TECHNISCHE UNIVERSITÄT WIEN
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Transport equations for confined structures derived from the Boltzmann equation

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New applications give rise to new mathematical problems—“never do what has been done before”

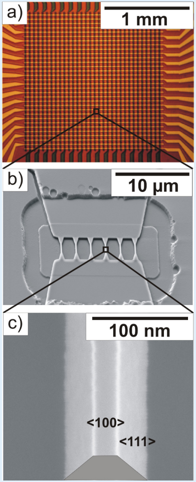
Nanotechnology is a very young field, and hence there are many open questions:

- nanowire field-effect biosensors,
- nanowire gas sensors,
- nanopores, etc.

Physics-based modeling leads to new mathematical problems:

- Homogenization:
  new multiscale problems arise in a natural manner.
- Uncertainty quantification:
  to go beyond the calculation of averages.

It is important to compare measurements with simulations. Optimal design.



Motivation: applications

- Ionic channels,
- Nanopores.

Motivation: modeling

- Molecular dynamics,
- Brownian dynamics,
- Drift-diffusion equations.

A transport equation for confined structures such as nanowires, nanopores, and ionic channels

Derivation and analysis of a classical sub-band type model for particle transport in narrowly confined geometries.

Confinement direction(s): treat particles on a microscopic level.
Unconfined direction(s): treat asymptotically on a much larger time scale.

Starting point is the 3D Boltzmann transport equation. We include the complex geometry of the confinement potential.

For 2D confinement and a harmonic confinement potential, explicit expressions for the transport coefficients in the diffusion-type equation were given.

Computationally, this yields an optimal reduction of the $(6+1)$-dimensional problem to a $(2+1)$-dimensional problem.

[C.H. and Christian Ringhofer. A transport equation for confined structures derived from the Boltzmann equation. *Commun. Math. Sci.*, 9(3):829–857, 2011.]

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The basic equation

We start from the Boltzmann equation in the form

$$\partial_t f + \{\mathcal{E}, f\}_{XP} + \mathcal{Q}[f] = 0,$$

where the Hamiltonian transport term is given by the Poisson bracket

$$\{g, f\}_{XP} := \nabla_P g \cdot \nabla_X f - \nabla_X g \cdot \nabla_P f.$$

The energy $\mathcal{E}(X, P)$ is given by

$$\mathcal{E}(X, P) := V(X) + \frac{|P|^2}{2m},$$

where $V(X)$ is the external potential, $|P|^2/(2m)$ the kinetic energy, and m the particle mass.

Confinement and scaling

We split the position variable X into $X = (x, y)$
and the momentum variable P into $P = (p, q) = (v, w)$,
where $x, p \in \mathbb{R}^d$ are coordinates in the longitudinal transport direction(s)
and $y, q \in \mathbb{R}^{3-d}$ are coordinates in the transverse confinement direction(s).

We split the potential V into two parts so that

$$V(x, y) = V_0(x) + V_1\left(x, \frac{y}{\epsilon}\right).$$

ϵ is the length scale of the structure in the (confined transverse) y-direction.
Hence $\epsilon \ll 1$ is the aspect ratio of the tube or plate.

V_1 is the confining potential and V_0 is an external, applied potential driving charged particles through the structure.

This scaling implies that $|\nabla_y V| = O(\frac{1}{\epsilon}|\nabla_x V|)$, i.e., the confining forces are much larger that the external forces driving the particles.

Confinement and scaling

Correspondingly, we split the energy and the Poisson bracket into

$$\begin{aligned}
\mathcal{E}(X,P) &:= \mathcal{E}_x(x,p) + \mathcal{E}_y(x,y,q), \\
\{g,f\}_{XP} &= \{g,f\}_{xp} + \{g,f\}_{yq}, \\
\mathcal{E}_x(x,p) &:= V_0(x) + \frac{|p|^2}{2m}, \\
\mathcal{E}_y(x,y,q) &:= V_1\left(x, \frac{y}{\epsilon}\right) + \frac{|q|^2}{2m}, \\
\{g,f\}_{xp} &= \nabla_x \cdot (f \nabla_p g) - \nabla_p \cdot (f \nabla_x g), \\
\{g,f\}_{yq} &= \nabla_y \cdot (f \nabla_q g) - \nabla_q \cdot (f \nabla_y g).
\end{aligned}$$

Then the Boltzmann equation becomes

$$\partial_t f + \{\mathcal{E}_x + \mathcal{E}_y, f\}_{xp} + \{\mathcal{E}_y, f\}_{yq} + \mathcal{Q}[f] = 0.$$

The collision operator

Due to the narrow confinement, collisions are much more likely to take place in the transport x-direction than in the confinement y-direction.

Therefore, we model collisions to be described by a relaxation operator $\mathcal{Q}$

- which locally conserves the transverse energy $\mathcal{E}_y(x, y, q)$ when averaged over y
- while relaxing the longitudinal kinetic energy $\mathcal{E}_x(x, p)$ against a Maxwellian distribution.

Hence, the collision operator $\mathcal{Q}$ is given by

$$\mathcal{Q}[f](x, y, p, q, t) := \frac{1}{\tau}\left(f - M(p)\frac{u_f(x, \mathcal{E}_y(x, y, q), t)}{N(x, \mathcal{E}_y(x, y, q))}\right),$$

where M is a Maxwellian, N is the density of states

$$N(x, \eta) := \int \delta(\mathcal{E}_y(x, y, q) - \eta)\, \mathrm{d}yq,$$

$$\text{and} \quad u_f(x, \eta, t) := \int \delta(\mathcal{E}_y(x, y, q) - \eta) f(x, y, p, q, t)\, \mathrm{d}ypq.$$

Summary of the setup

Now the Boltzmann equation becomes

$$\epsilon\partial_t f + \{\mathcal{E}_x + \mathcal{E}_y, f\}_{xv} + \frac{1}{\epsilon}\{\mathcal{E}_y, f\}_{yw} + \frac{1}{\epsilon\tau}\mathcal{Q}[f] = 0.$$

- Transport occurs in a narrow, irregular structure with aspect ratio ϵ.
- The confining forces are much larger than the external forces that drive the particles through the structure, i.e., $|\nabla_x V| = O(\epsilon|\nabla_y V|)$.
- Collisions with the background conserve the transverse energy $\mathcal{E}_y$ while dissipating the longitudinal energy $\mathcal{E}_x$ in the transport direction x.
- Collisions occur frequently on the time scale of transport in the longitudinal transport x-direction.

Chapman-Enskog expansion

First, we observe that the linear relaxation operator $\mathcal{Q}$ is a projection operator. We define the projection operator ¶ by

$$\P[f](x,y,v,w,t) := \frac{\rho_f(x,\mathcal{E}_y(x,y,w),t)}{N(x,\mathcal{E}_y(x,y,w))} M(v),$$

$$N(x,\eta) := \int \delta(\mathcal{E}_y(x,y,w)-\eta)\,\mathrm{d}yw,$$

$$\rho_f(x,\eta,t) := \int \delta(\mathcal{E}_y(x,y,w)-\eta) f(x,y,v,w,t)\,\mathrm{d}yvw,$$

where $M(v)$ is the Maxwellian and $N(x,\eta)$ is the density-of-states function.

We find that $\mathcal{Q} = \mathcal{I} - \P$ with $\mathcal{I}$ being the identity operator.

The projection ¶ projects onto the linear manifold of functions which are multiples of the Maxwellian $M(v)$ and depend on y and w only through the energy $\mathcal{E}_y(x,y,w)$.

Chapman-Enskog expansion

We split the density function $f(x, y, v, w, t)$ into

$$f = f_0 + \epsilon f_1,$$
$$f_0(x, y, v, w, t) := \P[f](x, y, v, w, t),$$
$$f_1(x, y, v, w, t) := \frac{1}{\epsilon}(\mathcal{I} - \P)[f](x, y, v, w, t).$$

Then we split the Boltzmann equation by applying the projections $\P$ and $\mathcal{I} - \P$.

Then various identities (Poisson bracket is a directional derivative; cyclicity of the commutator trace; $\{\mathcal{E}_y, \phi\}_{yw} = 0$ holds for any function ϕ which depends on y and w only through the energy $\mathcal{E}_y$) yield

$$\epsilon \partial_t f_0 + \P[\{\mathcal{E}_x + \mathcal{E}_y, f_0 + \epsilon f_1\}_{xv}] = 0,$$
$$\epsilon^2 \partial_t f_1 + (\mathcal{I} - \P)[\{\mathcal{E}_x + \mathcal{E}_y, f_0 + \epsilon f_1\}_{xv}] + \frac{1}{\epsilon}\{\mathcal{E}_y, f_0 + \epsilon f_1\}_{yw} + \frac{1}{\tau} f_1 = 0.$$

Chapman-Enskog expansion

Further simplifications are possible using again algebraic properties of the Poisson bracket and the projection operator ¶ so that we find

$$\epsilon \partial_t f_0 + ¶[\{\mathcal{E}_x + \mathcal{E}_y, \epsilon f_1\}_{xv}] = 0,$$

$$\epsilon^2 \partial_t f_1 + \{\mathcal{E}_x + \mathcal{E}_y, f_0 + \epsilon f_1\}_{xv} - ¶[\{\mathcal{E}_x + \mathcal{E}_y, \epsilon f_1\}_{xv}] + \frac{1}{\epsilon}\{\mathcal{E}_y, \epsilon f_1\}_{yw} + \frac{1}{\tau} f_1 = 0.$$

The first equation gives the evolution on the kernel manifold of the operator $\mathcal{Q}$; the second equation gives the evolution on the orthogonal complement.

The macroscopic approximation is obtained by formally dropping the $O(\epsilon)$ terms,

$$\partial_t f_0 + ¶[\{\mathcal{E}_x + \mathcal{E}_y, f_1\}_{xv}] = 0,$$

$$\{\mathcal{E}_x + \mathcal{E}_y, f_0\}_{xv} + \{\mathcal{E}_y, f_1\}_{yw} + \frac{1}{\tau} f_1 = 0.$$

In other words, the term ϵf_1 will stay small for all time assuming that we start on the kernel manifold.

The conservation law

The first equation can be written as a conservation law for the density ρ_{f_0}. From the weak formulation, we find that

$$\partial_t \rho_{f_0}(x, \eta, t) + \nabla_x \cdot F^x + \partial_\eta F^\eta = 0,$$

where the fluxes are

$$F^x(x, \eta, t) := \int \delta(\mathcal{E}_y - \eta) v f_1 \, \mathrm{d}yvw,$$

$$F^\eta(x, \eta, t) := \int \delta(\mathcal{E}_y - \eta)(\nabla_x V_1 \cdot v) f_1 \, \mathrm{d}yvw.$$

This is a conservation law for the mesoscopic fluid density ρ_{f_0}, which still depends on the free energy $\eta = \mathcal{E}_y$. The mesoscopic equation for ρ_{f_0} will contain second-order partial derivatives w.r.t. x and η.

The challenge is to compute the fluxes F^x and F^η, i.e., to compute the density f_1 for a given f_0 of the form $f_0(x, y, v, w, t) = M(v)\rho_{f_0}(x, \mathcal{E}_y, t)/N(x, \mathcal{E}_y)$.

An entropy estimate

There are two goals:

- To show well-posedness. We will show that there is a convex functional of the density ρ, an entropy, which decays in time.
- To make the system amenable to computations (stability). We will use a Galerkin approximation later.

We write the system as

$$\partial_t \rho(x,\eta,t) + \mathcal{L}_1[f_1](x,\eta,t) = 0,$$

$$\mathcal{L}_2[\rho](x,y,v,w,t) + \{\mathcal{E}_y, f_1\}_{yw} + \frac{1}{\tau} f_1 = 0$$

with the linear operators $\mathcal{L}_1$ and $\mathcal{L}_2$ defined by

$$\mathcal{L}_1[f_1](x,\eta,t) := \int \delta(\mathcal{E}_y(x,y,w) - \eta)\{\mathcal{E}_x + \mathcal{E}_y, f_1\}_{xv}\,\mathrm{d}yvw,$$

$$\mathcal{L}_2[\rho](x,y,v,w,t) := \left\{\mathcal{E}_x + \mathcal{E}_y, M(v)\frac{\rho(x,\mathcal{E}_y,t)}{N(x,\mathcal{E}_y)}\right\}_{xv}.$$

An adjoint property

Let $\mathcal{L}_1^{\mathrm{adj}}$ denote the adjoint of $\mathcal{L}_1$ with respect to the L^2 inner product.

Lemma (adjoint property for $\mathcal{L}_1$ and $\mathcal{L}_2$)

The operators $\mathcal{L}_1$ and $\mathcal{L}_2$ are related by the equation

$$\mathcal{L}_2[\rho](x,y,v,w,t) = -c\mathrm{e}^{-\mathcal{E}_{\boldsymbol{x}}-\mathcal{E}_{\boldsymbol{y}}}\mathcal{L}_1^{\mathrm{adj}}\left[\frac{\mathrm{e}^{V_0(x)+\eta}\rho(x,\eta,t)}{N(x,\eta)}\right](x,y,v,w,t).$$

Furthermore, the identity $\mathfrak{Re}\left(\int \mathrm{e}^{\mathcal{E}_{\boldsymbol{x}}+\mathcal{E}_{\boldsymbol{y}}} f^*\{\mathcal{E}_y, f\}_{yw}\,\mathrm{d}yw\right) = 0 \quad \forall x$ holds for all x and for all complex functions $f(y,w)$, where $\mathfrak{Re}$ is the real part.

Here the constant c denotes the normalization constant of the Maxwellian so that $M(v) = c\exp(-|v|^2/2)$ holds.

The entropy estimate

We use this lemma to rewrite the system as

$$\partial_t \rho(x,\eta,t) + \mathcal{L}_1[f_1](x,\eta,t) = 0,$$
$$-c\mathrm{e}^{-\mathcal{E}_x-\mathcal{E}_y}\mathcal{L}_1^{\mathrm{adj}}\left[\frac{\mathrm{e}^{V_0(x)+\eta}\rho(x,\eta,t)}{N(x,\eta)}\right] + \{\mathcal{E}_y, f_1\}_{yw} + \frac{1}{\tau}f_1 = 0$$

and can now proof the following entropy estimate.

Theorem (entropy estimate)

Solutions (ρ, f_1) of the system satisfy the entropy estimate

$$\frac{1}{2}\partial_t \int \frac{\mathrm{e}^{V_0(x)+\eta}}{N(x,\eta)}|\rho(x,\eta,t)|^2\,\mathrm{d}x\eta = -\frac{1}{c\tau}\int \mathrm{e}^{\mathcal{E}_x+\mathcal{E}_y}|f_1|^2\,\mathrm{d}xyvw \le 0.$$

The Galerkin approximation: eliminating the lateral momentum v

The dependence of the operator $\mathcal{L}_2$ on the momentum v takes the form of a multiple of the function $M(v)v$, i.e.,

$$\mathcal{L}_2[\rho](x, y, v, w, t) = M(v)v \cdot \left(\nabla_x \left(\frac{\rho(x, \mathcal{E}_y, t)}{N(x, \mathcal{E}_y)} \right) + \frac{\rho(x, \mathcal{E}_y, t)}{N(x, \mathcal{E}_y)} \nabla_x (V_0 + V_1) \right).$$

Since the Poisson bracket $\{\mathcal{E}_y, f_1\}_{yw}$ does not operate on the momentum component v, the second equation allows a solution of the form

$$f_1(x, y, v, w, t) = M(v)v \cdot g(x, y, w, t),$$

where the function $g(x, y, w, t) \in \mathbb{R}^d$ is vector valued for the case of a plate ($d = 2$) and scalar in the case of a tube ($d = 1$).

The adjoint property revisited

To exploit this structures of $\mathcal{L}_1$ and $\mathcal{L}_2$, we define the operators Λ_1 and Λ_2 as

$$\begin{aligned}
\Lambda_1[g](x,\eta,t) &:= \mathcal{L}_1[M(v)v\cdot g](x,\eta,t),\\
\mathcal{L}_2[\rho](x,y,v,w,t) &= M(v)v\cdot\Lambda_2[\rho](x,y,w,t),\\
\Lambda_2[\rho](x,y,w,t) &:= \nabla_x\left(\frac{\rho(x,\mathcal{E}_y,t)}{N(x,\mathcal{E}_y)}\right)+\frac{\rho(x,\mathcal{E}_y,t)}{N(x,\mathcal{E}_y)}\nabla_x(V_0+V_1).
\end{aligned}$$

Then the system becomes

$$\begin{aligned}
\partial_t\rho(x,\eta,t)+\Lambda_1[g](x,\eta,t) &= 0,\\
\Lambda_2[\rho](x,y,w,t)+\{\mathcal{E}_y,g\}_{yw}+\frac{1}{\tau}g &= 0.
\end{aligned}$$

Lemma (adjoint property for Λ_1 and Λ_2)

The operator Λ_1 equals

$$\Lambda_1[g](x,\eta,t) = \int \nabla_x \cdot \big(\delta(\mathcal{E}_y - \eta) g(x,y,w,t)\big) + \partial_\eta \big(\delta(\mathcal{E}_y - \eta)\nabla_x V_1(x,y)\cdot g\big)\,\mathrm{d}yw$$

and the operator Λ_2 is given in terms of the adjoint of Λ_1 by

$$\Lambda_2[\rho](x,y,w,t) = -\mathrm{e}^{-V_0-\mathcal{E}_y}\Lambda_1^{\mathrm{adj}}\left[\mathrm{e}^{V_0+\eta}\frac{\rho(x,\eta,t)}{N(x,\eta)}\right](x,y,w,t).$$

Furthermore the identity

$$\mathfrak{Re}\Big(\int \mathrm{e}^{\mathcal{E}_x+\mathcal{E}_y} g^H \{\mathcal{E}_y, g\}_{yw}\,\mathrm{d}yw\Big) = 0 \quad \forall x$$

holds for all complex functions $g(y,w)$.

The system

After eliminating the lateral momentum v and using the adjoint property for Λ_2, the system becomes

$$\partial_t \rho(x,\eta,t) + \Lambda_1[g](x,\eta,t) = 0,$$
$$-\mathrm{e}^{-V_0-\mathcal{E}_y}\Lambda_1^{\mathrm{adj}}\left[\mathrm{e}^{V_0+\eta}\frac{\rho(x,\eta,t)}{N(x,\eta)}\right](x,y,w,t) + \{\mathcal{E}_y, g\}_{yw} + \frac{1}{\tau}g(x,y,w,t) = 0.$$

In order to obtain a closed equation for the mesoscopic density $\rho(x,\eta,t)$, the second equation has to be inverted for g in terms of ρ.

For a general confinement potential $V_1(x,y)$, this can only be done approximatively. This approximation will take the form of a series expansion, i.e., Galerkin solution.

The variable transformation Γ and its inverse Ω

A crucial aspect is the usage of a bijective variable transformation that maps

$$(y, w) \in \mathbb{R}^{6-2d} \quad \text{to} \quad \big(u = \mathcal{E}_y(x, y, w), \theta\big),$$

where $u \in \mathbb{R}$ denotes an energy and $\theta \in \mathbb{R}^{5-2d}$ an angle.
(Recall $x, v \in \mathbb{R}^d$ and $y, w \in \mathbb{R}^{3-d}$.)

We write

$$\begin{aligned}
(u, \theta) &= \Gamma(x, y, w), \\
(y, w) &= \Omega(x, u, \theta), \\
\Gamma(x, \Omega(x, u, \theta)) &= (u, \theta), \\
\Omega(x, \Gamma(x, y, w)) &= (y, w),
\end{aligned}$$

since the variable transformation can depend on x.

Importantly,

$$\mathcal{E}_y(x, \Omega(x, u, \theta)) = u$$

holds.

The system after the variable transformation Γ

Three lemmata and a couple of pages later, we have calculated the transformed system

$$\partial_t \rho(x,\eta,t) + \mathcal{A}[g_1](x,\eta,t) = 0,$$

$$-\mathrm{e}^{-V_0-u}\mathcal{A}^{\mathrm{adj}}\left[\mathrm{e}^{V_0+\eta}\frac{\rho(x,\eta,t)}{N(x,\eta)}\right](x,u,\theta,t) + \sigma(S\cdot\nabla_\theta)g_1 + \frac{\sigma}{\tau}g_1(x,u,\theta,t) = 0,$$

where

$$\begin{aligned}
\mathcal{A}[g_1](x,\eta,t) &:= \int \nabla_x \cdot \big(\sigma g_1(x,\eta,\theta,t)\big) \\
&\qquad + \partial_\eta\big(\sigma(x,\eta,\theta)\nabla_1 V_1(x,\Omega_y(x,\eta,\theta))\cdot g_1\big)\,\mathrm{d}\theta, \\
S(x,u,\theta) &:= (\gamma_{21}\gamma_{12}^T - \gamma_{22}\gamma_{11}^T)(x,\Omega(x,u,\theta) \in \mathbb{R}^{5-2d}, \\
\sigma(x,u,\theta) &:= \left|\det(\partial\Omega(x,u,\theta))\right|, \\
\partial\Gamma(x,y,w) &= \frac{\partial(u,\theta)}{\partial(y,w)} =: \begin{pmatrix}\gamma_{11} & \gamma_{12}\\ \gamma_{21} & \gamma_{22}\end{pmatrix}.
\end{aligned}$$

Galerkin approximation: series expansions

To calculate solutions, we have to solve for g_1 in the second equation and substitute in the first to obtain an equation for the density ρ.

We choose an orthonormal system of basis functions $\kappa_K(\theta)$ with $K \in \mathcal{K}$ satisfying

$$\int \kappa_K(\theta)^* \kappa_{K'}(\theta) \, \mathrm{d}\theta = \delta_{KK'},$$

where K is a multiindex varying in a $(5-2d)$-dimensional index set $\mathcal{K}$.

We expand g_1 into the basis functions as

$$g_1(x, \eta, \theta, t) = \sum_{K \in \mathcal{K}} \kappa_K(\theta) G_K(x, \eta, t).$$

Lemma (entropy estimate)

Regardless of the choice of basis functions and the number of terms used in the Galerkin approximation, we have the inequality

$$\frac{1}{2}\partial_t \int \mathrm{e}^{V_0+\eta} \frac{|\rho(x,\eta,t)|^2}{N(x,\eta)}\,\mathrm{d}x\eta = -\int \frac{\sigma}{\tau}\mathrm{e}^{V_0+\eta}|g_1(x,\eta,\theta,t)|^2\,\mathrm{d}x\eta\theta \leq 0.$$

Galerkin approximation: summary

After the series expansion, the first equation (the conservation law) becomes

$$\partial_t \rho(x,\eta,t) + \sum_{K\in\mathcal{K}} \nabla_x \cdot \big(a_K(x,\eta) G_K(x,\eta,t)\big) + \partial_\eta \big(A_K(x,\eta)\cdot G_K(x,\eta,t)\big) = 0$$

and the second equation becomes

$$\begin{aligned} a_K(x,\eta)^* \mathrm{e}^{-V_0} \nabla_x \big(\mathrm{e}^{V_0} \tfrac{\rho}{N}\big) + A_K(x,\eta)^* \mathrm{e}^{-\eta} \partial_\eta \big(\mathrm{e}^{\eta} \tfrac{\rho}{N}\big) \\ + \sum_{K'\in\mathcal{K}} C_{KK'}(x,\eta) G_{K'}(x,\eta,t) = 0 \quad \forall K \in \mathcal{K}. \end{aligned}$$

Galerkin approximation: summary

The potential V_1 is given, however the variable transformation Γ can still be chosen in a suitable manner.

The coefficients, depending on V_1 and Γ, are

$$
\begin{aligned}
a_K(x,\eta) &= \int \kappa_K(\theta)\sigma(x,\eta,\theta)\,\mathrm{d}\theta,\\
A_K(x,\eta) &= \int \kappa_K(\theta)\sigma(x,\eta,\theta)\nabla_1 V_1(x,\Omega_y(x,\eta,\theta))\,\mathrm{d}\theta,\\
C_{KK'}(x,\eta) &= \int \kappa_K(\theta)^*\sigma(x,\eta,\theta)\big((S\cdot\nabla_\theta)\kappa_{K'}(\theta) + \frac{1}{\tau}\kappa_{K'}(\theta)\big)\,\mathrm{d}\theta,\\
S(x,\eta,\theta) &= (\gamma_{21}\gamma_{12}^T - \gamma_{22}\gamma_{11}^T)(x,\Omega(x,\eta,\theta)),\\
\sigma(x,\eta,\theta) &= \left|\det(\partial\Omega(x,\eta,\theta))\right|.
\end{aligned}
$$

Galerkin approximation: the conservation law

If the inverse of the matrix C exists, we can express the coefficients G_K in terms of ρ to find the conservation law

$$\partial_t \rho(x,\eta,t) + \nabla_x \cdot F^x(x,\eta,t) + \partial_\eta F^\eta(x,\eta,t) = 0,$$

where the d-dimensional flux vector F^x and the scalar flux F^η are

$$F^x(x,\eta,t) = -\sum_{K,K'\in\mathcal{K}} a_K(x,\eta) C^{-1}_{KK'}(x,\eta) \cdot \\ \cdot \Big(a_{K'}(x,\eta)^* \mathrm{e}^{-V_0} \nabla_x \big(\mathrm{e}^{V_0} \frac{\rho}{N}\big) + A_{K'}(x,\eta)^* \mathrm{e}^{-\eta} \partial_\eta \big(\mathrm{e}^{\eta} \frac{\rho}{N}\big)\Big),$$

$$F^\eta(x,\eta,t) = -\sum_{K,K'\in\mathcal{K}} A_K(x,\eta)^T C^{-1}_{KK'}(x,\eta) \cdot \\ \cdot \Big(a_{K'}(x,\eta)^* \mathrm{e}^{-V_0} \nabla_x \big(\mathrm{e}^{V_0} \frac{\rho}{N}\big) + A_{K'}(x,\eta)^* \mathrm{e}^{-\eta} \partial_\eta \big(\mathrm{e}^{\eta} \frac{\rho}{N}\big)\Big).$$

Galerkin approximation: goals and remarks

The actual computational challenge lies in computing the inconspicuous looking term $C^{-1}_{KK'}(x,\eta)$.
(K is a multiindex of the same dimension as the angular variable θ, and θ denotes an angle in the $(6-2d)$-dimensional (y,w)-space. Hence K and θ have $5-2d$ components.)

For the case of a plate where $d=2$, K is a scalar and the matrix $C(x,\eta)$ has to be inverted for every point (x,η).

For the case of a tube where $d=1$, the multiindex K has three components and the resulting tensor $C(x,\eta)$ is very large even if a moderate number of expansions terms are used in each component of θ. This is the computationally most demanding case.

Since our goal is to derive a simple macroscopic system, we treat the case of a tube ($d=1$) in the following. To make the calculations more concrete, we assume a harmonic confinement potential V_1 in the following.

Harmonic confinement potentials

A harmonic confinement potential V_1 has the quadratic form

$$V_1(x,y) = \frac{1}{2}\big(y - b(x)\big)^\top B(x)\big(y - b(x)\big),$$

where $y, b \in \mathbb{R}^2$ and the diagonal matrix $B(x)$ has the form

$$B(x) = \begin{pmatrix} B_1(x) & 0 \\ 0 & B_2(x) \end{pmatrix}.$$

(In order to approximate arbitrary confinement potentials, we can always minimize the difference in the forces, i.e., we minimize the functional

$$\int_{\mathcal{B}} \left| B(x)(y - b(x)) - \nabla_y V_1(x,y) \right|^2 \mathrm{d}y$$

for every value of x.)

Defining the variable transformation Ω

What is a suitable variable transformation?

1. First, we transform (y_j, w_j), $j \in \{1,2\}$, using polar coordinates. We set

$$y_j =: b_j + \sqrt{\frac{2r_j}{B_j}} \cos\theta_j, \quad w_j =: \sqrt{2r_j} \sin\theta_j$$

   with $r_j \in [0,\infty)$ and $\theta_j \in [-\pi,\pi)$ for $j \in \{1,2\}$.
2. Next, we use the transformation

$$\eta := r_1 + r_2, \quad \theta_3 := \frac{r_2 - r_1}{r_2 + r_1}, \quad r_1 = \eta\frac{1-\theta_3}{2}, \quad r_2 = \eta\frac{1+\theta_3}{2}$$

   with $\eta \in [0,\infty)$ and $\theta_3 \in [-1,1]$. We have $\mathcal{E}_y(x,y,w) = \eta$ as required.
3. Finally, combining the two transformations yields Ω as

$$\begin{pmatrix} y \\ w \end{pmatrix} = \Omega(x,\eta,\theta) = \begin{pmatrix} \Omega_y(x,\eta,\theta) \\ \Omega_w(x,\eta,\theta) \end{pmatrix} = \begin{pmatrix} b_1 + \sqrt{\frac{\eta(1-\theta_3)}{B_1}} \cos\theta_1 \\ b_2 + \sqrt{\frac{\eta(1+\theta_3)}{B_2}} \cos\theta_2 \\ \sqrt{\eta(1-\theta_3)} \sin\theta_1 \\ \sqrt{\eta(1+\theta_3)} \sin\theta_2 \end{pmatrix}.$$

Defining the basis functions

Having found a reasonable variable transformation, how should we choose the basis functions for the Galerkin approximation?

We define

$$\kappa_K(\theta) := \frac{1}{2\pi} \mathrm{e}^{\mathrm{i}k_1\theta_1 + \mathrm{i}k_2\theta_2} L_{k_3}(\theta_3), \quad K = (k_1, k_2, k_3) \in \mathbb{Z} \times \mathbb{Z} \times \mathbb{N},$$

where the $L_{k_3}(\theta_3)$ are Legendre polynomials of degree k_3 normalized in the L^2-norm on the interval $[-1, 1]$.

The success of our procedure still depends on the question if we can find usable/simple expressions for the coefficients a_K, A_K, C_{KK}, C^{-1}_{KK}, and hence the fluxes F^x and F^η.

The coefficients a_K, A_K, and $C_{KK'}$

The coefficient a_K simplifies to

$$a_K(x,\eta) = \int \kappa_K \sigma \,\mathrm{d}\theta = \sqrt{2}\pi \frac{\eta}{\sqrt{B_1 B_2}} \int \kappa_0^* \kappa_K \,\mathrm{d}\theta = \frac{\sqrt{2}\pi\eta}{\sqrt{B_1 B_2}} \delta_{0,K}.$$

The coefficient A_K "simplifies" to

$$\begin{aligned} A_K(x,\eta) = {}& \frac{\pi\eta}{2\sqrt{B_1 B_2}} \cdot \\ & \cdot \Big(\frac{1}{4}\eta\partial_x(\ln B_1)\delta_{k_2,0}(\delta_{k_1,-2} + 2\delta_{k_1,0} + \delta_{k_1,2})(\sqrt{2}\delta_{k_3,0} - \sqrt{2/3}\delta_{k_3,1}) \\ & + \frac{1}{4}\eta\partial_x(\ln B_2)\delta_{k_1,0}(\delta_{k_2,-2} + 2\delta_{k_2,0} + \delta_{k_2,2})(\sqrt{2}\delta_{k_3,0} + \sqrt{2/3}\delta_{k_3,1}) \\ & - \sqrt{\eta B_1}\partial_x b_1 \delta_{k_2,0}(\delta_{k_1,-1} + \delta_{k_1,1}) L^-_{k_3} - \sqrt{\eta B_2}\partial_x b_2 \delta_{k_1,0}(\delta_{k_2,-1} + \delta_{k_2,1}) L^+_{k_3} \Big), \end{aligned}$$

where

$$L^\pm_{k_3} := \int_{-1}^{1} \sqrt{1 \pm \theta_3}\, L_{k_3}(\theta_3)\,\mathrm{d}\theta_3.$$

The coefficients a_K, A_K, and $C_{KK'}$

We find

$$C_{KK'}(x,\eta) = \frac{\eta}{2\sqrt{B_1 B_2}} \left(\frac{1}{\tau} - \mathrm{i}k_1\sqrt{B_1} - \mathrm{i}k_2\sqrt{B_2} \right) \delta_{KK'}$$

after integrating out θ. Therefore C is a diagonal matrix.

Therefore we find the elements of the inverse matrix C^{-1} as

$$C^{-1}_{KK'}(x,\eta) = \frac{2\tau\sqrt{B_1 B_2}}{\eta} \frac{1+\tau(k_1\sqrt{B_1}+k_2\sqrt{B_2})\mathrm{i}}{1+\tau^2(k_1\sqrt{B_1}+k_2\sqrt{B_2})^2} \delta_{KK'}.$$

At this point, we have (more or less) determined the coefficients a_K, A_K, and $C_{KK'}$ that appear in the expressions for the fluxes F^x and F^η in the conservation law. Of course, they depend on the coefficients b_j and B_j of the harmonic confinement potential V_1.

The fluxes F^x and F^η

Recall the d-dimensional flux vector F^x and the scalar energy flux F^η:

$$F^x(x,\eta,t) = -\sum_{K,K'\in\mathcal{K}} a_K(x,\eta) C^{-1}_{KK'}(x,\eta)\cdot$$

$$\cdot\left(a_{K'}(x,\eta)^* \mathrm{e}^{-V_0}\nabla_x\left(\mathrm{e}^{V_0}\frac{\rho}{N}\right) + A_{K'}(x,\eta)^*\mathrm{e}^{-\eta}\partial_\eta\left(\mathrm{e}^{\eta}\frac{\rho}{N}\right)\right),$$

$$F^\eta(x,\eta,t) = -\sum_{K,K'\in\mathcal{K}} A_K(x,\eta)^T C^{-1}_{KK'}(x,\eta)\cdot$$

$$\cdot\left(a_{K'}(x,\eta)^* \mathrm{e}^{-V_0}\nabla_x\left(\mathrm{e}^{V_0}\frac{\rho}{N}\right) + A_{K'}(x,\eta)^*\mathrm{e}^{-\eta}\partial_\eta\left(\mathrm{e}^{\eta}\frac{\rho}{N}\right)\right).$$

Our Galerkin basis functions are $\kappa_K(\theta) := \dfrac{1}{2\pi}\mathrm{e}^{\mathrm{i}k_1\theta_1+\mathrm{i}k_2\theta_2} L_{k_3}(\theta_3)$.

The index set $\mathcal{K}$ is unfortunately still $\mathbb{Z}\times\mathbb{Z}\times\mathbb{N}$:
angles θ_1,θ_2: indices $k_1,k_2\in\mathbb{Z}$; Legendre polynomial L_{k_3}: index $k_3\in\mathbb{N}$.
Can we do better?

The fluxes F^x and F^η

First, we note the Kronecker delta in $a_K(x,\eta) = \frac{\sqrt{2}\pi\eta}{\sqrt{B_1 B_2}}\delta_{0,K}$.

Second, the coefficient A_K vanishes for $|k_1| > 2$ and $|k_2| > 2$, since the complex exponentials are orthogonal to $\cos\theta_j$ and $\cos^2\theta_j$ for all $j \in \{1,2\}$.

Therefore, regardless of the number of terms used in the expansion, the fluxes F^x and F^η are of the form

$$
\begin{aligned}
F^x(x,\eta,t) = -a_0(x,\eta)\,C_{00}^{-1}(x,\eta)\,\cdot& \\
&\cdot \left(a_0(x,\eta)^* \mathrm{e}^{-V_0}\nabla_x\big(\mathrm{e}^{V_0}\frac{\rho}{N}\big) + A_0(x,\eta)^* \mathrm{e}^{-\eta}\partial_\eta\big(\mathrm{e}^{\eta}\frac{\rho}{N}\big)\right), \\
F^\eta(x,\eta,t) = -\sum_{k_1=-2}^{2}\sum_{k_2=-2}^{2}\sum_{k_3=0}^{\infty} A_K(x,\eta)\,C_{KK}^{-1}(x,\eta)\,\cdot& \\
&\cdot \left(\delta_{0,K}\,a_0(x,\eta)^* \mathrm{e}^{-V_0}\nabla_x\big(\mathrm{e}^{V_0}\frac{\rho}{N}\big) + A_K(x,\eta)^* \mathrm{e}^{-\eta}\partial_\eta\big(\mathrm{e}^{\eta}\frac{\rho}{N}\big)\right).
\end{aligned}
$$

Now the index set is $\mathcal{K} = \{0\} \times \{-2,-1,0,1,2\}^2 \times \mathbb{N}$. Can we do better?

The flux F^x

To simplify notation, we define

$$T_1 := \mathrm{e}^{-V_0} \nabla_x \big(\mathrm{e}^{V_0} \frac{\rho}{N}\big) \qquad \text{and} \qquad T_2 := \mathrm{e}^{-\eta} \partial_\eta \big(\mathrm{e}^{\eta} \frac{\rho}{N}\big).$$

(cf. Slotboom, Scharfetter–Gummel).

We find

$$F^x(x, \eta, t) = -\frac{4\pi^2 \tau \eta}{\sqrt{B_1 B_2}} T_1 - \frac{\pi^2 \tau \eta^2}{\sqrt{B_1 B_2}} \big(\partial_x (\ln B_1) + \partial_x (\ln B_2)\big) T_2.$$

This is the explicit expression for F^x that can be conveniently used for numerical calculations.

The flux F^η

After summing over $k_1, k_2 \in \{-2,-1,0,1,2\}$ and simplifying, the energy flux F^η still contains the infinite sum over k_3:

$$
\begin{aligned}
F^\eta(x,\eta,t) = &-\frac{\pi^2\tau\eta^2}{\sqrt{B_1B_2}}\big(\partial_x(\ln B_1)+\partial_x(\ln B_2)\big)\,T_1 \\
&-\sum_{k_3=0}^{\infty}\frac{\pi^2\tau\eta^2}{24\sqrt{B_1B_2}}\Bigg(4\eta\partial_x(\ln B_1)\partial_x(\ln B_2)(3\delta_{k_3,0}-\delta_{k_3,1}) \\
&+\left(\frac{\eta(3+8\tau^2B_1)(\partial_x(\ln B_1))^2}{1+4\tau^2B_1}+\frac{\eta(3+8\tau^2B_2)(\partial_x(\ln B_2))^2}{1+4\tau^2B_2}\right)(3\delta_{k_3,0}+\delta_{k_3,1}) \\
&+\frac{24B_1(\partial_x b_1)^2}{1+\tau^2B_1}(L_{k_3}^-)^2+\frac{24B_2(\partial_x b_2)^2}{1+\tau^2B_2}(L_{k_3}^+)^2\Bigg)\,T_2.
\end{aligned}
$$

What do we know about the integrals $L_{k_3}^\pm = \int_{-1}^{1}\sqrt{1\pm\theta_3}\,L_{k_3}(\theta_3)\,\mathrm{d}\theta_3$?

Lemma

Let L_n be the Legendre polynomials on the interval $[-1, 1]$ normalized in the L^2-norm. Then the equation

$$L_n^{\pm} = \int_{-1}^{1} \sqrt{1 \pm x} L_n(x) \,\mathrm{d}x = \frac{-4(\mp 1)^n}{(2n+3)(2n-1)\sqrt{2n+1}} \qquad \forall n \in \mathbb{N}$$

holds.

Now we can sum the squares of the integrals to find

$$\sum_{k_3=0}^{K_3} (L_{k_3}^{+})^2 = \sum_{k_3=0}^{K_3} (L_{k_3}^{-})^2 = \frac{16(2K_3^4 + 8K_3^3 + 11K_3^2 + 6K_3 + 1)}{(4K_3^2 + 8K_3 + 3)^2},$$

whose limit as $K_3 \to \infty$ is clearly 2,

$$\sum_{k_3=0}^{\infty} (L_{k_3}^{+})^2 = \sum_{k_3=0}^{\infty} (L_{k_3}^{-})^2 = 2.$$

Theorem (Macroscopic transport equation for tubes ($d = 1$))

In a tube ($d = 1$) given by a harmonic confinement potential, diffusive transport is described by the conservation law

$$\partial_t \rho(x, \eta, t) + \partial_x F^x(x, \eta, t) + \partial_\eta F^\eta(x, \eta, t) = 0$$

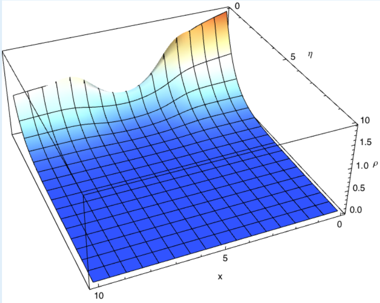
with the constitutive relations

$$F^x(x, \eta, t) = -\frac{4\pi^2 \tau \eta}{\sqrt{B_1 B_2}} T_1 - \frac{\pi^2 \tau \eta^2}{\sqrt{B_1 B_2}} \big(\partial_x(\ln B_1) + \partial_x(\ln B_2)\big) T_2,$$

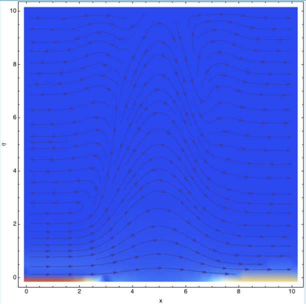
$$\begin{aligned} F^\eta(x, \eta, t) = & -\frac{\pi^2 \tau \eta^2}{\sqrt{B_1 B_2}} \big(\partial_x(\ln B_1) + \partial_x(\ln B_2)\big) T_1 \\ & - \frac{\pi^2 \tau \eta^2}{6\sqrt{B_1 B_2}} \bigg(\frac{12 B_1 (\partial_x b_1)^2}{1 + \tau^2 B_1} + \frac{12 B_2 (\partial_x b_2)^2}{1 + \tau^2 B_2} + 2\eta \partial_x(\ln B_1) \partial_x(\ln B_2) \\ & \qquad + \frac{\eta(3 + 8\tau^2 B_1)(\partial_x(\ln B_1))^2}{1 + 4\tau^2 B_1} + \frac{\eta(3 + 8\tau^2 B_2)(\partial_x(\ln B_2))^2}{1 + 4\tau^2 B_2} \bigg) T_2, \end{aligned}$$

where $\quad T_1 := \mathrm{e}^{-V_0} \partial_x \big(\mathrm{e}^{V_0} \frac{\rho}{N}\big) \quad$ *and* $\quad T_2 := \mathrm{e}^{-\eta} \partial_\eta \big(\mathrm{e}^{\eta} \frac{\rho}{N}\big).$

Numerical example no. 1 (no applied potential)



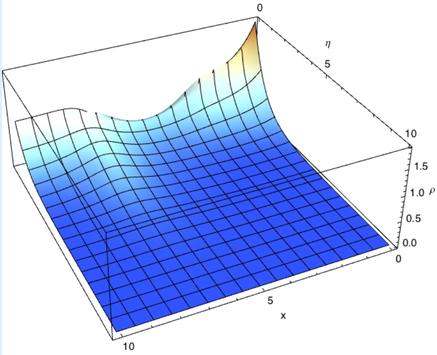
Concentration $\rho(x, \eta)$



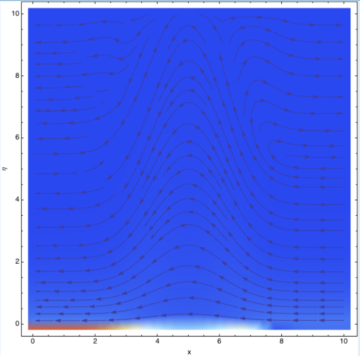
Streamlines plot of $F^x(x,\eta)\mathbf{e}_x + F^\eta(x,\eta)\mathbf{e}_\eta$

The concentration gradient between the two baths drives the current.
Current $\int F^x(10,\eta)\,\mathrm{d}\eta = 0.063\,120$.
$x \in [0, 10]$. $\eta \in [0, 10]$. $\tau := 1$. No applied potential: $V_0(x) := 0$.
Confinement: $B_1(x) := B_2(x) := 1 + 5\exp(-(x-5)^2/2)$. $b_1(x) := b_2(x) := 0$.
Boundary conditions: $\rho(0,\eta) := 2\exp(-\eta)$, $\rho(10,\eta) := \exp(-\eta)$.

Numerical example no. 2 (with applied potential)



Concentration $\rho(x,\eta)$



Streamlines plot of $F^x(x,\eta)\mathbf{e}_x + F^\eta(x,\eta)\mathbf{e}_\eta$

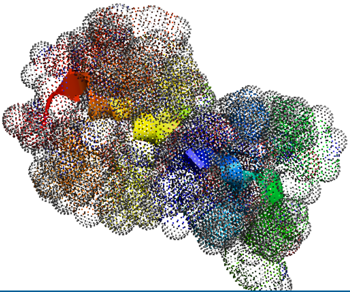
The applied potential works against the concentration gradient.
Current $\int F^x(10,\eta)\,\mathrm{d}\eta = -0.891\,181$.
Applied potential: $V_0(x) := x$, other parameters as before.

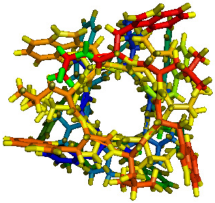
Application to ion channels: Gramicidin A

Gramicidin A is an antibiotic.

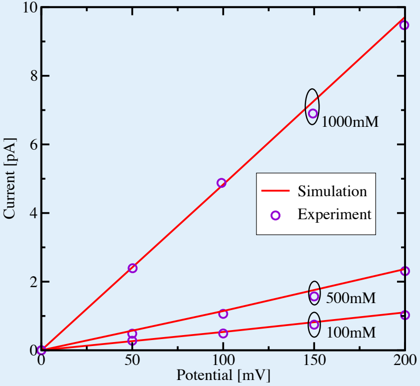
Gramicidin increases the permeability of bacterial cell membranes inducing a current of inorganic monovalent cations (e.g., Na^+).

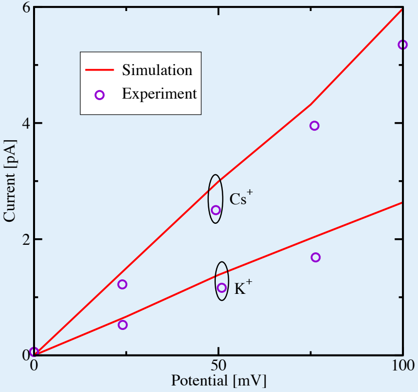
This lowers the ion gradient between the cytoplasm and the extracellular environment killing the bacteria.





Comparison of simulations with measured current-voltage characteristics of Gramicidin A



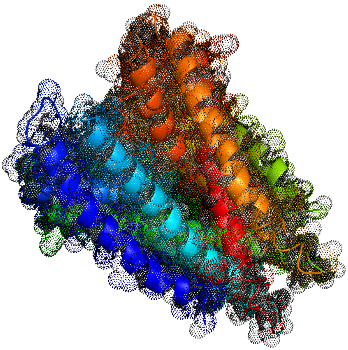


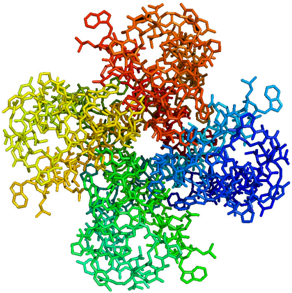
Left: three different ionic bath concentrations.
Right: selectivity between Cs^+ and K^+.

Application to ion channels: the KcsA channel

Ion channels such as KcsA are fundamental to signal conduction in nerves.

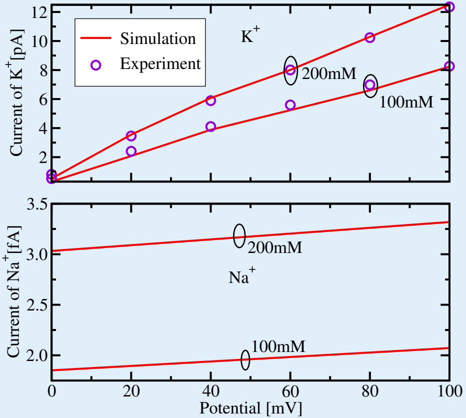
Na^+: smaller ion, but cannot pass through the channel;
K^+: larger ion, but can pass through the channel.



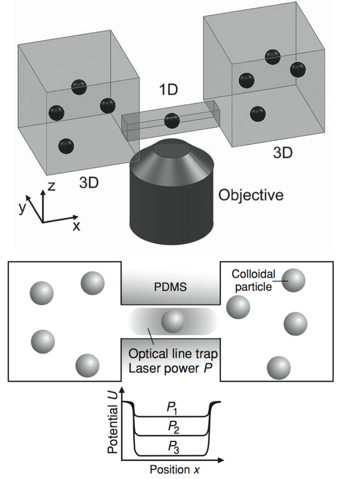


Comparison of simulations with measured current-voltage characteristics of KcsA

The simulated values agree very well with the observed selectivity between Na^+ and K^+ (three orders of magnitude). (Note the different units, pA and fA.)



Recent experimental realization of such confined structures

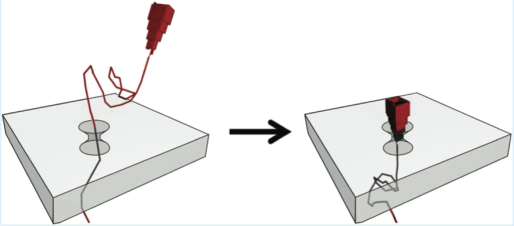


Ulrich Keyser (Cavendish Labs, Cambridge) has used optical tweezers to create a fully controlled and tunable environment to study diffusion.
[S. Pagliara, C. Schwall, and U.F. Keyser. Optimizing diffusive transport through a synthetic membrane channel. *Adv. Mater.*, 25:844–849, 2013.]

Another experiment:
[J.H. Park, J. He, B. Gyarfas, S. Lindsay, and P.S. Krstic. DNA translocating through a carbon nanotube can increase ionic current. *Nanotechnology*, 23:455107, 2012.]

Understanding nanopores for DNA sequencing and single-molecule sensing

Hagan Bayley (Oxford) and Oxford Nanopore Technologies use certain nanopores as the platform for next-generation DNA sequencing and single-molecule sensing.



Ulrich Keyser (Cavendish Labs, Cambridge) also fabricates artificial, reproducible nanopores for biosensing applications. [N.A.W. Bell et al. DNA origami nanopores. *Nano Letters*, 12(1):512–517, 2012.]

Acknowledgments: students

Master's students:

- Claus Aichinger: April 2013.
- Marina Rehrl: Sep 2011.
- Klemens Katterbauer: Dec 2010.
- Stefan Baumgartner: July 2009.

PhD students:

- Amirreza Khodadadian, MSc: Nov 2012 – present.
- Mag. Gerhard Tulzer: Sep 2011 – present.
- Mag. Stefan Baumgartner: *PDE models for field-effect sensors*, Aug 2009 – Dec 2012.
- Mag. Alena Bulyha: *Modeling and simulation of field-effect biosensors*, Oct 2008 – July 2011 (co-advised).

Postdoc:

- Dipl.-Ing. Dr. Martin Vasicek: Jan 2010 – Jan 2012.

Acknowledgments: funding

Nov 2013 – 2019 (projected):

FWF START Prize and Project PDE models for nanotechnology. (9 out of 96 proposals were funded in an international competition among all areas of science.)

Jan 2010 – Dec 2013:

High-potential project funded by WWTF (Viennese Science and Technology Fund), Mathematics and nanosensors.

Jan 2009 – Feb 2013:

FWF project Mathematical models and characterization of BioFETs.

Apr 2008 – Jun 2009:

Jubilee-fund project of the ÖAW (Austrian Academy of Sciences), Multiscale modeling and simulation of field-effect nano-biosensors. (2 out of 30 proposals were selected for funding.)

Thank you for your attention!

Homepage (with list of publications, reprints, and preprints):
http://Clemens.Heitzinger.name/.