Directed Brownian Motion?
Thermo-molecular transport mechanisms in longitudinally asymmetric microchannels (LAMs)

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Advanced Separation

- fluid dynamics
- membranes
- electrokinetics & dielectrics

Tailored Reaction Systems

- multi-phase reactions
- $\mu$-reactors
- foam catalysts
- membrane-reactors
Main question

How **gas specific** can transport be in long and longitudinally asymmetric microchannels (LAMs)?

\[ \frac{d}{L} < 0.001 \]
Temperature driven transport mechanism in microchannels

Thermal creep (TC)
\[ \frac{dn_{TC}}{dt} = G \cdot n \cdot \frac{dT}{dL}_{wall} \]

Convective transport (CT)
\[ \frac{dn_{CT}^i}{dt} = K_D \cdot \frac{p}{RT} (p_j - p_i) \]

Effusion
\[ \frac{dn_i}{dt} = n_i \sqrt{\frac{kT_i}{2\pi m}} \]

T: temperature, t: time
n: number density
amount of material in moles
m: mass of atom/molecule
Temperature driven transport mechanism in microchannels

Hypothesis 1:
Long asymmetric μ-channels provide

- high $\Delta l$
- strong TC

\[ I = \frac{2 - \sigma}{\sigma} \text{Kn} \]
\( I: \text{Slip length} \)
\( \sigma: \text{TMAC} \)
Hypothesis 2:
Long asymmetric $\mu$-channels can direct Brownian motion gas specifically ($Kn > 0.01$)

\[ l = \frac{2 - \sigma}{\sigma} Kn \]

\( l \): Slip length
\( \sigma \): TMAC
Temperature driven transport mechanism in microchannels

DBM: directed Brownian motion
Experimental testing of LAMs

Long Asymmetric Microchannels

Glass capillary bundle of app. 200 3D-LAMs
CT-scan

3D-LAM

$\alpha = 0.028^\circ$

$d \sim 1 \mu m$

$L = 15,000 \mu m$
Trapezoidal µ-channels: 2D-LAM

Schematic of geometries

1,000 – 15,000 µm

2.4 µm +/- 0.3 µm
Batch set-up
Effect of channel length

@ $\Delta T = T_{\text{tip}} - T_{\text{Base}} = 8 \pm 0.9 \, \text{K}$
Longitudinal asymmetry enhances thermal creep

Here: hot gas, cold wall

\[ G = f(\text{Kn}) \]

\[ \frac{dn^{TC}}{dt} = \frac{G}{L_{eq}} \cdot \bar{n} \cdot \Delta T \]

- \( dT/dL_{eq} = \text{const} \)

\[ G/L_{eq} = a \Delta T^2 + b \Delta T \]

**Graph**

- **Graph** showing the relationship between \( G/L_{eq} \) and \( \Delta T \) for different pressures (50 kPa and 102 kPa).

**Diagram**

- Difference in slip length \( \Delta l \) increases.
- Slip and transition range, \( T_1 \)
- Continuum range, \( T_2 \)
- High momentum transfer
- Zero momentum transfer \( (l = 0) \)

**Equation**

\[ G/L_{eq} = a \Delta T^2 + b \Delta T \]
Directed Brownian motion?

Change in number density in tip chamber

\[ \Delta T = T_{\text{tip}} - T_{\text{Base}} \]

Rate of material transport from tip to base at \( t = 0 \) s

- Batch pressure measurements
- Simulation
Quantitative macro-scale model

\[ dp_i = \left( \frac{\partial p_i}{\partial T_i} \right)_n dT_i + \left( \frac{\partial p_i}{\partial n_i} \right)_T dn_i \]

\[ dn_i = dn_i^{BM} - dn_j^{BM} + dn^{TC} + dn_i^{CT} \]

\[ \frac{dn_i^{BM}}{dt} = -K_i \cdot n_i \sqrt{\frac{kT_i}{2\pi \cdot m}} \]

\[ \frac{dn^{TC}}{dt} = G \cdot \bar{n} \cdot \frac{dT}{dL}_{wall} \]

\[ \frac{dn_i^{CT}}{dt} = K_D \cdot \frac{\bar{p}}{RT} (p_j - p_i) \]

Chambers i and j

p: pressure, T: temperature, n: amount of material in moles, t: time

Change in number of molecules (initially \( n_{0,i} \)), in particular through directed brownian motion (BM), thermal creep (TC), and conservation of momentum (Convective transport, CT)

k: Boltzmann constant
K_j: direction specific molecule permeability

G: thermal transpiration coefficient
Parameter K and G used in simulation

\[ K = K_{\text{Tip} \rightarrow \text{base}} / K_{\text{base} \rightarrow \text{Tip}} \]

Order of magnitude

\[ K_{\text{base} \rightarrow \text{Tip}} = 1 \times 10^{-10} \text{ m}^{-1} \]

Again: hot gas, cold wall

\[ G = f(K_n) \]

\[ \frac{dT}{dL_{eq}} = \text{const} \]

\[ \frac{dn^{TC}}{dt} = \frac{G}{L_{eq}} \cdot n \cdot \Delta T \]

\[ G/L_{eq} = a \Delta T^2 + b \Delta T \]

\[ d/L \leq 0.001 \]
Sreening of asymmetric channels

No such effects observed
for \( d/L > 0.001 \)
Validation with continuous plant still lacking

Holder for 2D-LAMs
Molecular dynamics simulations

(1) surface with gas (xsd-file) → (2) run simulation (perl-file) → (3) trajectories of gas (xtd-file) → (4) analyse xtd-file (perl-file) → (5) results (txt-file)

In cooperation with
L. Colombi Ciacchi, Bremen, Germany
A. Chaffee, Monash University, Australia

CO₂

-OH

silicon
Molecular dynamics simulations

Scattering Angle (beta) [deg]

- **Ar/OH - 298K; 45deg**
  - Mean beta: 46.18°

- **N₂/OH - 298K; 45deg**
  - Mean beta: 46.71°

- **CO₂/OH - 298K; 45deg**
  - Mean beta: 41.38°

- Specular scattering
- Mixed
  - Specular / diffuse scattering
Conclusions

- In long asymmetric channels
  - surprisingly strong thermal creep was observed at low $\Delta T$

- it appears that wall scattering can direct Brownian motion *gas specifically*

- The effects have not yet been validated in a continuous set-up
In cooperation with:

- Membranotec
- E.ON
- RWE
- Universität Bremen

We acknowledge financial support by

- BMWI
- DFG

and

PoreNet

GRADUIERTENKOLLEG
Longitudinal asymmetry enhances thermal creep

\[ \text{Kn} \approx \text{const} \rightarrow l \approx \text{const} \]

**Difference in slip length \( \Delta l \) increases**
DBM – the mechanism

Different gas molecules have different interactions with a surface

because of different adsorption enthalpy, Lennard-Jones parameters, ...

Knudsen cosine law
\[ \frac{1}{\pi} \cdot n \cdot \cos \phi \cdot d\phi \]

[Knudsen 1915]

Back scattering  Forward scattering  Surface diffusion
Membrane

cone angle $\alpha = 0.25^\circ$

depth of channel = 7 $\mu$m

number of channels = 75
Thermo-molecular transport in long asymmetric microchannels (LAMs).

Test gas: CO₂

Dominating effect
thermal-creep

Δp = p_{Tip} - p_{Base}

DBM

Relaxation due to continuous steady temperature difference ΔT = 8 ± 0.9 K
p_{abs} varying from 25 to 102 kPa, i.e. Kn_{Tip} = 0.111 to 0.027 respectively.
Continuous plant measures reliably in continuum range.