University of Bremen

Predicting Rarefied Gas Flow Through Surface Functionalized Channels

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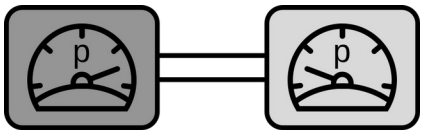
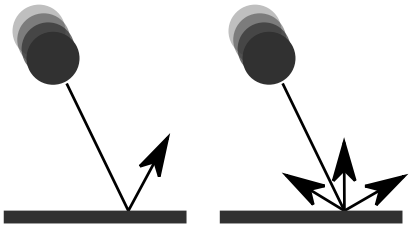
Seoul 06.07.2022

CHEMISCHE VERFAHRENS-TECHNIK

Overview

$$f(x) \rightarrow \dot{m}$$





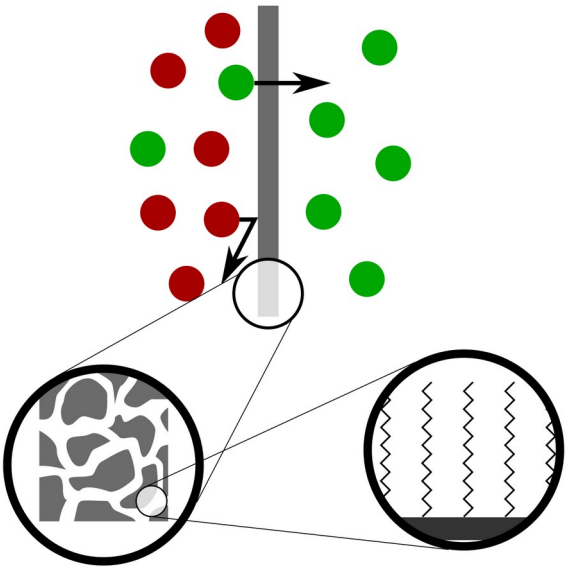
There are numerous numerical methods to describe rarefaction effects. But, to efficiently describe the flow of rarefied gases, an analytical expression is desirable.

We will cover the development of such a fully predictive analytical model to describe rarefied gas flow for all Knudsen numbers in straight channels.

We will combine this with experimental data and discuss the resulting implications regarding the surface interaction, as characterized by the tangetial momentum accommodation coefficient.

So, what does this have to to with porous media?

Functionalized Porous Media



In many industrial processes, we often face the challenge that it must be avoided that exhaust gases are released into the atmosphere.

An example would be a power plant, releasing carbon dioxide, which is a greenhouse gas. To avoid releasing such gases into the atmosphere, one option is to separate it from the exhaust gas for further storage or processing.

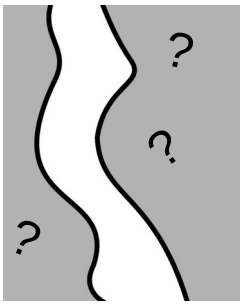
This can be done by using gas separation membranes. These membranes are permeable for specific gases but retain others.

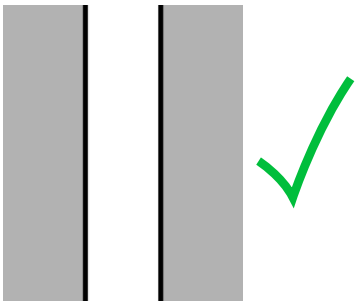
They are made from a porous structure.

The surface of these pores is functionalized by attaching molecules onto it which interact selectively with the gases.

While this process is widley used, the exact mechanisms are not clearly understood. This is because different effects such as rarefied gas flow and interaction with the surface functionalization are present. Here, we will focus on these two aspects of such membranes.

Keep it simple





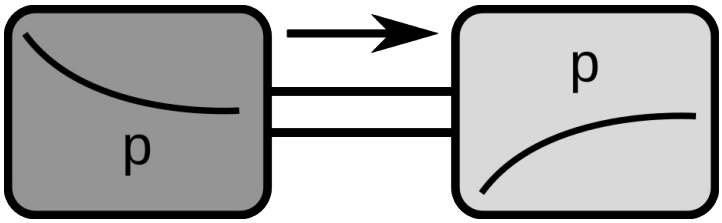
$$f(x) \rightarrow \dot{m}$$

Then, there is also the irregularity of porous media.

To exclude this influence and to focus on the underlying transport mechanisms, we consider a simple, straight channel here. Think of it as an idealized model of a porous medium.

The analytical model we cover today will be able to describe rarefied gas flow in such straight channels.

The experiments



P. Perrier, I. Graur – IUSTI, University Aix-Marseille

For measuring the mass flow at various Knudsen numbers, we use two different experimental setups.

One is shown here. It is located at the University Aix-Marseille and is used in cooperation with Pierre Perrier and Irina Graur.

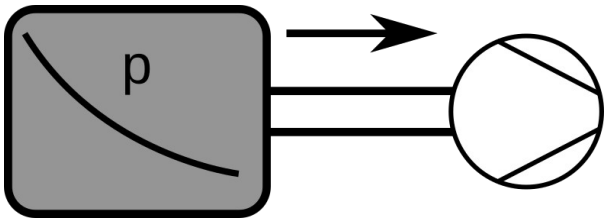
We have two constant volumes connected by a channel.

In the left volume, the pressure is high, in the right volume, the pressure is low.

When gas flows through the channel, the pressure in the first volume decreases, and it increases in the second volume.

The pressure slope can then be used to determine the mass flow.

The experiments



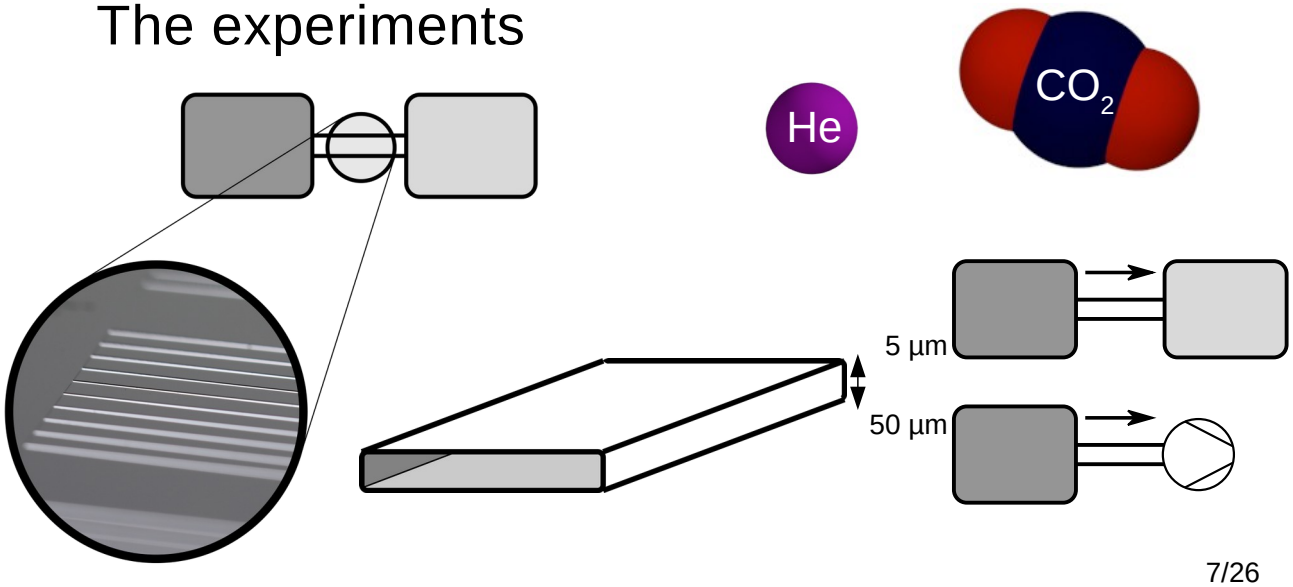
S. Varoutis, C. Day – ITEP, Karlsruhe Institute of Technology
S. Varoutis *et al* 2012 *J. Phys.: Conf. Ser.* **362** 012027

The second setup is located at the Karlsruhe Institute of Technology and is used in cooperation with Stylianos Varoutis and Christian Day.

This method is slighty different by using a vacuum pump at the right side of the channel instead of a second volume.

Here, only the pressure drop in the first volume is considered for mass flow calculation.

The experiments



We investigate rectangular channels etched into a silicon wafer.

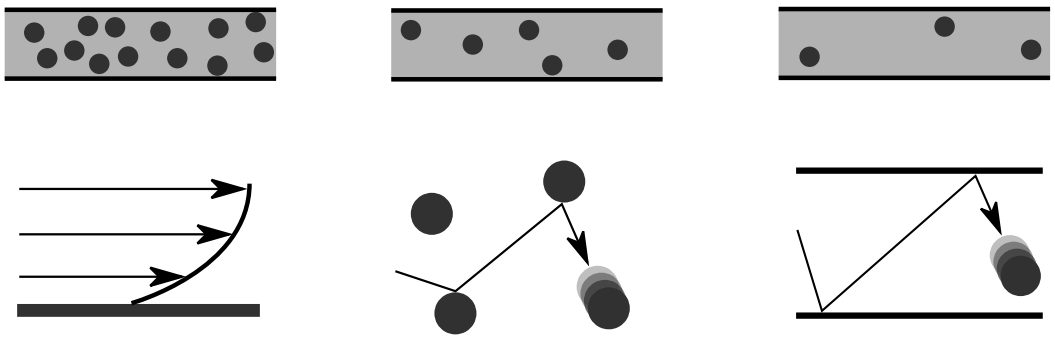
We use channels with a much larger width than height, because these exhibit an interesting characteristic, as we will see later.

They have a height of around 5 µm for the experiments in Marseille and around 50 µm for the experiments in Karlsruhe.

This is larger than the pores in a gas separation membrane, but still only one tenth of or equal to the thickness of a typical human hair.

To observe a potential selectivity in regard to gas species, helium and carbon dioxide is used, while each experimental run only uses one gas at a time.

The model



Kunze, S., Groll, R., Besser, B., Thöming, J. Molecular diameters of rarefied gases. *Sci Rep* **12**, 2057 (2022)

The approach for analitically modeling the mass flow is to divide the rarefied gas flow into three regimes which each have their own analytical expression.

For now, we consider a plain channel without surface functionalization.

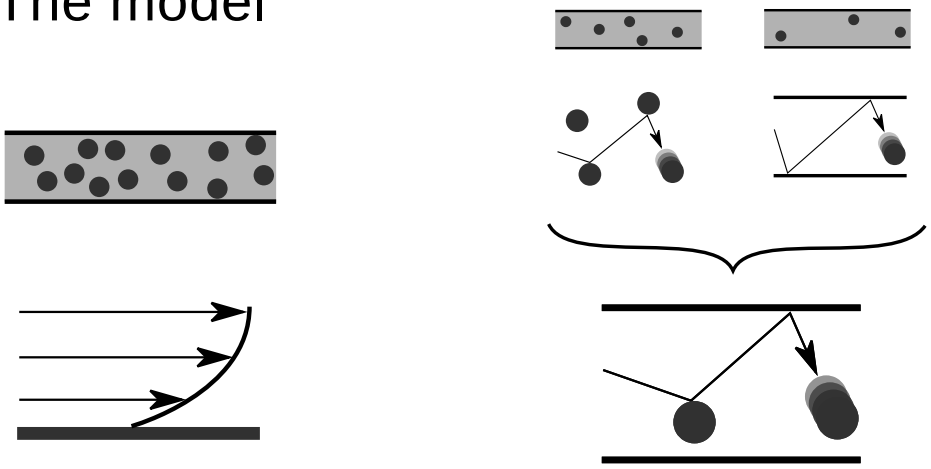
At small Kn numbers, convective flow dominates. However, for slightly rarefied gases, slip flow is prevalent which is convective flow corrected with a slip boundary condition. A classical first order slip boundary condition is modified to include the influence of the channel walls at very high Knudsen numbers, which would otherwise introduce errors.

At high Kn numbers, the molecules are free to move without intermolecular collision. This is called the Free Molecular regime and the molecules are only interacting with the surrounding geometry, resulting in free molecular diffusion. This behavior is well-described by the Smolukowski expression.

In between, at medium Kn numbers, the regime is classically termed “transition regime”. Here, bulk diffusion is the main transport mechanism and is described by Fickian diffusion.

Note that these three parts of the model are always present in all regimes, albeit to varying extent which is implied in their analytical expression.

The model

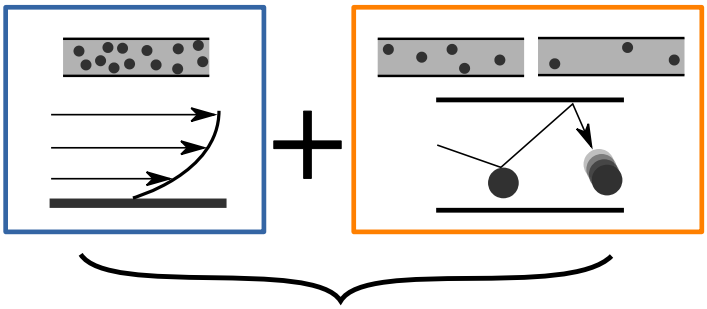


Kunze, S., Groll, R., Besser, B., Thöming, J. Molecular diameters of rarefied gases. *Sci Rep* **12**, 2057 (2022)

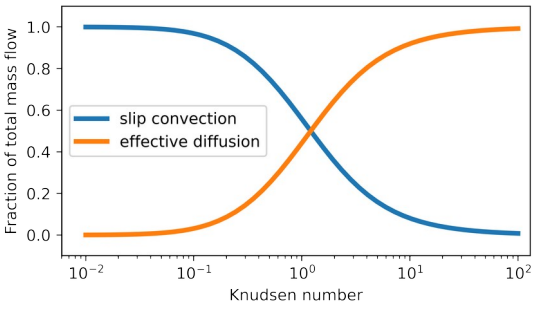
We now have different mechanisms at hand. We need to combine them to a total mass flow.

The Fickian diffusion and the free molecular diffusion can be combined to yield an “effective” diffusion. This effective diffusion takes into account the interaction between the molecules as well as the interaction with the surrounding geometry at the same time.

The model



$$f(x) \rightarrow \dot{m}$$

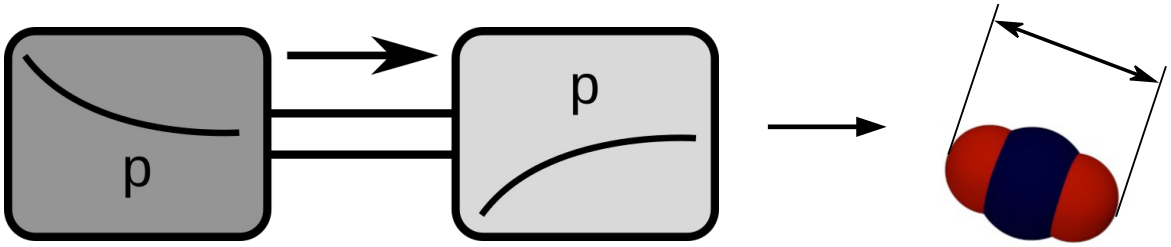


Kunze, S., Groll, R., Besser, B., Thöming, J. Molecular diameters of rarefied gases. *Sci Rep* **12**, 2057 (2022)

The slip convection and the effective diffusion are just added to yield the final mass flow.

On the right is a visualization of the contribution of the slip convection and the effective diffusion as a function of the Knudsen number. The convection vanishes for high Knudsen numbers, while the diffusion becomes more important, having a cross-over at around Knudsen = 1.

The model

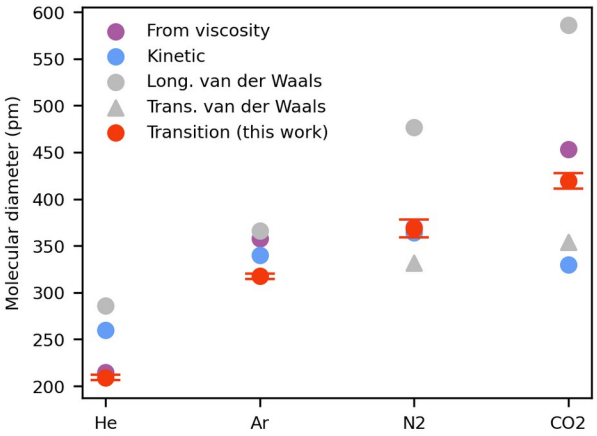


Kunze, S., Groll, R., Besser, B., Thöming, J. Molecular diameters of rarefied gases. *Sci Rep* **12**, 2057 (2022)

The model is then “calibrated” for a certain gas using experimental flow data, resulting in a unique molecular diameter suitable to describe rarefied gases across all Knudsen numbers.

This diameter is different to other commonly used diameters which have each their own way of measurement and their specific applications.

The model



Kunze, S., Groll, R., Besser, B., Thöming, J. Molecular diameters of rarefied gases. *Sci Rep* **12**, 2057 (2022)

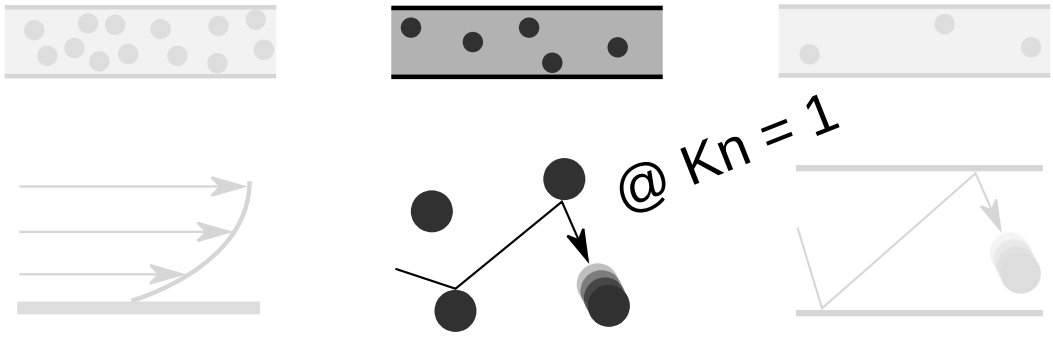
The results using literature data for helium, argon, nitrogen and carbon dioxide are shown here.

This diameter, termed “transition” diameter, is shown in red, and blends well into the range of the other diameters for each gas.

As soon as that is done, the model is transferable to any pressure conditions, temperatures and channel cross sections.

The diameter determined using literature data is used for the model to compare it to our experimental data. The diameter was not re-calculated using the experimental data acquired here.

Dimensionless mass flow



Now, to visualize mass flow for different Knudsen numbers because the mass flow becomes increasingly small for large Knudsen numbers, it is reasonable to use a dimensionless mass flow which is the actual mass flow divided by another mass flow.

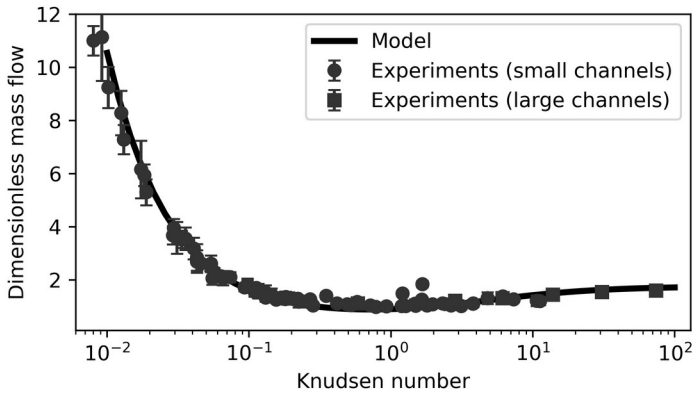
For this, the diffusive mass flow can be used. In particular, we use the diffusive mass flow that corresponds to conditions at Knudsen equals 1.

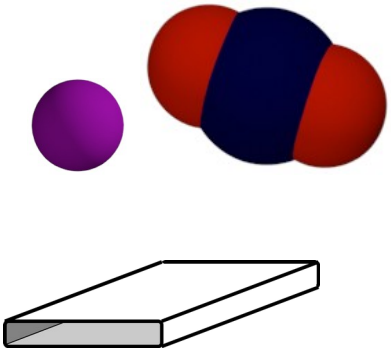
For circular channels, this recovers Knuden's original expression, often called Knudsen diffusion.

However, because rectangular geometries are more interesting, we have a look at those here. Note that the model however works for circular cross sections just as well.

If we normalize our actual mass flow this way, we get this result:

Dimensionless mass flow





We see here the dimensionless mass flow over the Knudsen number in a rectangular channel.

There is a clear minimum at around Knudsen equal 1.

After that minimum, the dimensionleses mass flow reaches a plateau.

This behavior is the before-mentioned “interesting characteristic” of such a high ratio rectangular channel, and it is an expected behavor as we see when comparing with experimental data, here for both helium and carbon dioxide.

Because in our system, the gas molecules interact a lot with the surface, we now want to have a more detailed look at that interaction.

TMAC

0 1

When a gas molecule hits a wall, it can be reflected in different ways.

On extreme is specular reflection. The molecule gets reflected at the angle of incidence.

The other extreme is diffuse reflection, where the molecule gets scattered in a random direction.

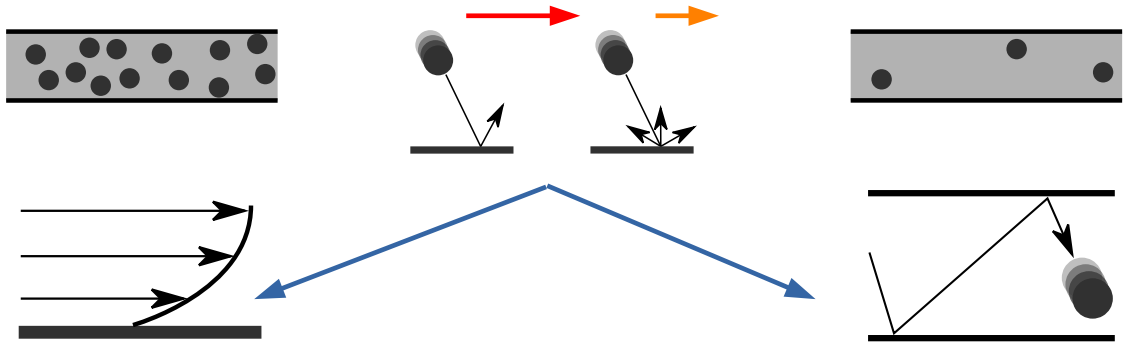
This can be characterized by the Tangential Momentum Accommodation Coefficient, or TMAC.

It is Zero for specular reflection, and One for diffuse reflection.

A real reflection can also be anywhere in between.

Specular reflection results in a faster gas flow, because the tangential momemtum is preserved. Diffuse reflection results in slower gas flow.

TMAC



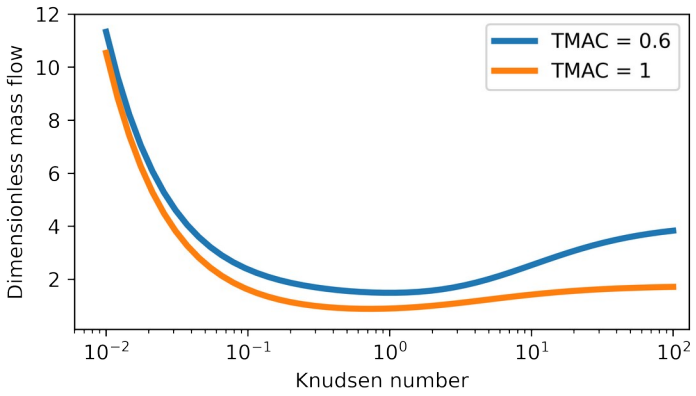
The TMAC therefore influences two aspects of the model, where direct interaction with the surface is considered:

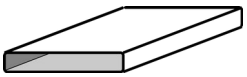
The slip flow and the free molecular flow.

Both these components are getting larger for smaller TMACs, that is more specular reflection.

Now, we are lucky because we can easily adjust the TMAC in our model and watch the results.

TMAC sensitivity





We see here what happens when we lower the TMAC.

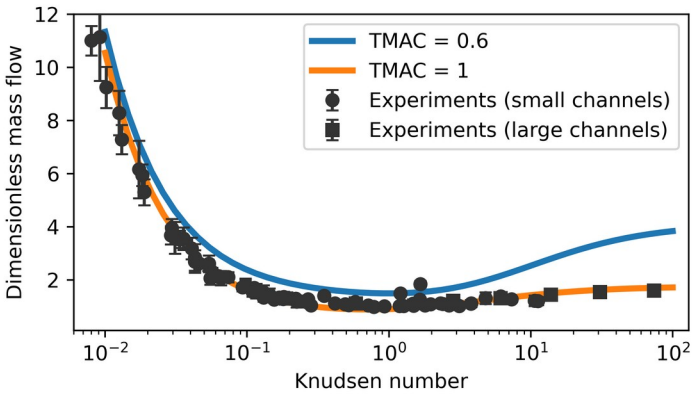
The mass flow rises the more specular reflection we have.

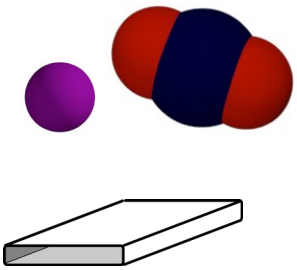
This is particularly pronounced at high Knudsen numbers, where we have the free molecular regime.

Now, the question is: which TMAC is correct?

Let’s again look at the experimental data.

Which TMAC is correct?





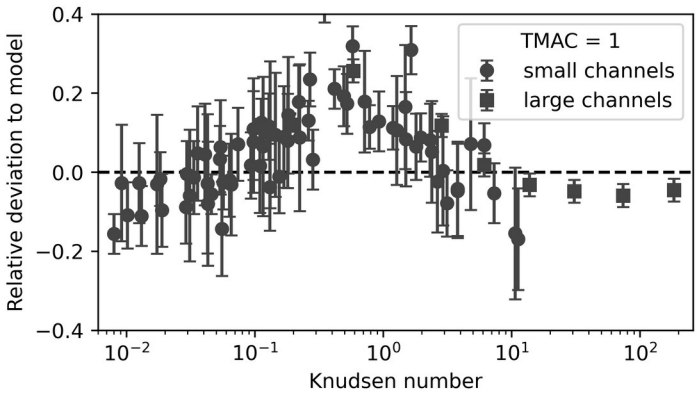
The experimental data clearly shows that a TMAC of 1 is most likely correct.

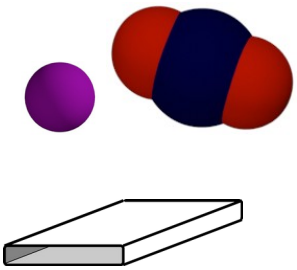
This is particularly convincing in the free molecular regime, where the flow is almost exclusively described by the Smoluchowski equation. There is also almost no influnce of the before-mentioned molecular diameter here.

A TMAC of 1 is in contradiction with results seen in literature, where often a TMAC of around 0.8 is stated.

But since generally, the TMAC is determined not using the free molecular flow but data for smaller Knudsen numbers, let’s see what happens if we change the TMAC for only the slip convection.

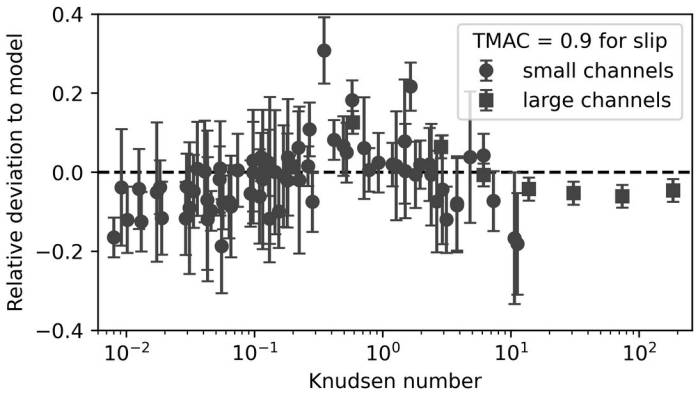
Which TMAC is correct?

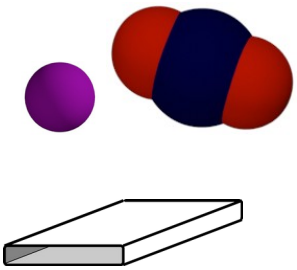




We see here the deviation of experiments from the model, with a TMAC of 1 for both the slip and the free molecular part. A positive deviation means that the measured mass flow is higher than the predicted mass flow by the model.

Which TMAC is correct?





Here, we see the result if we change the TMAC just for the slip convection to 0.9.

The results are slightly better, especially for the region around Kn = 1. Note that the TMAC for the free molecular regime stays at 1 for the whole time.

Which TMAC is correct?

Now, again, the question is, which is the correct TMAC?

Is it the TMAC of 0.9, the one of the slip flow expression, with a partially specular reflection?

Or is it the TMAC of 1, which is present in the free molecular regime?

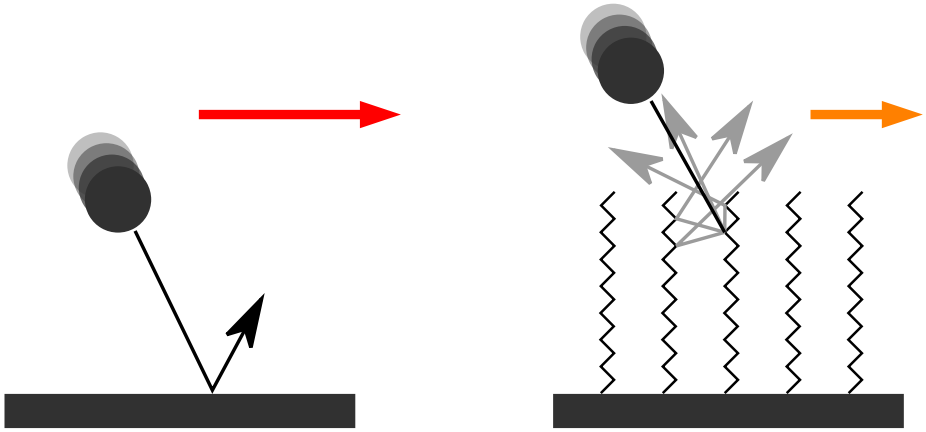
Functionalization

To investigate the interaction with the surface in more detail, we performed experiments with a functionalized channel surface.

For this, we used chemical vapor deposition to attach hydrocarbon silanes to the channel surfaces.

These hydrocarbons can be used in gas seperation membranes to achieve a selectivity with regard to the gas species.

Functionalization

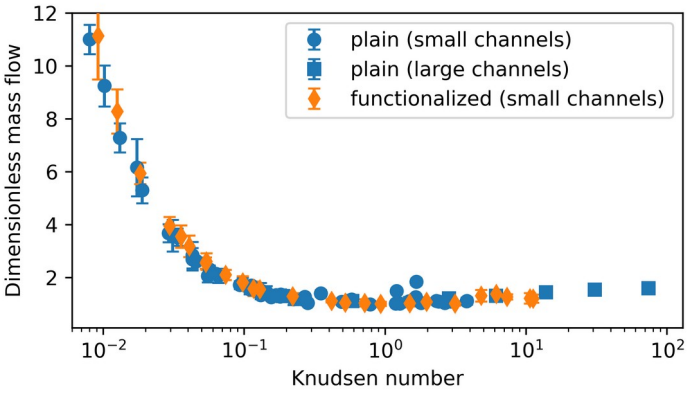


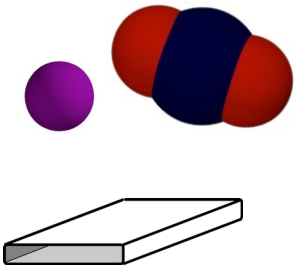
The functionalization introduces a significant irregularity, or roughness, onto the surface.

If there was any specular reflection on the surface before this procedure, it should now be more diffusive or even fully diffusive with the functionalization.

This should be detectable because a change of the TMAC results in a change of mass flow, as discussed before.

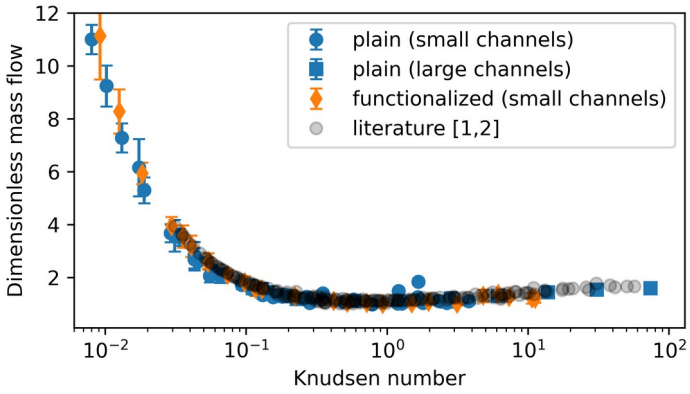
Functionalization

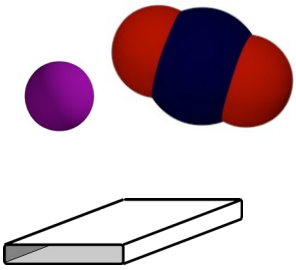




But, as can be seen here, there is just no difference in mass flow between a plain and a functionalized channel.

Functionalization





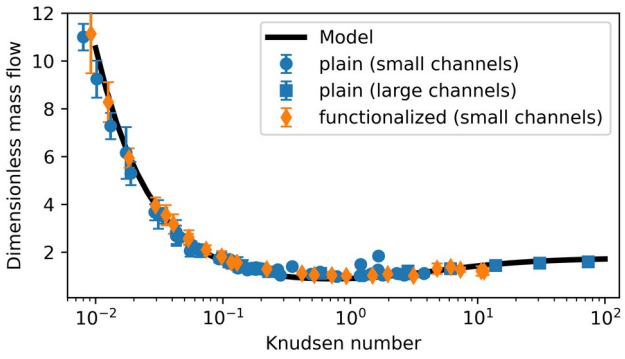
[1] Ewart, T., Perrier, P., Graur, I. A. & Méolans, J. G. Mass flow rate measurements in a microchannel, from hydrodynamic to near free molecular regimes. J Fluid Mech 584, 337 (2007).
[2] Graur, I. A., Perrier, P., Ghozlani, W. & Méolans, J. G. Measurements of tangential momentum accommodation coefficient for various gases in plane microchannel. Phys Fluids 21, 102004 (2009).

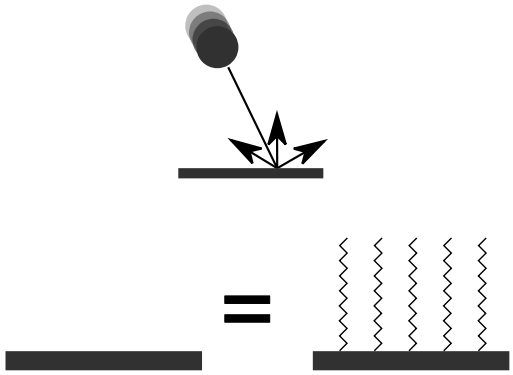
And all these results are in agreement with experimental values from the literature.

So indeed, the TMAC should be 1 everywhere in the first place. Why would a TMAC of 0.9 for the slip expression give a better result?

We suggest that this may be due to a flawed slip expression yielding an unprecise result. The actual TMAC even for smaller Knudsen numbers should still be 1.

Conclusion





$f(x) \rightarrow \dot{m}$ ✓

So, to sum things up:

We can confidently say that the TMAC is one for our experiments as well as the literature values used for comparison. We therefore only observe diffuse reflection, which is reasonable for technical surfaces.

At the scale of the channels considered here, a surface functionalization does not have an effect as opposed to effects clearly observed in membranes.

And: the analytical model is able to reliably describe the gas flow through these rectangular channels for all Knudsen numbers.