Flow Conductance of a Single Nanohole

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The mass flow conductance of single nanoholes with diameter ranging from 75 to 100 nm was measured using mass spectrometry. For all nanoholes, a smooth crossover is observed between single-particle statistical flow (effusion) and the collective viscous flow emanating from the formation of a continuum. This crossover is shown to occur when the gas mean free path matches the size of the nanohole diameter. As a consequence of the pinhole geometry, the breakdown of the Poiseuille approximation is observed in the power-law temperature exponent of the measured conductance.

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The concept of resistance to flow, or conversely the flow conductance \(G\), dates back to the early development of fluid mechanics. Given a transport channel with a specific geometry connected to two reservoirs, a source \(S\) and drain \(D\), a mass flow current \(Q = G \cdot \Delta P\) is induced whenever a pressure difference \(\Delta P\) is provided across the channel. This pressure-mass current relationship is analogous to the electrical current flowing in a resistor with a resistance \(R = G^{-1}\) when a voltage drop is supplied across it, \(I = G \cdot \Delta V\). Despite fundamental differences in the nature of the constituents forming the reservoir, i.e. electrons carry a charge whereas particles in a fluidic system are usually neutral, much of the transport processes are very alike and the problem often reduces to the measurement and/or the calculation of the conductance of the channel. Here, we report on the first measurement of the gas flow conductance of a single hole of nanometric size. A direct observation of Knudsen effusion \(\text{[1]}\) is made whose crossover transition is found to occur when the mean free path of the gas matches the nanohole diameter, as expected.

\textit{A priori} the concept of conductance remains well-defined for transport channels as large as a macroscopic conductor or pipe, or as small as a nano-fabricated channel. With the recent progress made in microfluidics \(\text{[2]}\) and the push towards nanofluidics \(\text{[3]}\) for molecular detection \(\text{[4, 5]}\), experimental investigation of the transport properties of fluids at the nanoscale becomes more accessible. With the exception of a few experiments involving quantum fluids \(\text{[6, 7, 8, 9]}\) and DNA sensing \(\text{[10]}\), most experimental investigations have so far been restricted to either a single pipe in the micron range \(\text{[11]}\), or to porous membranes with sizes and properties averaged over the very large number of nanostructures \((e.g. \sim 10^{11} \text{ nanochannels/cm}^2) \text{[12, 13]}\). The properties of flow, hence the conductance, for a single nano-fabricated hole has been left out between these two limits, not by lack of interest \(\text{[14, 15]}\), but rather by the difficulties of measuring the very small flow emanating from a single nanochannel.

Figure 1A shows a realistic drawing of the experimental cell used for the gas flow measurements and Fig. 1B shows a field-emission transmission electron microscope (FE-TEM) image of the nanohole with a circle of diameter 101±2 nm which best fits the aperture. The FE-TEM was also used to drill the hole through a 50 nm thick window of dimension 30 × 40 micrometer, made of low-stress Silicon Nitride (SiN). The wafer was then epoxy-sealed on a sample holder (see Fig. 1A middle piece) that was subsequently inserted into the body of the experimental cell. Both the lid (top part of cell in Fig. 1A) and the sample holder were sealed with soft indium o-rings to protect against leaks to the outside and leaks around the holder, respectively. The drain pressure below the membrane \((P_D)\) is kept at vacuum through continuous pumping and helium gas is introduced in the top part of the cell creating a pressure gradient \(\Delta P = P_S - P_D \approx P_S\) which induces a mass flow \(Q\). This flow was detected with a Pfeiffer vacuum Smart Test HLT560 calibrated with an external standard leak of \(2.79 \times 10^{-8} \text{ atm-cc/s ±10−15%}\). A cartoon representation of the whole experiment is shown in Fig. 1C. The two reservoirs are depicted by a capillary conductance \(G_S\) and \(G_D\), in series before and after the nanohole with a conductance \(G_{nh}\). The mass spectrometer is denoted by \(A_M\) and measures the total mass current \(Q\) when the drain side of the set-up is kept under a vacuum, typically below \(\sim 2 \times 10^{-3} \text{ mbar}\). With our technique, the total conductance \(G_T^{-1} = G_S^{-1} + G_D^{-1} + G_{nh}^{-1}\) of the circuit is measured. The source and drain conductance can be estimated using the infinite pipe approximation for Poiseuille flow \((G_S \sim 10^{-11} \text{ m-s at } t \sim 1 \text{ bar})\) and Knudsen free-molecular diffusion \((G_D \sim 10^{-13} \text{ m-s at } t \sim 10^{-3} \text{ mbar})\). These conductances are several orders of magnitude larger than the nanohole conductance which has a typical value \(G_{nh} \sim 10^{-18} \text{ m-s}\) (see Fig. 2B). We therefore can approximate \(G_T \approx G_{nh}\) in our measurement circuit to a very good accuracy.

Typical measurements of the mass flow through the nanohole are shown in Fig. 2A for pressures up to 38 bar and at temperature \(T = 77\ K\). These data are the raw output of the mass spectrometer which measures flows in units of \([\text{mbar-l/s}]\), and plotted versus the source pressure \(P_S\). The uncertainty in the calibration of the spectrometer induces a small offset in the measured...
To correct for this instrumental artifact, a constant was added to the measured mass flow so that the condition \( Q \to 0 \) with \( P_S \to 0 \) was enforced. Three distinct pressure ranges are shown to emphasize the linearity (shown with a dotted line) of the mass flow with pressures in the range \( P_S \approx 0 - 55 \) mbar, and the strong and weak departure from linearity for pressures \( P_S \approx 0.69 - 5 \) bar and \( P_S > 6.2 \) bar. The non-linear departure of the flow with applied pressure is the first indication of a non-constant conductance, i.e. evolving with a functional dependence \( G = G(P_S) \) in the pressure range \( P_S = 0 \sim 38 \) bar.

In a classical fluidic system, a dimensionless number can be used to sort out the relevant formalism to be applied for the calculation of flow across a channel. This parameter is known as the Knudsen number \( Kn \) and is defined for a pinhole geometry as the ratio of the inter-particle mean free path \( \lambda \) to the hole diameter \( D \). At small Knudsen numbers \( Kn \ll 1 \), inter-particle collisions dominate, the transport is collective and a formalism describing continuous media should be used. In the case of a viscous fluid, the Navier-Stokes equations of fluid dynamics can be used to describe the flow. For \( Kn \gg 1 \), inter-particle collisional events are rare, the transport of particles is individual and a formalism based on the kinetic theory of statistical mechanics best describes the flow. In the case of an ideal pinhole, the problem is very similar to that of a photon escaping a black box: transport of particles is given by a Maxwell-Boltzmann speed distribution with each particle’s escape probability contributing to the current flow out. In the context of molecular diffusion or fluidic transport, this mechanism is known as effusion for a hole, and Knudsen diffusion for a tube.

The mean free path in a gas can be calculated from kinetic theory with the relation \( \lambda^{-1} = \sqrt{\frac{2}{\pi}} \cdot \frac{d^2}{n_v} \), where \( \pi d^2 \) is the effective cross-section of collisions and \( n_v \) is the volumic density determined from the pressure and temperature of the gas. In our experiment, we use helium which has \( d = 2.2 \times 10^{-10} \) m and a density calculated with the ideal gas law corrected with known virial coefficients [16]. The mean free path can thus easily be tuned to be smaller or larger than the hole size. In order to study the nonlinearity of the mass flow as the pressure is increased, we extract the conductance \( G_{nh} \equiv Q/\Delta P = Q/P_S \) from the measured flow. The resulting conductances are plotted versus the Knudsen number extracted from \( P_S \) in Fig. 2B (at \( T = 77 \) K). Two distinct regimes can be seen in the data, one for \( Kn > 1 \) for which \( G_{nh} \) is constant, and one for \( Kn < 1 \) where the conductance is continuously evolving. These data, spanning a measurement of \( G_{nh} \) over four orders of magnitude, indicate that the mechanism at small Knudsen number for a hole, and Knudsen diffusion for a tube.

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magnitude in $Kn$, unambiguously show that a crossover transition in the mass flow occurs when the inter-particle mean free path approaches the nanohole diameter, as expected. For completeness, the inset of Fig.2B shows the crossover transition observed at $Kn \simeq 1$ in a 77 nm diameter nanohole. Our results extend those reported in an array of silicon nanochannels [1] (with pore density $\sim 10^{11}$ cm$^{-2}$) to the single hole limit, revealing a clear picture of the dynamics of the flow in the crossover region.

At low $Kn$, where the fluid is described by a continuum, the flow in a macroscopic capillary of radius $R$ and length $L$ can be modeled by the Navier-Stokes equations. For example, when $L \gg R$, one obtains the well-known pressure-dependent Poiseuille conductance of viscous flow, $G_{\text{viscous}}^{\text{Poiseuille}} = \frac{\pi R^4}{8\eta L}$, where $\rho = \rho(P,T)$ is the density of the fluid and $\eta = \eta(T)$ its dynamic viscosity, which depends mostly on temperature. However, in a pinhole geometry where $R \sim L$, a model for short pipes must instead be used. Sherman has modeled the flow in short pipes [17] by linearizing the Navier-Stokes equations, from which we can extract a conductance $G_{\text{finite viscous}} = \frac{8\pi mL}{\alpha^2} \left(\sqrt{1 + \frac{\Delta P^2}{P_c^2}} - 1\right) \frac{1}{\Delta P}$, with $P_c = \sqrt{\frac{8\pi^2 L^2 k_B T}{\alpha m R^3}}$ defining a critical pressure (and associated critical Knudsen number $Kn_c$) containing a geometry-dependent factor $\alpha$ accounting for the acceleration of the fluid at the boundary. As a consequence of finite-size effects, we note that at large $\Delta P$ the conductance reduces to $G_{\text{viscous}}^{\text{finite}} = \frac{\pi R^2}{\sqrt{\alpha m R^3}}$, which is pressure and viscosity independent. At high $Kn$, when the gas is very dilute and the mean free path is large compared to the capillary diameter, the gas is no longer forming a continuum and the formalism of fluid mechanics should be replaced by a statistical approach. This leads to a Knudsen effusive flow given by $G_{\text{Knudsen}}^{\text{finite}} = \frac{\kappa L^3}{8R} \left(\sqrt{\frac{32\pi m \kappa}{9k_B T}} \frac{R^2}{L}\right)$, where $\kappa$ is the Clausing factor which goes from 0 to 1 as the ratio $L/R$ goes from infinity to 0.

In order to deepen our understanding of fluidic transport in the transitional region, the temperature dependence of the conductance between 77 K and 297 K was studied in detail. A fixed amount of gas was introduced in the cell and the temperature was slowly lowered to 77 K over the course of several hours, and then warmed back up to room temperature while the mass flow was monitored. Upon cooling, both the volume and number of atoms were kept constant, so the pressure in the experimental cell was reducing according to the ideal gas law. For example, the top (squares) cooldown data shown in the inset of Fig. 3 varied in pressure from 6 bar at 77 K over the course of several hours, and then warmed back up to room temperature while the mass flow was monitored. Upon cooling, both the volume and number of atoms were kept constant, so the pressure in the experimental cell was reducing according to the ideal gas law.

Using the conductance data (above $Kn = 10$) for Knudsen flow (using a fixed pore length of 50 nm), we find a fitted radius (using the Knudsen conductance) of $50.0 \pm 0.2$ nm, which is within 1% of the radius determined by means of TEM microscopy. Moreover, using the semi-phenomenological unified flow model given by Eq. 1, a fit of the conductance data (at 77 K) is shown in Fig. 2B with a dashed line and with fitted parameters $\alpha = 4.69 \pm 0.06$ and $\sigma = 5.3 \pm 0.1$. The agreement with the data is excellent, and the individual contributions from Knudsen (with cut-off) and viscous flow to the conductance are shown with a dotted and dash-dotted line, respectively. This good agreement between theory and data confirms the Knudsen theory predictions for a $\sim 100$ nm nanohole both qualitatively (observation of pressure-independent conductance) and quantitatively (by direct extraction of the nanohole radius with the model).

In order to deepen our understanding of fluidic transport in the transitional region, the temperature dependence of the conductance between 77 K and 297 K was studied in detail. A fixed amount of gas was introduced in the cell and the temperature was slowly lowered to 77 K over the course of several hours, and then warmed back up to room temperature while the mass flow was monitored. Upon cooling, both the volume and number of atoms were kept constant, so the pressure in the experimental cell was reducing according to the ideal gas law. For example, the top (squares) cooldown data shown in the inset of Fig. 3 varied in pressure from 6.6 bar at 297 K to 6.08 bar at 77 K. This corresponds to Knud-
sen numbers decreasing by a factor of $\sim 3.4$ from 0.286 to 0.083, respectively, therefore averaging to $\overline{Kn} = 0.18$. For each cooling/warming procedure, we determine such a mean Knudsen number $\overline{Kn}$. The temperature of the gas during the procedure was inferred from a continuous measurement of the gas pressure, thereby forming a gas thermometer. The extracted conductances at initial pressures $P = 6.6$ bar ($\overline{Kn} = 0.18$) and $P = 97$ mbar ($\overline{Kn} = 12.2$) are shown on a log-log plot in the inset of Fig. 3 as green diamonds and blue circles, respectively. The linear behavior on the log-log scale allows us to write a power law of the form $\mathcal{G}_{nh} \propto T^{-\alpha}$, where $\alpha$ is a power law exponent for the temperature dependence of the conductance. The power exponent $\alpha$ extracted at each pressure and shown in the main panel of Fig. 3 is therefore plotted against $\overline{Kn}$ for each cooling (circles) and warming (triangles) procedures. Above $\overline{Kn} \approx 10$, the power-law exponent $\alpha$ recovers the square root behavior expected for Knudsen flow including finite-size effects, $\mathcal{G}_{Knudsen} \propto T^{-\frac{1}{2}}$. For $\overline{Kn} < 10$, a clear departure from an inverse square root is observed, with a peaking power $\alpha \approx 0.67$ at $\overline{Kn} \approx 0.2$. At lower Knudsen number, a falling off of the exponent down to $\sim 0.58$ at $\overline{Kn} \approx 0.03$ is seen, which corresponds to the highest differential pressure that the SiN membrane could support prior to reaching the breaking point.

The fall-off trend below $\overline{Kn} \approx 0.2$ can easily be interpreted as the onset of finite-size conductance in the viscous regime. Interestingly, in the high-pressure limit where $\Delta P \to \infty$, the conductance should asymptotically reach $\mathcal{G}_{viscous} \propto T^{-\frac{3}{2}}$ as a pure consequence of finite-size effects. To support our interpretation, we have indicated in Fig. 3 by a grey bar (and its uncertainty by its width) the critical Knudsen number $Kn_c$ obtained from the $\alpha$ parameter fitted to the data in Fig. 2 (and similar fit for data at 297K). From high-to-low Knudsen number, the rise and peak in the exponent $\alpha$ in the transitional regime is consistent with the onset of viscous flow towards the Poiseuille limit, up to $Kn_c$. Beyond this point, the failure of the Poiseuille approximation and the onset of finite-size effects forces the departure from the Poiseuille regime and the fall-off of the exponent towards the finite-size, high-flow limit. We therefore conclude that $i)$ the expected temperature dependence for Knudsen flow is recovered above $\overline{Kn} \approx 10$, in complete agreement with the conductance data of Fig. 2 and $ii)$ the crossover from an extended to a finite-size viscous flow in the conductance of a single nanohole is observed at $Kn$ in the vicinity of the critical Knudsen number, $Kn_c$.

In conclusion, we have made a direct observation of the smooth crossover between the collective transport of particles emanating from a continuum to a single-particle statistical flow occurring in a single nanohole. Future experiments will focus on reducing the size of the nanofluidic channel even further, towards the one-dimensional limit, where quantum ballistic transport should give rise at low temperatures to a conductance quantized in unit of $G_m = 2e^2/h$, the quantum of conductance for mass flow.

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