles of these fields with values based on the experiment described by Majumder et al [10]. The re-casted Navier–Stokes pressure profile is seen to deviate from the classical linear pressure drop predicted by the Navier–Stokes equations.

4.2. Mass flow rate

For calculation of the mass flow rate, we emphasize that the total mass flux \( \rho_u \) as defined through equation (4) consists of the advective mass flux \( \rho u_x \) as well as the diffusive mass flux \( \rho u_z \nabla \ln p \). The (dimensional) tangential
component of this flux to zeroth order in $\varepsilon$ is

$$\rho U_{m_0,0} = \rho U_{b,0} + \rho \kappa_p \frac{d\ln p_0}{dz}. \quad (59)$$

Using equations (57)–(58) and integrating the mass flux $\rho u_{m_0,0}$ over a cross-section of the tube then gives the (constant) rate of mass transport:

$$M_{RNS} = 2\pi \rho \int_0^R r u_{m_0,0} dr = 2\pi \rho \int_0^R \left( r u_{F,0} - r \kappa_p \frac{d\ln p_0}{dz} \right) dr \quad (60)$$

$$= 2\pi \rho \int_0^R \left[ \frac{1}{4\mu} (r^3 - r R^3) \frac{dp_0}{dz} - r \kappa_p \frac{d\ln p_0}{dz} \right] dr \quad (61)$$

$$= 2\pi \rho \left[ - \frac{R^4 \frac{dp_0}{dz}}{16\mu} - \frac{1}{2} \kappa_p R \frac{d\ln p_0}{dz} \right] \quad (62)$$

$$= \pi \rho R^4 \frac{\Delta P}{8\mu L} + \frac{8\mu \kappa_p}{R^2} \ln (P). \quad (63)$$

In the last step towards obtaining equation (63), we have made use of the pressure distribution (58). We recall further that the mass flow rate according to the classical no-slip Hagen-Poiseuille flow law is given by,

$$M_{HP} = \frac{\pi \rho R^4 \Delta P}{8\mu L}. \quad (64)$$

This allows our new mass flow rate to be expressed as:

$$M_{RNS} = M_{HP} + \frac{\pi \rho R^2 \kappa_p \ln (P)}{L} = (1 + \gamma) M_{HP}, \quad (65)$$

where the flow enhancement factor $\gamma$ is defined by,

$$\gamma = \frac{M_{RNS} - M_{HP}}{M_{HP}} = \frac{8\mu \kappa_p \ln (P)}{R^2 \Delta P}. \quad (66)$$

This definition of flow enhancement is slightly different from the ratio $M_{RNS}/M_{HP}$ used in previous studies [35].

5. Discussion and comparison with experimental data

Considering analytical expressions for the mass flow rate as given in equations (65) and (66), several key features can be uncovered. First, we note that the flow enhancement factor $\gamma$ is directly proportional to the viscosity coefficient, $\mu$, and the diffusivity coefficient, $\kappa_p$, while depending inversely on the square of the tube radius $R$. This ensures that the classical Hagen-Poiseuille flow law is recovered at large radii where surface effects become negligible. For a simple numerical illustration, let us take a diffusivity coefficient $\kappa_p = 10^{-8} \text{ m}^2 \text{ s}^{-1}$, a dynamic
viscosity \( \mu = 10^{-3} \text{ kg/ms} \) (approximately that of water) and inlet/outlet pressures \( P_{\text{in}} = 2 \cdot 10^5 \text{ Pa} \), \( P_{\text{out}} = P_{\text{atm}} \approx 1 \cdot 10^5 \text{ Pa} \). In a tube of radius \( R = 1 \text{ nm} \), we then have a flow enhancement factor \( \gamma \approx 500 \). Increasing the tube radius to 100 nm, we find \( \gamma \approx 0.05 \), or about 5% enhancement over the Hagen-Poiseuille flow rate. This would explain why no enhancement was measured when investigating water flow through channels of 200 nm diameter and 800 nm diameter [9].

Second, equation (66) is explicitly dependent on the inlet and outlet pressures via:

\[
\frac{\ln \left( \frac{P}{\Delta P} \right)}{\Delta P} = \frac{1}{\Delta P} \ln \left( \frac{P_{\text{out}} + \Delta P}{P_{\text{out}}} \right). \tag{67}
\]

To investigate the influence of the inlet/outlet ratio \( P \) on the flow enhancement in more detail, let us fix the outlet pressure as \( P_{\text{out}} = 1 \cdot 10^5 \text{ Pa} \) and view equation (67) as a function of \( \Delta P \). Figure 3 shows the graph of this function (and hence \( \gamma \)) as well as the corresponding flow rates for pressure differences varying from \( \Delta P = 0 \text{ Pa} \) to \( \Delta P = 1 \cdot 10^6 \text{ Pa} \). The 1 bar pressure difference used in the experiments of Majumder et al [10] and Holt et al [13] is highlighted on these plots. It can be seen that, for fixed values of \( \mu, \kappa_p, R \), the enhancement decreases as the applied pressure \( P_{\text{in}} \) is increased further from this point. On the other hand, if \( P_{\text{in}} \) is reduced, the enhancement increases. For \( \Delta P \ll 1 \text{ bar} \), equation (67) may be approximated as \( \ln \left( \frac{P}{\Delta P} \right) / \Delta P \approx 1/P_{\text{out}} \). In fact, with \( \Delta P \to 0 \), we find \( \gamma \to \frac{\mu p_{\text{in}}}{R^2 P_{\text{out}}} \). This limiting enhancement value is of course meaningless, as there is no flow in this case (\( \ln P = \ln 1 = 0 \) in equation (63)).

Suppose now that we fix \( \Delta P \) instead and consider the effect of the ambient pressure on \( \gamma \). From equation (67), it is clear that a lower \( P_{\text{out}} \) leads to a higher value of \( \gamma \). Thus, the diffusive mechanism in our model becomes more important in a lower pressure environment.

The dependence of the mass flow rate on \( 1/R^2 \) and the logarithmic term \( \ln \left( \frac{P}{\Delta P} \right) \) appears also in several models for rarefied gas flow. In fact, equation (65) and its derivation are synonymous to Dadzie and Brenner’s equation (24) in [28] for gas flow in a rectangular micro-channel of width \( w \) and height \( h \):

\[
\dot{M} = \frac{wh^2 P_{\text{out}}^2}{24 L \mu RT} (P^2 - 1) \left[ 1 + 12 K_{\text{slip}} Kn_\gamma \frac{1}{P + 1} + \frac{24}{Pr K_\gamma} Kn_\gamma^2 \ln \frac{P}{P^2 - 1} \right]. \tag{68}
\]

This expression for the mass flow rate was derived on the basis of Brenner’s Bi-velocity model. The common factor outside the square brackets in equation (68) is the generalization of the Hagen-Poiseuille flow law for a compressible gas, where \( P_{\text{out}} (P^2 - 1) \) replaces the pressure difference \( \Delta P \). The second term inside the brackets arises because of an explicit Maxwell slip-condition imposed on the volume velocity. Setting \( K_{\text{slip}} = 0 \) (i.e. no explicit Maxwell slip on the volume velocity), we obtain the mass flow rate which is analogous to our equation (65).

The flow enhancement term \( \gamma \dot{M}_{\text{slip}} \) in equation (65) can also be compared to an expression derived by Veltze and Thöming [36] to account for surface diffusion in their model for moderately rarefied gases:

\[
\dot{m}_{\text{S}} = \frac{A}{L} D s q^* M \ln \left( \frac{P_{\text{in}} K_\gamma + 1}{P_{\text{out}} K_\gamma + 1} \right). \tag{69}
\]
Equation (69) was derived using a phenomenological approach based on an adsorption/desorption mechanism described by the Langmuir isotherm [37]. The authors subsequently add this term to the Hagen-Poiseuille flow law for a compressible gas, together with a term representing Knudsen diffusion.

Solving the original incompressible Navier-Stokes equations written in terms of the mass velocity, equation (2), subject to the slip boundary condition on the mass velocity as given in equation (21), we obtain exactly the new mass flow equation (65). Equation (21), which originates from the no-slip condition on the pressure diffusion velocity, $U_p$, appears as a slip condition on the mass velocity written in terms of a pressure gradient rather than in terms of a tangential velocity gradient as in a traditional Maxwell’s slip expression [18]. We conclude therefore that, in this case, re-casting the Navier-Stokes equations is an alternative to introducing additional physics such as mass velocity slip or other surface diffusion effects at the wall.

To compare our new theoretical results with data available in the literature, the measured flow velocity, $U_{exp}$, and the Hagen-Poiseulle predicted velocity, $U_{HP}$, are used to define the flow enhancement factor, $\gamma_{exp}$ as:

$$
\gamma_{exp} = \frac{U_{exp} - U_{HP}}{U_{HP}}.
$$

This experimentally determined enhancement factor is then used in equation (66) to compute the corresponding values of the new molecular diffusivity coefficient, $\kappa_p$, and consequently the dimensionless parameter, $\alpha^* = \frac{\kappa_p}{\rho/\mu}$. Results are reported in table 1.

For the water flow experiments listed in table 1, we calculated $\alpha^*$-values to be of the order of magnitude between $10^{-2}$ and $10^{-1}$ when using data from the experiments by Holt et al in 2 nm diameter CNTs. $\alpha^*$-values based on the data of Majumder et al in carbon nano-tubes (CNT) of 7 nm diameter is found to be in the order of magnitude of $10^{-1} - 10^2$. On the other hand, $\alpha^*$-values based on Whitby et al in 44 nm diameter CNTs experiments is again found to be in the order of magnitude of $10^{-1}$.

To validate our new theory with the 1.66 nm to 44 nm diameter CNT experimental data in table 2 we collect existing measurement values and molecular dynamic simulation results for water. The quoted enhancement factors for CNT diameters between 1.66 nm and 44 nm are presented in figure 4. A significant discrepancy can be seen between the enhancement factors quoted by Du et al [12] (light green square) and Zhang et al [38] (red square) for the 10 nm diameter experiments. It has been suggested that the extremely large enhancement values reported by Majumder et al (dark green squares) and Du et al (light green squares) represent an over-estimation [39] and could be the result of an uncontrolled external variable such as an electric field [40]. In general, experiments involving flow through CNT membranes are prone to showing errors due to practical challenges in
Table 2. Flow enhancement data for water.

Summary of water flow enhancement data from experiments and molecular dynamics simulations

| Experimental study | Pore diameter $d$ (nm) | Membrane thickness $L$ (μm) | Pressure difference $\Delta P$ (bar) | Enhancement factor $\gamma_{exp}$ | Pressure diffusivity $K_p$ ($\times 10^{-7}$ m$^2$/s) | Dimensionless parameter $\alpha^*$ | Dimensionless parameter $\alpha^{**}$ |
|--------------------|-------------------------|----------------------------|-------------------------------------|----------------------------------|-------------------------------------------------|-----------------------------|-----------------------------|
| Thomas and McGaughey (MD) | 1.66 | 0.08 | 150–638 | 87–162 | 0.39–0.9 | 0.039–0.09 | 0.93–1.6 |
| Holt et al (experiment) | 2.00 | 2 | 1 | 560–8400 | 0.1–1.5 | 0.01–0.15 | 1.3–2.9 |
| Thomas and McGaughey (MD) | 2.77 | 1 | 1300–2900 | 98–190 | 4.6–10 | 0.46–1.0 | — |
| Thomas and McGaughey (MD) | 4.99 | 1 | 1300–2600 | 53–60 | 7.9–13 | 0.79–1.3 | 3.9–6.8 |
| Majumder et al (experiment) | 7.00 | 126 | 1 | $6.1 \times 10^3 – 2.8 \times 10^5$ | 140–630 | — | 7.7–13 |
| Du et al (experiment) | 10.00 | 4000 | 1 | $3.8 \times 10^3$ | 1750 | — | 0.44 |
| Zhang et al (experiment) | 10.00 | 120 | 0.13 | 2100 | 6.9 | 0.69 | — |
| Whitby et al (experiment) | 44.00 | 78 | 0.071 | 20–37 | 1.3–2.3 | 0.13–0.23 | 0.07–0.13 |
the estimation of parameters such as permeability and average pore size. Additionally, partial blockage of pores can easily lead to significant over- or under-estimation of the volumetric flow rate through a single tube. For this reason, to compare our theory with the existing data, a uniform average value of $\alpha^* = 0.47$ was first determined from table 2 by excluding the $\alpha^*$-values for the experiments by Majumder et al and Du et al (as indicated by the empty spaces in table 2). This average $\alpha^*$-value corresponds to a pressure diffusivity coefficient $\kappa_p$ in the order of magnitude between $10^{-7}$ and $10^{-6}$, which is comparable to the kinematic viscosity $\nu$ of water ($\approx 1 \times 10^{-6}$ m$^2$ s$^{-1}$). The theoretical results for enhancement factor $\gamma = 8\alpha^* \mu^2 \ln(\mathcal{P})/\rho R^2 \Delta P$, with $\alpha^* = 0.47$, are superimposed on figure 4 as blue filled circles joined by straight line segments. One can observe on this plot that our theoretical predictions using equation (66) are close to most of the various experimental and MD enhancement values except those of Majumder et al [11] and Du et al [12], for which the predictions are about two orders of magnitude less than the measured values. For the smaller diameter CNTs, it is noted that a reduced viscosity in a ‘depletion layer’ existing approximately within 0.7 nm of the tube wall may become significant and it has been modelled previously by Myers [35] in an attempt to explain the high flow rates without resorting to wall-slip conditions. If considered in our model, a reduced viscosity zone near the wall would lead to an overall decrease in the flow enhancement $\gamma$. This might explain why the theoretical prediction in figure 4 lies above the experimental data for the 1.66 nm and 2 nm channels.

As the experimental and molecular dynamics simulation data in table 2 involve a wide range of diameters and tube lengths, we also conducted another analysis based on the full dataset, this time including the highest $\alpha^*$-values in table 2. From the $\alpha^*$-values in table 2 we identify an average to be $\alpha^* = 0.0028$, excluding the lower enhancement value for the 10 nm channel by Zhang et al. Based on this second analysis, the corresponding theoretical prediction given by equation (66) is represented on figure 4 by the filled purple circles joined by straight line segments. We again observe a reasonably good theoretical prediction of the experimental data that includes those of Majumder et al and Du et al.

6. Conclusion

We performed a theoretical analysis of isothermal pressure-driven liquid flows in nano-channels. The new equations used for the analysis termed re-casted Navier–Stokes equations are obtained by a change of variable on the mass velocity $U_m$ appearing in the classical conservation equations of mass and momentum. The specific form of this transformation is assumed to be determined by the main driving mechanism of the flow. For the problem of isothermal pressure-driven liquid flow discussed in the present paper, the mass velocity $U_m$ was written as the sum of a new velocity $U_p$ (the pressure diffusion velocity) and a diffusive term, $\kappa_p \nabla p/\rho$, involving the pressure gradient. A regular perturbation expansion in the channel aspect ratio was used to derive a simpler set of equations for the flow configuration. These were then solved analytically subject to a no-slip condition on $U_p$, resulting in a theoretical expression for the mass flow rate. This expression was seen to be the classical Hagen-Poiseuille flow law with an additional extra mass transport term resulting from the mass diffusion at the wall. It was therefore noted that the re-casting methodology introduces new physics in the solutions. The theoretical mass flow rate was compared with existing literature data from experiments and molecular dynamic simulations reported on enhanced flow rates of liquid flows in nanotubes. The new equations and analytical solutions provide an alternative physical explanations of the data. The methodology may therefore be deployed to interpret other similar anomalous flow experiments.

Acknowledgments

This research is supported by the UK’s Engineering and Physical Sciences Research Council (EPSRC) under grant no. EP/R008027/1 and The Leverhulme Trust, UK, under grant reference RPG-2018-174.
ORCID iDs
Alexandros Stamatiou https://orcid.org/0000-0002-4587-3150
S. Kokou Dadzie https://orcid.org/0000-0001-8557-0595
M. H. Lakshminarayana Reddy https://orcid.org/0000-0003-2421-409X

References
[1] Colin S 2010 Microfluidics ISTE (New York: Wiley) (https://doi.org/10.1007/9781118599839)
[2] Karniadakis G E, Beskos A and Aluru N 2005 Microflows and Nanoflows (New York: Springer) (https://doi.org/10.1007/0-387-28676-4)
[3] Ague P 2004 Aquaporin water channels (noble lecture) Angew. Chem. Int. 43 4328–90
[4] Zhang L, Shan B, Zhao Y, Du J, Chen J and Tao X 2018 Gas transport model in organic shale nanopores consideringlangmuir slip conditions and diffusion: pore confinement, real gas, and geomechanical effects Energies 11 223
[5] Knudsen M 1909 Die Gesetze der Molekularströmung und der inneren Reibungsströmung der Gase durch Röhren Ann. Phys. 333 75–130
[6] Arkilic E B, Schmidt M A and Breuer K S 1997 Gaseous slip flow in long microchannels J. Microelectromech. Syst. 6 167–78
[7] Maurer J, Tabeling P and Flandre S 2003 Second-order slip laws in microchannels for helium and nitrogen Phys. Fluids 15 2613–21
[8] Ewart T, Perrier P, Graur I and Meolans J M 2007 Mass flow rate measurements in a microchannel, from hydrodynamic to near free molecular regimes J. Fluid Mech. 584 337–56
[9] Pfälzer J, Harlej J, Bau H and Zemel J 1990 Liquid transport in micron and submicron channels Sensor. Actuat. A 22 431–41
[10] Majumder M, Chopra N, Andrews R and Hinds B J 2005 Enhanced flow in carbon nanotubes Nature 438 44
[11] Majumder M, Chopra N, Andrews R and Hinds B J 2011 Mass transport through carbon nanotube membranes in three different regimes: ionic diffusion and gas and liquid flow Nano 5 3867–77
[12] Du F, Qu L, Xia Z, Feng L and Dai L 2011 Membranes of vertically aligned superelong carbon nanotubes Langmuir 27 8437–43
[13] Holt J K, Park H G, Wang Y, Stadtermann M, Aryukhina A B, Grigoropolous C P, Noy A and Bakajin O 2006 Fast mass transport through sub-2-nanometer carbon nanotubes Science 312 1034–7
[14] Qin X, Yuan Q, Zhao Y and Si L and Zhi Z 2011 Measurement of the rate of water translocation through carbon nanotube Nano Lett. 11 2173–7
[15] Whitby M, Cagnon L, Thanou M and Quirke N 2008 Enhanced fluid flow through nanoscale carbon pipes Nano Lett. 8 2632–7
[16] Walther J H, Ritos K, Cruz-Chu E R, Megaridis C M and Koumoutsakos P 2013 Barriers to superfast water transport in carbon nanotube membranes Nano Lett. 13 1910–4
[17] Thomas J A and McGaughey A J H 2009 Water flow in carbon nanotubes: transition to subcontinuum transport Phys. Rev. Lett. 102 184502
[18] Maxwell J C 1879 On stresses in rarefied gases arising from inequalities of temperature Proc. R. Soc. London 27 304–8
[19] Arlemark E J, Dadzie S K and Reese J M 2010 An extension to the Navier–Stokes equations to incorporate gas molecular collisions with boundaries J. Heat Transfer 132 041006
[20] Veltzke T and Thoiming I 2012 An analytically predictive model for moderately rarefied gas flow J. Fluid Mech. 698 406–22
[21] Ottinger H C 2005 Beyond Equilibrium Thermodynamics (Hoboken, New Jersey: Wiley) (https://doi.org/10.1002/047127903)
[22] Dadzie S K, Reese J M and McLines C R 2008 A continuum model of gas flows with localized density variations Physica A 387 6079–94
[23] Sheretov Y V and Elizarova T G 2001 Theoretical and numerical investigation of quasigasdynamic and quasihydrodynamic equations Comput. Math. Math. Phys. 41 219–34
[24] Graur I A, Meolans J G and Zeltoun D E 2006 Analytical and numerical description for isothermal gas flows in microchannels Microfluid Nanofluid 2 64–77
[25] Brenner H 2012 Beyond Navier–Stokes Int. J. Eng. Sci. 54 67–98
[26] Chakraborty S and Durst F 2007 Derivations of extended Navier–Stokes equations from upscaled molecular transport considerations for compressible ideal gas flows: towards extended constitutive forms Phys. Fluids 19 11–59
[27] Svärd M 2018 A new Eulerian model for viscous and heat conducting compressible flows Physica A 506 350–75
[28] Dadzie S K and Brenner H 2012 Predicting enhanced mass flow rates in gas microchannels using nonkinetic models Phys. Rev. E 86 036318
[29] Lv Q, Liu X, Wang E and Wang S 2013 Analytical solution to predicting gaseous mass flow rates of microchannels in a wide range of Knudsen numbers Phys. Rev. E 88 030107
[30] Christou C and Dadzie S K 2018 On the numerical simulation of rarefied gas flows in micro-channels J. Phys. Commun. 2 035002
[31] Reddy M H L, Dadzie S K, Ocone R, Borg M K and Reese J M 2019 Recasting Navier–Stokes equations J. Phys. Commun. 3 105009
[32] Reddy M H L and Dadzie S K 2019 Reinterpreting shock wave structure predictions using the Navier-Stokes equations arXiv:1909.02631
[33] Korteweg D 1901 Sur la forme que prennent les equations du mouvements des densite en presence des forces capillaires causees par des variations de densite considérables mais connues et sur la théorie de la capillarité dans l'hypothese d’une variation continue de la densite Arch. Neerl. Sci. Ex. Nat. (ii) 6 1–24
[34] Heida M and Malek J 2010 On compressible Korteweg fluid–like materials Int. J. Eng. Sci., special issue in Honor of K. R. Rajagopal 48 1313–24
[35] Myers T G 2010 Why are slip lengths so large in carbon nanotubes? Microfluid. Nanofluid. 10 1141–5
[36] Veltzke T 2013 On Gaseous Microflows Under Isothermal Conditions (PhD Thesis) University of Bremen
[37] Myong R S 2004 Gaseous slip models based on the langmuir adsorption isotherm Phys. Fluids 16 104–17
[38] Zhang L, Zhao B, Jiang C, Yang J and Zheng G 2015 Preparation and transport performances of high-density, aligned carbon nanotube membranes Nanoscale Res. Lett. 10 266
[39] Borg M K, Lockerby D A, Ritos K and Reese J M 2018 Multiscale simulation of water flow through laboratory-scale nanotube membranes J. Membr. Sci. 567 115–26
[40] Thomas J A and McGaughey A J H 2008 Reassessing fast water transport through carbon nanotubes Nano Lett. 8 2788–93