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It is well-known that the Poiseuille mass flow rate along microchannels shows a stationary point as the fluid density decreases, referred to as the Knudsen minimum. Surprisingly, if the flow characteristic length is comparable to the molecular size, the Knudsen minimum disappears, as reported for the first time by Wu *et al.* (*J. Fluid Mech.*, vol. 794, 2016, pp. 252-266). However, there is still no fundamental understanding why the mass flow rate monotonically increases throughout the entire range of flow regimes. Although diffusion is believed to dominate the fluid transport at the nanoscale, here we show that the Fick's first law fails in capturing this behaviour, and so diffusion alone is insufficient to explain this confined flow phenomenon. Rather, we show that the Knudsen minimum disappears in tight confinements because the decay of the mass flow rate due to the decreasing density effects is overcome by the enhancing contribution to the flow provided by the fluid velocity slip at the wall.

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## 1. Introduction

Fluids confined within geometries of molecular dimensions are commonly encountered in geological and biological systems (Bocquet & Charlaix 2010), as well as in many engineering applications, e.g., membrane science (Mistry *et al.* 2021), that have been constantly growing in recent years — fostered by the technological progress in the fabrication of nanofluidic devices (Kavokine *et al.* 2021). In these flows, three significant length scales can be identified: the diameter of fluid constituent particles $\sigma$, the flow characteristic length $d$, which is related to the channel size, and the molecular mean free path (MFP) $\lambda$, which represents the average distance travelled by particles between two consecutive collisions. The interplay of phenomena occurring at these scales leads to complex fluid behaviour. Indeed, the continuum approach based on the Navier-Stokes equations breaks down with increasing rarefaction ($\lambda \sim d$), since the local thermodynamic equilibrium condition is not fulfilled. Likewise,

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the standard kinetic theory description is no longer accurate at the nanoscale where dense ($\lambda \sim \sigma$) and confinement ($d \sim \sigma$) effects come into play, implying that the Boltzmann equation must be replaced by more complicated kinetic models, such as the Enskog equation (Kremer 2010).

Despite the availability of computational procedures to describe the flow of confined fluids, the fundamental understanding of many phenomena occurring under tight confinement is still lacking. A notable example is that, for simple fluids, the Poiseuille mass flow rate (MFR) is found to monotonically increase in channels of molecular dimensions when the fluid density decreases, by using numerical solutions of the Enskog equation (Wu *et al.* 2016) and event-driven molecular dynamics simulations (Sheng *et al.* 2020). This behaviour is in sharp contrast with the long-standing recognition of flow mechanics in microchannels, which instead exhibits a non-monotonic variation of the MFR and the formation of a stationary point referred to as the "Knudsen minimum" (Cercignani & Sernagiotto 1966), as long as the channel is sufficiently long and does not contain any bends (Ho *et al.* 2020).

A possible explanation of the Knudsen minimum disapperance is that the transport in dense fluids changes from convection to molecular diffusion under tight confinements. Here, *molecular diffusion* is referred to as the diffusive mechanism which is driven by the interactions between fluid particles in the continuum limit ($\lambda \ll d$), and it is distinguished from the *Knudsen diffusion* that takes place in the free molecular limit ($\lambda \gg d$), where particles only collide ballistically with the wall (Xiao & Wei 1992). The dominance of diffusive transport at the nanoscale is known to take place for long alkanes in porous media, where the hydrodynamic description breaks down, although doubt remains for single-site gas molecules (Falk *et al.* 2015). Despite there is no unequivocal evidence that this behaviour also occurs for non-tortuous channels, some hints supporting the diffusive nature of Poiseuille flow transport in tight geometries are provided by the analysis of velocity profiles. These are no longer parabolic as expected for force/pressure-driven flows, but show a plug-like behaviour instead, suggesting the predominance of diffusive mechanisms (Firouzi & Wilcox 2013). However, a conclusive proof regarding a crossover from convection to molecular diffusion in these systems, that is triggered by the fluid confinement, has still not been given.

The aim of this work is to perform a detailed investigation of the Knudsen minimum disappearance in straight nanochannels, and elucidate the underpinning physical reasons. There are two main findings. First, despite the molecular-like confinements, we show that diffusion does not dominate transport, and so the convective flow contribution cannot be neglected outside the free molecular regime. Second, we show that the monotonic increase of MFR can be attributed to the larger relative importance of the velocity slip at the wall, compared to the other physical mechanisms that are normal contenders at the microscale. The rest of the paper is organised as follows. In section 2 we outline the simulation approach used to numerically study the transport process. In section 3.1 we show that the Knudsen minimum vanishing in straight nanochannels cannot be attributed to diffusive processes, whereas in section 3.2 we prove that the contribution of the fluid slippage at the confining solid surface provides a satisfactory explanation of this recently discovered feature. A summary of the main results and conclusions follow in section 4.

## 2. Methodology

We consider force-driven Poiseuille flows inside a long tubular geometry with diameter $d$, where the fluid is modelled using a system composed of hard-sphere particles with molecular diameter $\sigma$. The wall is assumed to be a structureless cylindrical surface and the fluid-wall interactions are described by the Maxwell scattering kernel with full tangential momentum accommodation coefficient, where impinging particles are diffusely reflected after being

thermalised with the wall. The exact time evolution of the monatomic hard-sphere system is simulated using event-driven molecular dynamics (EDMD). In these simulations, the state of the system jumps from one time to another corresponding to the upcoming collision through three basic steps: (a) evaluating the time of the earliest collision event, (b) moving ballistically all particles for that time interval, and (c) updating the velocity of the particles that have collided with another particle or the wall, according to elastic hard-sphere dynamics or the Maxwell scattering kernel, respectively. Note that the time step is not constant throughout the simulation run, like in regular MD simulations, as it depends on the spatial coordinates and velocities of all molecules in the system. More information on the simulation setup can be found in Corral-Casas *et al.* (2021).

Three dimensionless groups can be identified to systematically describe the different transport processes that may take place in this system, namely the reduced density, the confinement ratio, and the Knudsen number. The reduced density $\eta = n\pi\sigma^3/6$, where $n$ is the number density, represents the number of fluid particles in the theoretical volume occupied by one hard-sphere. This first dimensionless group allows to differentiate between dense (large $\eta$ values) and rarefied (low $\eta$ values) gas flows. The confinement ratio $R = d/\sigma$ provides information about the degree of fluid inhomogeneity that arises because of the presence of walls, where tight confinements (low $R$ values) are associated with a more prominent molecular layering next to the confining surface and, therefore, with an increase of the collision frequency of fluid particles with the wall. Finally, the Knudsen number $Kn = \lambda/d$ quantifies the departure of the fluid from its local quasi-equilibrium case. The continuum approach can be used for $Kn \lesssim 0.01$, while non-equilibrium effects come progressively into play in the following three regimes: slip ($0.01 < Kn \lesssim 0.1$, where the continuum model still holds but different boundary conditions are needed to capture the "slippage" of fluid particles at the solid surface), transition ($0.1 < Kn \lesssim 10$, where the continuum description breaks down and kinetic equations must be used instead), and free molecular ($Kn > 10$, where molecules move ballistically between collisions with the confining wall). The expression of the MFP, derived from kinetic theory, is given by (Kremer 2010)

$$\lambda = \frac{16}{5\pi}\frac{\mu}{P}\sqrt{\frac{\pi kT}{2m}}, \tag{2.1}$$

where $m$ is the molecular mass and $P$ is the pressure, related to the density through $P = nkTZ$, in which $k$ is the Boltzmann constant, $T$ the temperature of the system, and $Z$ is the fluid compressiblity factor that can be accurately approximated by the equation of state for the hard-sphere fluid proposed in Carnahan & Starling (1969)

$$Z = \frac{P}{nkT} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}. \tag{2.2}$$

According to the Enskog theory, the shear viscosity $\mu$ of a hard-sphere fluid is given by

$$\mu = \frac{5}{16\sigma^2}\sqrt{\frac{mkT}{\pi}}\mu_f = \frac{5}{16\sigma^2}\sqrt{\frac{mkT}{\pi}}\frac{1}{\chi}\left[1+\frac{16}{5}\eta\chi+\frac{64}{25}\left(1+\frac{12}{\pi}\right)\eta^2\chi^2\right], \tag{2.3}$$

where $\mu_f$ is the dense gas correction for the viscosity of a rarefied gas, and $\chi$ represents the contact value of the pair correlation function in a hard-sphere fluid in uniform equilibrium, which from the aforementioned equation of state reads

$$\chi = \frac{1}{nb}\left(\frac{P}{nkT}-1\right) = \frac{1}{2}\frac{2-\eta}{(1-\eta)^3}, \tag{2.4}$$

where $b = 2\pi\sigma^3/3$ is the second virial coefficient (Kremer 2010).

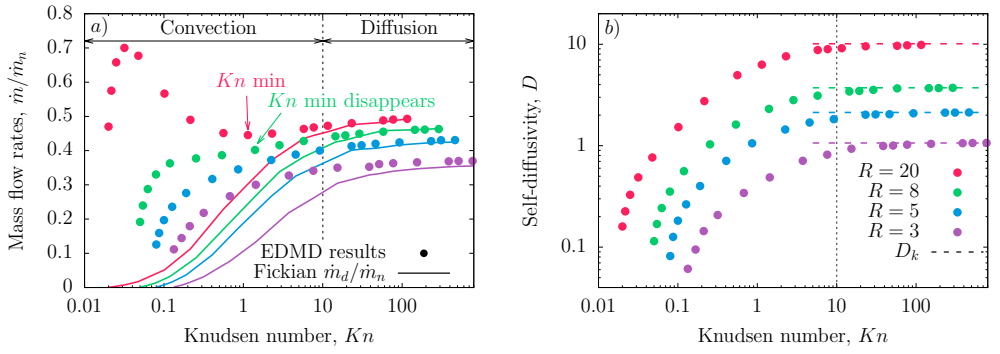


Figure 1: *(a)* Comparison between the dimensionless MFR provided by non-equilibrium simulations (symbols) and the theoretical predictions assuming Fickian diffusion, as given by Eq. (3.1) (lines). There is good agreement in the free molecular regime ($Kn \geqslant 10$), whilst Fick's law underestimates MFR elsewhere, which imply that convective transport transport terms cannot be neglected at any confinement. *(b)* Dependence of the self-diffusivity $D$ on the Knudsen number $Kn$ and the confinement ratio $R$. Dashed horizontal lines represent the theoretical value of the Knudsen self-diffusivity from Eq. (3.2) for each confinement ratio.

## 3. Results and discussion

### 3.1. *Knudsen minimum disappearance: analysis based on diffusion*

The Knudsen minimum disappearance, which was initially presented for the slit geometry in Wu *et al.* (2016), is demonstrated for a cylindrical pipe in this work, where it is seen to occur between $R = 20$ and $R = 8$ in figure 1*(a)*. Here, we show transport results from non-equilibrium EDMD simulations that are performed in the presence of an external unidirectional force $F$ along the axis of the channel, whose value is assumed to be sufficiently low so that the flow remains in the linear response regime — the artificial addition of heat is adequately dissipated by the wall. The numerical evaluation of the MFR for each case, depending on $\eta$ and $R$, is obtained from a spatial integration of local densities and velocities.

As mentioned in section 1, the Knudsen minimum vanishing might be explained by supposing that, under molecular confinements, a crossover from convective to diffusive transport takes place up to the late transition regime ($Kn \lesssim 10$). This hypothesis is tested by comparing the actual MFR with the analytical estimate assuming that the transport is solely driven by diffusion, which is based on the Fick's first law where the MFR of diffusing particles $\dot{m}_d$ follows a linear response with the density gradient along the axial $z-$direction $dn/dz$

$$\dot{m}_d = -\frac{\pi d^2}{4} m D \frac{dn}{dz} = -\frac{D\pi d^2 m}{4kT\left(Z + \eta \frac{dZ}{d\eta}\right)} \frac{dP}{dz}, \tag{3.1}$$

in which $D$ is the self-diffusion coefficient. Note that the number density $n$ and pressure $P$ are interconnected using Eq. (2.2), with the pressure gradient being identified with the force $F$ through the fundamental relation given by $-dP/dz = nF$.

However, before comparing the MFR simulation results with the predictions given by Eq. (3.1), self-diffusion results $D$ are needed as this information is unavailable in the literature for the cylindrical geometry. Therefore, a set of equilibrium EDMD simulations is carried out, see details in Corral-Casas *et al.* (2021), where the self-diffusion coefficients are determined by means of the Einstein relation in the entire range of flow regimes, for different confinement ratios of interest. These simulation results are shown in figure 1*(b)*, where it can be seen that, from a qualitative standpoint, self-diffusivities increase with Knudsen number because the

MFP becomes larger and therefore particles have more mobility before colliding with another entity in the system. At the same time, self-diffusivities increase with the flow characteristic length for a given $Kn$, as large $R$ values imply less collisions with the diffuse wall model that hinder the molecular displacement in the streamwise direction. Note that in the free molecular limit, where there are just diffuse collisions with the wall, numerical results perfectly agree with the analytical Knudsen self-diffusivity prediction from kinetic theory (Xiao & Wei 1992)

$$D_k = \frac{2d}{3}\sqrt{\frac{2kT}{\pi m}}. \tag{3.2}$$

As presented in figure 1*(a)*, it is found that the Fick's first law unsurprisingly reproduces the MFR simulation results very well in the free molecular regime. The slight disagreement in the tightest of confinements (for $R = 3$) can be attributed to the transition from Fickian to anomalous diffusion (e.g., of single-file type) as particles cannot overtake each other when moving along the channel. However, it is evident that Eq. (3.1) underestimates the mass transport along the remaining flow regimes ($Kn \lesssim 10$), and therefore the governing mechanism in this range of $Kn$ is no longer purely diffusive. This clearly proves that, in straight channels, the supposed crossover from convection to diffusion does not occur even under tight confinements and, consequently, cannot explain the Knudsen minimum disappearance. Note that these results do not imply that diffusion is not the governing transport mechanism within more complex geometries, such as in microporous media, which will need to be addressed separately.

### 3.2. *Knudsen minimum disappearance: analysis based on slip*

As discussed so far, there are a number of mechanisms that influence the MFR through a channel, and so the best explanation for describing the features of the MFR dynamics can be inferred in the limits of the continuum ($Kn \approx 0$) and free molecular ($Kn \sim \infty$) regimes, as we illustrate in figure 2. As suggested by the analysis from section 3.1, the fluid flow is convective in nature in the continuum regime, regardless of $R$. When moving towards the free molecular regime (i.e., decreasing density values), the MFR initially increases as the viscosity decreases, implying that the fluid velocity arising as a response to a given external driving force will be larger. By contrast, the fluid flow is driven by Knudsen diffusion in the free molecular regime. This means that, when moving back towards the continuum regime (i.e., increasing density values), the MFR decreases as the molecular MFP shortens, implying lower self-diffusivities as observed in figure 1*(b)*.

Under a sufficiently loose confinement ($R \gtrsim 60$ as shown in Appendix A), the Knudsen minimum existence follows from these two limiting behaviours. The MFR in the continuum regime is always larger than that in the free molecular regime and, therefore, the MFR curve must show two stationary points as depicted by the orange curve in figure 2, namely the Knudsen maximum and the Knudsen minimum. If the confinement is tighter, the continuum MFR is lower than the free molecular one. Accordingly, the flow transport curve may either form two stationary points, given by the blue dotted line, or else could show a monotonic increase throughout the entire range of Knudsen numbers, as represented by the blue solid line. It is then clear that, for the confined case, a necessary and sufficient condition for the Knudsen minimum to appear is that the Knudsen maximum shows up as well. Therefore, proving the disappearance of the Knudsen minimum is equivalent to demonstrating the Knudsen maximum vanishing. The latter question is easier to address as this local maximum falls in the continuum/slip regime ($Kn \lesssim 0.1$), where it can be tackled analytically using the Navier-Stokes equations with the first-order velocity slip boundary condition, which in its dimensionless form (a step-by-step derivation of this mathematical expression is presented

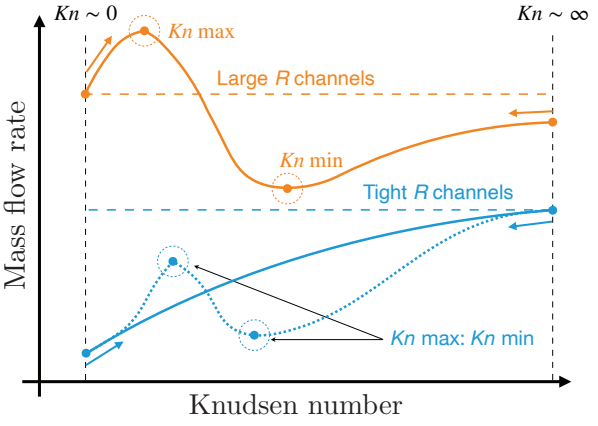


Figure 2: Qualitative analysis of the dimensionless MFR curves against the Knudsen number. Due to the governing transport mechanisms in the limiting flow regimes, the MFR will always increase/decrease when decreasing/increasing density in the continuum/free molecular regime. In sufficiently *large* channels (orange colour), where the continuum transport is larger than the free molecular one, the MFR curve must develop two stationary points as a response. On the other hand, for tighter confinements (blue colour) where the free molecular flow is larger than the continuum one, the MFR curve could either show the two stationary points or follow a monotonic increase instead, where the Knudsen minimum disappears.

in Appendix A) reads

$$\dot{m} = \frac{\dot{m}_h}{\dot{m}_n} = \frac{3R\eta}{5\sqrt{\pi}\mu_f}\left(1 + 8\alpha Kn\right). \tag{3.3}$$

Note that two symplifying assumptions have been implicitly made. First, the slip coefficient $\alpha$ is assumed to be constant and equal to that of a rarefied gas, albeit slip phenomena are known to be more complicated when dealing with liquid-like densities (Martini *et al.* 2008; Hadjiconstantinou 2021). The validity of this assumption will be discussed later. Second, the velocity slip boundary condition at the wall is based on the strain rate and not on the stress tensor, leading to less accurate results if the wall is not at rest (Lockerby *et al.* 2004).

Eq. (3.3) clearly shows that there are three physical terms contributing to the MFR, namely the viscosity (i.e., via $\mu_f$), the density (i.e., via $\eta$), and the slip (i.e., via $1 + 8\alpha Kn$). These terms vary with the reduced density but, for the following analysis, we find it more convenient to study the MFR with respect to the reduced specific volume $\nu = 1/\eta$, as in this way there is a one-to-one direct correspondence between $\nu$ and $Kn$. It should be stressed that this choice does not limit the generality of the conclusions. The relative importance of these terms can be singled out by evaluating their corresponding partial rates of change

$$\frac{d\dot{m}}{d\nu} = \frac{d\eta}{d\nu}\left(\frac{\partial\dot{m}}{\partial\mu_f}\frac{d\mu_f}{d\eta} + \frac{\partial\dot{m}}{\partial\eta} + \frac{\partial\dot{m}}{\partial Kn}\frac{dKn}{d\eta}\right) = \frac{1}{\nu^2}\left(Q_\mu + Q_\eta + Q_\alpha\right), \tag{3.4}$$

where

$$Q_\mu = \frac{3R\eta\left(1 + 8\alpha Kn\right)}{5\sqrt{\pi}\mu_f^2}\frac{d\mu_f}{d\eta}, \tag{3.5}$$

$$Q_\eta = -\frac{3R\left(1 + 8\alpha Kn\right)}{5\sqrt{\pi}\mu_f}, \tag{3.6}$$

$$Q_\alpha = \frac{24R\eta\alpha}{5\sqrt{\pi}\mu_f}\frac{dKn}{d\eta}. \tag{3.7}$$

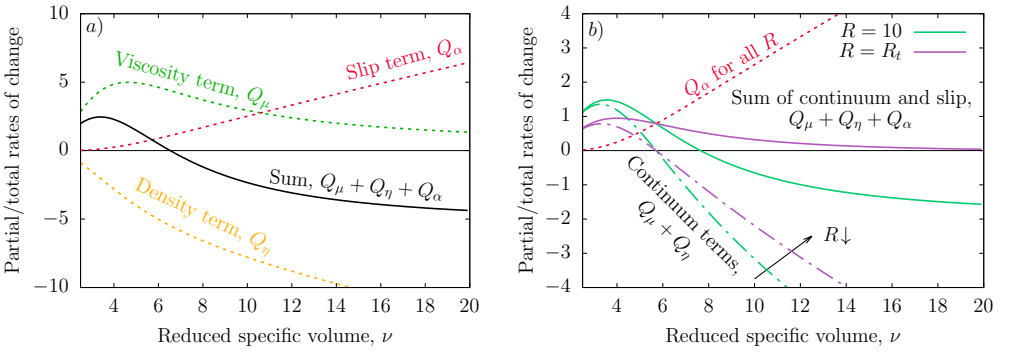


Figure 3: *(a)* Partial rates of change against the reduced specific volume, for $R = 20$, under the continuum framework of fluid modelling, which capture how flow transport is affected by a change of each of the underlying contributions. *(b)* Interplay between the continuum (dash-dotted) and the slip (dotted) contributions for different $R$. For sufficiently large $R$ values, the continuum contribution dominates and the sum of all rates of change (solid) cross the $x-$axis, i.e., the Knudsen maximum appears. However, for tight channels, the continuum contribution is less relevant whereas slip remains the same, driving the overall rate of change to be positive throughout the entire range of $\nu$ values, with the Knudsen maximum disappearing as a consequence.

These individual contributions are presented in figure 3*(a)* for $R = 20$, in a range of $\nu$ values corresponding to $Kn \lesssim 0.1$, namely the slip regime. Here, the plot of Eq. (3.5) shows that the partial derivative of the MFR with respect to the viscosity, $Q_\mu$, is always positive with increasing reduced specific volume. In particular, the rate of change is higher for low $\nu$ values, whereas its value decreases for large reduced specific volumes. Eq. (3.6) shows that the MFR partial derivative with respect to the density, $Q_\eta$, is always negative with increasing reduced specific volume. If the slip contribution is temporarily disregarded, the density is seen to become relevant over the viscosity at $\nu \approx 6$, and drives the MFR to decrease monotonically with further increase in the reduced specific volume. Eq. (3.7) shows that the MFR partial derivative with respect to the slip, $Q_\alpha$, is always positive with increasing specific volume. In particular, the rate of change is almost negliglible in the continuum regime while it becomes larger in the slip regime ($\nu \gtrsim 3.33$), where rarefaction effects become more prominent and the fluid slippage at the wall increasingly contributes to the overall MFR.

Three important observations are in order and presented in figure 3*(b)*, that helped us to understand why the Knudsen minimum disappears only when confinements are tight. The first remark is that the viscosity and density contributions exactly counterbalance at the same $\nu$ regardless of $R$. This can be easily proved using Eqs. (3.5) and (3.6), and it is clearly shown by dashed lines, representing the sum of viscosity and density rates of change (dubbed the *continuum contribution* from here onwards), which always crosses the $x-$axis at $\nu = 5.711$. A second remark is that the magnitude of the rate of change of the continuum contribution reduces with tighter channels and so its absolute value decreases with lower $R$ for a given $\nu$ value, as could also be deduced from Eqs. (3.5) and (3.6). The third remark is that the slip contribution (dotted line) is independent of $R$, as it is seen in Eq. (3.7), and so its relative importance grows when the confinement ratio reduces.

The interplay between the three aforementioned contributions (denoted by solid lines in figure 3*(b)*, representing the sum of continuum and slip terms) significantly depends on the size of the channel, and we can mainly distinguish between two types of flow behaviours. For *large* channel sizes and starting from the continuum regime (low $\nu$), the viscosity contribution initially dominates and leads the MFR to increase with $\nu$. The region corresponding to low $\nu$ values can then be referred to as viscosity dominated since this contribution overcomes that

of density, and here the slip term is negligible. Unlike the viscosity term that gets weaker as the fluid rarefaction increases, the density term becomes progressively more important and causes the Knudsen maximum to form by eventually driving the MFR to decrease.

For tight confinements, viscosity is initially dominant and drives the MFR increase as in the previous case. However, now there is an interplay between density and slip in the region where the transport was previously density dominated, as the relative contribution of slip becomes more and more important for decreasing $R$. Indeed, as emphasised by the magnitude of the continuum and slip contributions in figure 3*(b)*, there might be a threshold confinement ratio $R$ at which the latter overcomes the former, preventing the formation of the expected Knudsen maximum. Therefore, the velocity slip at the boundary impels the MFR curve to monotonically increase throughout the entire range of flow regimes, with the Knudsen maximum (and so, the Knudsen minimum) disappearing as a consequence.

It is worth noticing that, within the simplified solution represented by Eq. (3.4), the Knudsen minimum disappearance can be determined by a simple argument. As the rate of change of the MFR is a continuous function that takes positive values in the continuum limit, a sufficient condition for the MFR to cross the $x-$axis could be defined by the Bolzano theorem

$$\lim_{\nu\to\infty}\left(Q_\mu + Q_\eta + Q_\alpha\right) = \frac{8\sqrt{2}\alpha - 3R}{5\sqrt{\pi}} \leqslant 0. \tag{3.8}$$

Numerical evidence shows that this condition is not only sufficient but also necessary, and hence one may conclude that the threshold confinement ratio $R_t$ for the Knudsen minimum disappearance is $R_t < 8\sqrt{2}\alpha/3$.

The analysis carried out in this section is based on two main simplifying considerations. The first assumption consists on using nominal values for density and viscosity in the Navier-Stokes equations, despite it is well-known that, under tight confinement, density is non-uniform across the channel and viscosity is no longer a local property of the position along the channel (Travis *et al.* 1997). However, there is a large body of evidence demonstrating that the hydrodynamic framework is valid down to nanoscale confinements (Bocquet & Charlaix 2010), and our numerical simulations also showed an agreement (within 4.5% for $Kn \lesssim 0.01$) with the non-slip Hagen-Poiseuille solution, using nominal values of the fluid properties. The second assumption involves the use of a constant slip coefficient although, unlike the rarefied case, numerical evidence shows that it depends on the channel size, e.g., larger $\alpha$ with decreasing $R$ values. However, the validity of the presented analysis is not undermined as the slip enhancement at lower $R$ just results in the Knudsen minimum disappearance at a larger $R_t$, and therefore the results in figure 3*(b)* correspond to the worst case scenario.

## 4. Conclusions

We have studied the Knudsen minimum disappearance that occurs for Poiseuille flows in tight cylindrical geometries. High-fidelity EDMD simulations have been carried out in a wide range of reduced fluid densities $\eta$ and channel confinement ratios $R$, in both equilibrium (to obtain the self-diffusivities needed in the Fickian framework) and non-equilibrium (directly evaluating the mass flow rate) setups. Although diffusion is supposed to be the main transport mechanism at the nanoscale, we found that the convective contribution to the mass flow rate cannot be disregarded — even under confinements of molecular dimensions. This convection-dominated transport, which is analytically studied using the Hagen-Poiseuille solution with first-order slip, is decoupled into its three fundamental contributions, namely viscosity, density, and slip. The individual influence of each of them on transport is assessed for different fluid rarefaction states and confinement ratios, which revealed that the disappearance of the

Knudsen minimum is a consequence of the interplay between these contributions. More specifically, the combined contribution of viscosity and density weakens in tight geometries, whereas the slip term remains the same when $R$ decreases, and so its relative importance increases in this context. Therefore, the Knudsen minimum vanishing under tight confinement can be explained by the more accentuated importance of the fluid slippage at the wall. The relevance of this work underpins in its qualitative explanation of dense flow mechanisms at the molecular scale, which may help to better understand how slip, from a fundamental standpoint, affects the flow of dense gases/liquids confined within tight geometries, such as high-pressure methane transport in unconventional shale rocks or water transport in nano-structured filtration membranes.

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**Declaration of interests.** The authors report no conflict of interest.

**Data availability statement.** The data that supports the findings of this study are openly available in Edinburgh DataShare repository at http://doi.org/[doi], reference number to be added during proofs' stage.

## Appendix A.

The Navier-Stokes equations for the incompressible flow of a Newtonian fluid through an infinite cylindrical channel simplify to

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{du_z}{dr}\right) = \frac{1}{\mu}\frac{dP}{dz}, \tag{A 1}$$

where $u_z$ is the fluid macroscopic velocity in the streamwise direction, and $r$ is the radial direction. The first-order slip at the wall, $r = d/2$, can be written as

$$u_s = -\alpha\lambda\left.\frac{du_z}{dr}\right|_{r=d/2}, \tag{A 2}$$

where $u_s$ is the slip velocity, and $\alpha = 2/\sqrt{\pi}$ is the velocity slip coefficient (Gibelli 2012). The straightforward solution of the boundary value problem from Eqs. (A 1), (A 2) reads

$$u_z(r) = \frac{1}{4\mu}\frac{dP}{dz}\left(r^2 - d\alpha\lambda - \frac{d^2}{4}\right). \tag{A 3}$$

The spatial integration of the velocity field over the cross section yields the Hagen-Poiseuille solution for the MFR

$$\dot{m}_h = mn\int_0^{d/2} u_z(r)2\pi r dr = -\frac{mn\pi d^4}{128\mu}\frac{dP}{dz}\left(1 + 8\alpha Kn\right). \tag{A 4}$$

Independently on the confinement ratio $R$, the MFR increases/decreases with the increasing/decreasing of the Knudsen number in the continuum/free molecular regimes (see discussion in the beginning of section 3.2). A sufficient condition for the Knudsen minimum to appear can be thus easily determined by imposing the MFR in the continuum regime to be larger than that in the free molecular regime. The dimensionless MFR in the continuum limit ($Kn \approx 0$) is given by Eq. (A 4) with $\alpha = 0$, i.e., the non-slip solution

$$\frac{\dot{m}_h}{\dot{m}_n} = \frac{3R\eta_0}{5\sqrt{\pi}f_\mu}, \tag{A 5}$$

where it is assumed that the fluid is at its freezing point, corresponding to $\eta_0 = 0.494$ for a fluid of hard-spheres (Sigurgeirsson & Heyes 2003). The normalising MFR here and elsewhere in the text, for instance explicitly in figures 1*(a)*, 2, and Eq. (3.3), is

$$\dot{m}_n = -mn_0 \frac{\pi d^2}{4} \frac{1}{m} \frac{1}{n_0} \frac{dP}{dz} \frac{d}{\sqrt{kT/m}} = -\frac{\pi d^3}{4\sqrt{kT/m}} \frac{dP}{dz}, \tag{A 6}$$

From the dimensionless MFR in the free molecular limit ($Kn \sim \infty$), provided by Eq. (3.1) with the Knudsen self-diffusivity from Eq. (3.2) as the proportionality factor and $Z = 1$ from Eq. (2.2)

$$\frac{\dot{m}_d}{\dot{m}_n} = \frac{D_k}{d} \sqrt{\frac{m}{kT}} = \frac{2}{3} \sqrt{\frac{2}{\pi}}, \tag{A 7}$$

it is easily derived that the aforementioned (A 5) $\geqslant$ (A 7) condition is always satisfied for $R \gtrsim 60$, represented by the orange curve in figure 2 depicting the behaviour in *large* channels.

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