The linearized Poisson-Nernst-Planck system as heat flow on the interval under non-local boundary conditions

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Abstract

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1 Introduction

The Poisson -Nernst-Planck (PNP) system [7] is a fundamental model for electrodiffusion and is one of the main tools in modeling ion channels in cell membrane(see, e.g. [12]). In one of its simplest forms, it contains a pair of drift-diffusion equations for positive and negatively charged ions, coupled with the equation for the electric field induced by the charges.

We concentrate on the case of two types of ions (positively (C_+) and negatively (C_-) charged) and a closed channel, where the flux of $C_\pm$ is zero at the ends of the channel, hence the number of ions of each type (and, in particular, the total charge $C_+ - C_-$) is preserved in time.

The physical model behind the PNP is a drift diffusion for charged particles, where the diffusion is due to independent Brownian motions of the ions,

and the drift is due to the external field induces by the potential difference between the ends of the channel, and the mean electric field generated by the moving ions.

Thus, the PNP can be considered as a system of Kolmogorov forward equation, [9, 10], whose solutions represent the probability distribution of a test particle for each type of ions in the system.

In the case of zero external field, the neutral case ($C_+ = C_-$) induces a steady, uniform distribution for both charges. A linearization of this equation around this constant neutral case is reduced, up to a re-scaling of the time, into the naive looking damped diffusion equation [11, 12][1] for the *local charge* $u \approx C_+ - C_-$:

$$u_t = u_{xx} - \kappa^2 u \ , \ 0 < x < 1, \quad t \geq 0 \tag{1}$$

where the interval $[0, 1]$ is the channel, $u(x, t)$ is the local charge at $x \in [0, 1], t \geq 0$ and κ^2 is the inverse Debye screening length. This looks like a fairly naive equation. However, the boundary conditions are

$$(u_x + (k^2/\epsilon)E)_{x=0,1} = 0 \tag{2}$$

where the electric field E is given by the Poisson equation

$$-\epsilon E_x = u, \qquad \int_0^1 E dx = V \ , \tag{3}$$

driven by the voltage difference V across the end points $x = 0, 1$. These are non-local boundary conditions. Indeed, we show that (2, 3) can be reduced to the following

$$u_x(0) = -k^2 \int_0^1 (1 - s)u(s)ds + \kappa^2 V \ , u_x(1) = \kappa^2 \int_0^1 su(s)ds + \kappa^2 V \ .$$

The steady state for the linearized problem can easily be obtained:

$$\bar{u}(x) = \frac{\kappa V}{\cosh(\kappa/2)} \sinh(\kappa(x - 1/2)) \tag{4}$$

so we can subtract it from the solution u of equation to get a homogeneous boundary conditions

$$u_x(0) = -k^2 \int_0^1 (1 - s)u(s)ds \ , u_x(1) = \kappa^2 \int_0^1 su(s)ds \ . \tag{5}$$

[1] I wish to thank Dr. Doron Elad for turning my attention to this formulation

Some versions of parabolic equations under non-local boundary conditions were studied by several authors (see, e.g.[1, 6]). A stochastic interpretation of linear diffusion equations under non-local boundary conditions goes back to Feller [5]. In that paper he extended his seminal paper [4] to non-local boundary conditions, and interpreted the diffusion equation in terms of a Brownian particle which may undergo a jump from a point on the boundary of the interval to a distributed position at the interior. This extension was later studied by several authors, see e.g [6, 8, 13]. However, in all these cases the process is allowed to jump from a boundary point to the interior, and not the other way around. This will be the case if, e.g., κ^2 is replaced by $-\kappa^2$ in (5).

The boundary conditions (5) associated with the operator $d^2/dx^2 - \kappa^2$ suggests a diffusion process which jump at a random Poisson time of mean κ^2 from an *inner* point $x \in (0,1)$ and reflected at the endpoint $x = 0$ with probability $1 - x$, and at the endpoint $x = 1$ with probability x. In this sense, it is a *forward* Kolmogorov equation representing the evolution of a probability distribution of the charge. [2]

The *heat kernel* $K(x, y, t)$ of such an equation generates the solutions

$$u(x,t) = \int_0^1 K(x,y,t)u(y,0)dy \ .$$

This kernel represents the probability of the particle to be at position x at time $t + s$, conditioned that it was at point y at time s. In particular

$$K(x,y,t) \geq 0, \quad \text{for} \quad (x,y) \in (0,1) \times (0,1), \ t > 0, \quad \int_0^1 K(x,y,t)dx = 1$$

and $\lim_{t \downarrow 0} K(x,y,t) = \delta_{x-y}$.

The adjoint equation, then, represents the backward Kolmogorov equation of the process. In general, it is also a diffusion equation of the same form and adapted boundary condition, whose kernel K^* is given by the interchange of x and y: $K^*(x,y,t) = K(y,x,t)$. However, in the case of b.c (5), an explicit form of the adjoint operator is not clear.

In this paper we attempt to calculate the spectral expansion of the heat kernel. The information encoded in this expansion contains the eigenvalues, as well as the eigenfunctions of both the operator and its adjoint.

To obtain this, we take advantage on the explicit solutions of the *resulvent* $R = R(\lambda, x, y)$ where $\lambda \in \mathbb{C}$, $(x, y) \in (0,1) \times (0,1)$:

$$\partial_x^2 R + \lambda R + \delta_{x-y} = 0$$

[2] Even though u is not necessarily of definite sign, we can consider the positive and negative parts of u independently, using the linearity of this equation.

where δ_{x-y} is the Dirac delta function and R satisfies the boundary conditions (5) in the x variable. These solutions can be expressed locally as a combination of the trigonometric functions $\sin(\lambda^{1/2}x)$ and $\cos(\lambda^{1/2}x)$. It turns out that the solution of the resulvent equation exists whenever $Re(\lambda) < -\kappa^2$. This resulvent R can also be written in terms of the heat kernel K (see [3], and also the review in the Appendix):

$$R(\lambda, x, y) = \int_0^\infty e^{(\lambda+\kappa^2)t} K(x, y, t) dt \ . \tag{6}$$

It turns out that R is a meromorphic function of λ in the complex plane, analytic if $Re(\lambda) < -\kappa^2$, and admits a countable number of simple poles in the half plane $Re(\lambda \geq -\kappa^2)$ (including $\lambda = -\kappa^2$).

Under some conditions which we can verify (c.f. Appendix) we can recover the heat kernel form (6) using the inverse Laplace transform via

$$K(x, y, t) = e^{-\kappa^2 t} \frac{1}{2\pi i} \oint_\Gamma e^{-\lambda t} R(\lambda, x, y) d\lambda$$

where Γ is a contour enclosing all the poles of R. Then, we use the Residue theorem [2] to evaluate the contour integral.

The main results are summarized below:

Theorem 1.1. *The heat kernel of (1, 5) is given by*

$$\begin{aligned} K(x, y, t) = & \frac{\kappa \cosh(\kappa/2) \cosh(\kappa(x - 1/2))}{2 \sinh(\kappa/2)} \\ & + \sum_{n=1}^\infty \frac{\kappa^2 A(\lambda_n, y)(\sqrt{\lambda_n} + \kappa^2/\sqrt{\lambda_n})}{2\sqrt{\lambda_n} Det'(\lambda_n)} \sin\left(\frac{\sqrt{\lambda_n}(1 - 2x)}{2}\right) e^{-(\lambda_n+\kappa^2)t} \\ & + \frac{1}{2} \sum_{n=1}^\infty \cos(2n\pi x) \left(\cos(2n\pi y) + \frac{1}{n\pi(4n^2\pi^2 + \kappa^2)}\right) e^{-(4n^2\pi^2+\kappa^2)t} \end{aligned} \tag{7}$$

where λ_n are the roots of

$$2 \tan(\lambda_n^{1/2}/2) = \lambda_n^{1/2} \kappa^{-2} (\lambda_n + \kappa^2) \ ,$$

Det is given by (15) and

$$A(\lambda, y) := \frac{1}{\pi^2} \sum_{m=1}^\infty \frac{2 \cos((2m + 1)\pi y)}{(2m + 1)^2(\pi^2(2m + 1)^2 - \lambda)} \ .$$

In particular,

$$K_0(x,y,t) := \frac{\kappa\cosh(\kappa/2)}{2\sinh(\kappa/2)}\psi_0(x)\phi_0(y)e^{\kappa^2 t} + \sum_{n=1}^{\infty}\frac{\kappa^2(\sqrt{\lambda_n}+\kappa^2/\sqrt{\lambda_n})}{2\sqrt{\lambda_n}Det'(\lambda_n)}\psi_n^{(1)}(x)\phi^{(1)}(y)e^{-\lambda_n t} + \frac{1}{2}\sum_{n=1}^{\infty}\psi_n^{(2)}(x)\phi_n^{(2)}(y)e^{-4n^2\pi^2 t} \quad (8)$$

is the heat kernel for the operator $\mathcal{L}_0 = d^2/dx^2$ on the domain (5), where

- $\psi_n^{(1)}(x) = \cos(2n\pi x)$,
- $\psi_n^{(2)}(x) = \sin(\lambda_n^{1/2}(x-1/2))$
- $\psi_0(x) = \cosh(\kappa(x-1/2))$

are the eigenstates of $\mathcal{L}_0$, and

- $\phi_n^{(1)}(y) = \cos(2n\pi y) + \frac{1}{n\pi(4n^2\pi^2+\kappa^2)}$,
- $\phi_n^{(2)}(y) = A(\lambda_n, y)$,
- $\phi^{(0)}(y) = 1$

are the eigenstates of its adjoint $\mathcal{L}_0^\dagger$. This poses a challenging question regarding the formulation of this problem, since (except of the constant), $\phi_n^{(1)}$, $\phi_n^{(2)}$ are not solutions of $\phi_{xx} + \lambda\phi = 0$ for any $\lambda \in \mathbb{C}$. It seems that the adjoint operator may not be given by a differential one, *and the non locality of the boundary conditions leaks into the operator itself.* (c.f Section 5).

Remark 1.1. *All eigenvalues λ_k for $k > 0$ are real and positive (excluding the "ground" eigenvalue $\lambda_0 = -\kappa^2$.*

2 The linearized PNP system

The one dimensional PNP equation takes the form [11]

$$C_{+,t} = D_+\left[C_{+,x} + \frac{ze}{k_BT}EC_+\right]_x$$

$$C_{-,t} = D_-\left[C_{-,x} - \frac{ze}{k_BT}EC_-\right]_x$$

on the interval $[0,1]$, where $C_\pm$ is the concentration of positive/negative ions, and E is the electric field given in terms of the concentrations $C_\pm$ and the potential difference V:

$$-\epsilon E_x = ze(C_+ - C_-), \quad \int_0^1 E(x,t)dx = V$$

The special case of non penetrating charges corresponds to zero flux on the boundary

$$C_{+,x}(0,t) + \frac{ze}{k_B T} C_+(0,t)E(0,t) = C_{-,x}(1,t) - \frac{ze}{k_B T} C_-(1,t)E(1,t) = 0 \ .$$

In the neutral case $C_+ = C_- = \eta$ and $E = 0$. We linearize this system :

$$C_+ = \eta + c_+, \quad C_- = \eta + c_-, \quad E << 1$$

and ignore all terms of second order in $Ec_\pm$ to obtain

$$u_t = D(u_{xx} - \kappa^2 u) + Bc_{xx}$$

$$c_t = B(c_{xx} - \kappa^2 u) + u_{xx}$$

$$-\epsilon E_x = u$$

where $D = \frac{D_+ + D_-}{2}$, $B = \frac{D_+ - D_-}{2}$, $\kappa^2 = \frac{2\eta ze}{k_B T}$, $u = ze(c_+ - c_-)$,
$c = ze(c_+ + c_-)$, subject to
$\int_0^1 E dx = V$, $(u_x + (\kappa^2/e)E)_{x=0,1} = 0$, $(c_x)_{x=0,1} = 0$.

Here we concentrate in the case $B = 0$ which reduces to a single equation on u. Without loss of generality we also assume $D = 1$:

$$-\epsilon E_x = u \ , \qquad \int_0^1 E dx = V, \quad (u_x + (\kappa^2 \epsilon)E)_{x=0,1} = 0 \ . \tag{9}$$

$$u_t = u_{xx} - \kappa^2 u \ . \tag{10}$$

Lemma 2.1. *The three b.c (9), together with the constraint $-\epsilon E_x = u$ can be introduced as a pair of non-local conditions:*

$$u_x(0,t) = -\kappa^2 \int_0^1 (1-s)u(s,t)ds - \epsilon\kappa^2 V, \quad u_x(1,t) = \kappa^2 \int_0^1 su(s,t)ds - \epsilon\kappa^2 V$$

Proof. By the field equation and the boundary condition (9, 5) admits a classical C^2 solution and $u(x,0) \geq 0$

$$E(x) = E(0) + \int_0^x E'(s)ds = \kappa^{-2}\epsilon^{-1}u_x(0) - \epsilon^{-1}\int_0^x u(s)ds$$

From $\int_0^1 E = V$ we get

$$V = \kappa^{-2}\epsilon^{-1}u_x(0) - \epsilon^{-1}\int_0^1\int_0^x u(s)dsdx = \epsilon^{-1}\left(\kappa^{-2}u_x(0) - \int_0^1 (1-s)u(s)ds\right) .$$

Likewise

$$E(x) = E(1) - \int_x^1 E^{'}(s)ds = \kappa^{-2}\epsilon^{-1}u_x(1) + \epsilon^{-1}\int_x^1 u(s)ds$$

and so

$$V = \epsilon^{-1}\kappa^{-2}u_x(1) + \epsilon^{-1}\int_0^1\int_x^1 u(s)dsdx = \epsilon^{-1}\left(\kappa^{-2}u_x(1) + \int_0^1 su(s)ds\right) .$$

□

3 Properties of the linrarized PNP

We start from the following We start from the following

Proposition 3.1. *If equation (1, 5) admits a classical solutions then*

a. The integral $\int_0^1 u(x,t)dx$ is preserved.

b. If $u(\cdot,0)$ is non-negative then $u(\cdot,t)$ is non-negative for any $t > 0$.

c. For any $t > 0$, $\|u(\cdot,t)\|_\infty \leq \cosh(\kappa/2)\|u(\cdot,0)\|_\infty$.

Proof. (a): Follows immediately upon integration, taking advantage of the fact that the kernels of the integrals in (5) $(1-x)$ and x sums to one.
(b): Follows from an elementary observation involving the maximum principle. Indeed, let u_ϵ be a solution of the equation $u_{\epsilon,t} = u_{\epsilon,xx} + \kappa^2 u + \epsilon$, under the boundary condition (5), where $\epsilon > 0$. Evidently $u_\epsilon \to u$ where $\epsilon \to 0$. Let $u(x,0)$ be strictly positive, and let $x_0 \in [0,1]$, $t_0 > 0$ such that $u_\epsilon(x,t) > 0$ for any $t \in [0,t_0)$, $x \in [0,1]$ and $x \neq x_0$, $t = t_0$, while $u_\epsilon(x_0,t_0) = 0$. From the boundary conditions we obtain that $u_{\epsilon,x}(0,t_0) < 0$, $u_{\epsilon,x}(1,t_0) > 0$, so $x_0 \neq 0,1$. However, $u_{\epsilon,xx}(x_0,t_0) \geq 0$ since x_0 is an inner minimum. In particular $u_{\epsilon,t} \geq \epsilon$ by the equation. It follows that u_ϵ is, indeed strictly positive for any $\epsilon > 0$, and the weak inequality is preserved in the limit $\epsilon = 0$.
(c): Assume, without limitation of generality, that $u(\cdot,0) \geq 0$. Using Lemma 3.2, or by a direct substitution, we obtain that $d^2\psi_0/d^2x - \kappa^2\psi_0 = 0$ where

$\psi_0 = \cosh(\kappa(x-1/2))$. Thus, $u(x,0) \le \|u(\cdot,0)\|_\infty \psi_0(x)$ for any $x \in [0,1]$. In particular, $w(x,0) := \|u(\cdot,0)\|_\infty \psi_0(\cdot) - u(\cdot,0)$ is non-negative. Since w satisfies (1, 5) it follows by (b) that $w(\cdot,t)$ is non-negative for any $t > 0$. Hence $0 \le u(x,t) \le \|u(\cdot,0)\|_\infty \psi_0(\cdot) \le \|u(\cdot,0)\|_\infty \cosh(\kappa/2)$ for any $t \ge 0$.

□

Let u be a solution of (1, 5). Substitute

$$v(x,t) = e^{\kappa^2 t} u(x,t) \ . \tag{11}$$

Then v is a solution of

$$\begin{aligned} &v_t = v_{xx} \ , x \in [(0,1), t > 0 \\ &v(\cdot,t) \in \mathcal{D} := \left\{ w \in C^1[0,1] \cap C^2(0,1); w_x(0) = -\kappa^2 \int_0^1 (1-s) w(s) ds, \quad w_x(1) = \kappa^2 \int_0^1 s w(s) ds \right\} . \end{aligned} \tag{12}$$

3.1 Eigenvalues and eigenfunctions

The eigenfunctions of the operator d^2/dx^2 are given by $a\sin(\lambda^{1/2}x) + b\cos(\lambda^{1/2}x)$. Substitute this in (12) we get

$$a\left(\lambda^{1/2} + \kappa^2\lambda^{-1/2} - \frac{\kappa^2}{\lambda}\sin(\lambda^{1/2})\right) \ + \ b\kappa^2\left(\frac{1-\cos\lambda^{1/2}}{\lambda}\right) \quad = \quad 0 \tag{13}$$

$$\begin{aligned} &a\left(\lambda^{1/2}\cos(\lambda^{1/2}) - \frac{\kappa^2\sin(\lambda^{1/2})}{\lambda} + \frac{\kappa^2\cos(\lambda^{1/2})}{\lambda^{1/2}}\right) \\ &\qquad + b\left(-\lambda^{1/2}\sin(\lambda^{1/2}) - \frac{\kappa^2\sin(\lambda^{1/2})}{\lambda^{1/2}} - \frac{\kappa^2\cos(\lambda^{1/2}) - 1}{\lambda}\right) = 0 \end{aligned} \tag{14}$$

The system (13, 14) is a linear system for the coefficients a, b. The determinant of this system is

$$\begin{aligned} Det(\lambda) &= 2\kappa^2\lambda^{-1/2}(1-\cos(\lambda^{1/2}))\left(1+\frac{\kappa^2}{\lambda}\right) - \sin(\lambda^{1/2})\left(\frac{\kappa^2}{\lambda^{1/2}} + \lambda^{1/2}\right)^2 \\ &= \sin(\lambda^{1/2})\left(1+\frac{\kappa^2}{\lambda}\right)\left(\frac{2\kappa^2}{\lambda^{1/2}}\tan(\lambda^{1/2}/2) - \kappa^2 - \lambda\right) \end{aligned} \tag{15}$$

Lemma 3.1. *$\lambda^{1/2}Det(\lambda)$ is a meromorphic function on the complex plane. The roots of $Det(\lambda) = 0$ are given by $(2k\pi)^2$ where $k \in \mathbb{Z}$. In addition λ_m, $m \in \mathbb{N}$ where $\{\lambda_m\}$ are the roots of*

$$2\tan(\lambda_m^{1/2}/2) = \lambda_m^{1/2}\kappa^{-2}(\lambda_m + \kappa^2) \ . \tag{16}$$

In addition, $\lambda = 0$ is a root of $Det(\lambda)$ only if $\kappa^2 \neq 12$, and it coincides with a root $\lambda_1(\kappa)$ of (16) as $\kappa^2 \to 12$.

In addition, $\lambda = -\kappa^2$ is the only negative root of Det, and it is a simple one.

Proof. The case of non-zero roots follows directly from (15).

To evaluate the case $\lambda = 0$, let us rewrite the leading Taylor expansion of the right side of (15) as a function of $\lambda^{1/2}$. Using $\tan(\lambda^{1/2}) = \lambda^{1/2} + \lambda^{3/2}/3 + 2\lambda^{5/2}/15\ldots$, we expand (15) and obtain that the leading terms in powers of $\lambda^{1/2}$ are

$$\sin(\lambda^{1/2})(1+\kappa^2/\lambda)\left[\frac{2\kappa^2}{\sqrt{\lambda}}(\sqrt{\lambda}/2 + (\sqrt{\lambda}/2)^3/3 + 2(\sqrt{\lambda}/2)^5/15 + \ldots) - \kappa^2 - \lambda\right] =$$

$$\sin(\lambda^{1/2})(1 + \kappa^2/\lambda)\left[(\frac{\kappa^2}{12} - 1)\lambda + \kappa^2\lambda^2/(120) + \ldots\right] \ .$$

□

Conjecture: *All rots of (16) are real and simple.*

At this stage we can only show that there exists $R(\kappa) > 0$ such that all roots of (16) outside the disc $\{|z| < R(\kappa)\}$ are real and simple. Numerical test verifies, for all selected values of κ, that all roots inside the disc are real and simple as well.

Proof. Substitute $z = \lambda^{1/2}/2$ and set $f(z) = \tan(z)$, $g(z) = z\kappa^{1/2}(4z^2 + \kappa^2)$ and $h(z) = g(z) - f(z)$. Consider the orbit Γ_n in the complex plan obtained by the edges of the square whose vertices are at $(n\pi, n\pi)$, $(-n\pi, n\pi)$, $(-n\pi, -n\pi)$, $(n\pi, -n\pi)$ where $n \in \mathbb{N}$ is large enough. The function f is bounded uniformly along this orbit, while $|g| \to \infty$ uniformly on Γ_n where $n \to \infty$. In particular, for n large enough, $|g(z)| > |f(z)|$ for any $z \in \Gamma_n$. By the argument principle,

$$\frac{1}{2\pi}\oint_{\Gamma_n}\frac{h'}{h}dz = \frac{1}{2\pi}\oint_{\Gamma_n}\frac{g'}{g}dz = \{number\ of\ zeroes\ of\ g\}$$

so

$$\frac{1}{2\pi}\oint_{\Gamma_n}\frac{h'}{h}dz = \#\{zeroes\ of\ h\} - \#\{poles\ of\ h\} = \#\{zeroes\ of\ g\}$$

in the interior of the square whose boundary is Γ_n. Since g is a polynomial of order 3, the number of zeroes of g inside the square is 3 for any n large enough. Since all the poles of h are identical to the poles of f, which are given by $(\pm k + 1/2)\pi$ on the real line, $k \in \mathbb{N} \cup \{0\}$, there are exactly two poles of h in $inter(\Gamma_{k+1}) - inter(\Gamma_k)$ for all k large enough, namely at $x = (\pm k + 1/2)\pi$. Thus, there are exactly two zeroes (or one zero of order 2) in $inter(\Gamma_{k+1}) - inter(\Gamma_k)$. Evidently, there are two real roots in this domain, one in each interval $(k\pi, (k+1)\pi)$ and $(-(k+1)\pi, -k\pi)$. Thus these are the only roots in $inter(\Gamma_{k+1}) - inter(\Gamma_k)$. It follows, in particular, that h has only real roots outside a large enough square. □

Lemma 3.2. *The eigenvalues of the operator d^2/dx^2 under boundary conditions (12) are $\mu_k = (2k)^2\pi^2$, the roots λ_m of (16) and $\lambda_0 = -\kappa^2$.*

The corresponding unnormalized *eigenfunctions are:*

- $\mu_k = (2k\pi)^2$: $\quad \psi_k^{(1)}(x) = \cos(2k\pi x).\ k \in \mathbb{N} \cup \{0\}.$
- λ_m (16) : $\quad \psi_m^{(2)}(x) = \sin(\lambda_m^{1/2}(x - 1/2)),\ \ m \in \mathbb{N}.$
- $\lambda_0 = -\kappa^2$: $\quad \psi_0(x) = \cosh(\kappa(x - 1/2)).$
- *If $\kappa^2 = 12$ then $\lambda_1 = 0$ and*
  $\psi_1^{(2)}(x) = x - 1/2 = \lim_{\lambda\to 0}\lambda^{-1/2}\sin(\lambda^{1/2}(x - 1/2)).$

Proof. The proof follows by Lemma 3.1 and (13, 14). If $\kappa^2 \neq 12$ then 0 is *not* an eigenvalue, even though it is a root of *Det*. The reason is that the coefficients of (13, 14) are degenerate in that case. However, if $\kappa^2 = 12$ then the first root λ_1 of (16) is zero, and the eigenfunction follows by substitution. □

3.2 The resolvent

The resolvent operator for Neumann problem on $[0, 1]$ is expressed in terms of the eigenvalues and eigenfunctions of the operator:

$$R_N(\lambda, x, y) = \frac{1}{\lambda} + \frac{1}{2}\sum_{k=1}^{\infty}\frac{\cos(k\pi x)\cos(k\pi y)}{\lambda - k^2\pi^2}$$

and

$$\int_0^1 (1-s)R_N(\lambda,s,y) = \frac{1}{2\lambda} - A(\lambda,y)\ ,$$

$$\int_0^1 sR_N(\lambda,s,y) = \frac{1}{2\lambda} + A(\lambda,y) \quad (17)$$

where

$$A(\lambda,y) := \frac{1}{\pi^2}\sum_{m=1}^{\infty} \frac{2\cos((2m+1)\pi y)}{(2m+1)^2(\pi^2(2m+1)^2-\lambda)}\ . \quad (18)$$

The resolvent R corresponding to the boundary condition (12) can be written as

$$R(\lambda,x,y) = R_N(\lambda,x,y) + a(\lambda,y)\sin(\lambda^{1/2}x) + b(\lambda,y)\cos(\lambda^{1/2}x)$$

From the boundary conditions of (12) and (17) we obtain

$$a\left(\lambda^{1/2} + \kappa^2\lambda^{-1/2} - \frac{\kappa^2}{\lambda}\sin(\lambda^{1/2})\right) + b\kappa^2\left(\frac{1-\cos\lambda^{1/2}}{\lambda}\right) + \kappa^2\left[\frac{1}{2\lambda} - A(\lambda,y)\right] = 0 \quad (19)$$

$$a\left(\lambda^{1/2}\cos(\lambda^{1/2}) - \frac{\kappa^2\sin(\lambda^{1/2})}{\lambda} + \frac{\kappa^2\cos(\lambda^{1/2})}{\lambda^{1/2}}\right) + b\left(-\lambda^{1/2}\sin(\lambda^{1/2}) - \frac{\kappa^2\sin(\lambda^{1/2})}{\lambda^{1/2}} - \frac{\kappa^2\cos(\lambda^{1/2})-1}{\lambda}\right) - \kappa^2\left[\frac{1}{2\lambda} + A(\lambda,y)\right] = 0 \quad (20)$$

We can now solve (19,20) for any $\lambda \neq 0$ which is not a root of Det,

$$a(\lambda,y)=\kappa^2 Det^{-1}(\lambda)\left\{\frac{1}{2\lambda}\left[\sin(\lambda^{1/2})\left(\lambda^{1/2}+\frac{\kappa^2}{\lambda^{1/2}}\right)-2\kappa^2\frac{1-\cos(\lambda^{1/2})}{\lambda}\right]\right.$$
$$\left.-A(\lambda,y)\sin(\lambda^{1/2})\left(\lambda^{1/2}+\frac{\kappa^2}{\lambda^{1/2}}\right)\right\}$$
$$b(\lambda,y)=\kappa^2 Det^{-1}(\lambda)\left\{\frac{1}{2\lambda}\left[\left(\lambda^{1/2}+\frac{\kappa^2}{\lambda^{1/2}}\right)(1+\cos(\lambda^{1/2}))-\frac{2\kappa^2\sin(\lambda^{1/2})}{\lambda}\right]\right.$$
$$\left.+A(\lambda,y)\left(\lambda^{1/2}+\frac{\kappa^2}{\lambda^{1/2}}\right)(1-\cos(\lambda^{1/2}))\right\} \quad (21)$$

After some trigonometric manipulations on (21, 15) we obtain

$$R(\lambda,x,y)-R_N(\lambda,x,y)=a(\lambda,y)\sin(\lambda^{1/2}x)+b(\lambda,y)\cos(\lambda^{1/2}x)=$$
$$\frac{\kappa^2\sin(\lambda^{1/2}/2)A(\lambda,y)(\lambda^{1/2}+\kappa^2/\lambda^{1/2})}{Det(\lambda)}\sin\left(\frac{\lambda^{1/2}(1-2x)}{2}\right)$$
$$-\frac{\kappa^2\cos(\lambda^{1/2}(x-1/2))}{2\lambda^{1/2}\sin(\lambda^{1/2}/2)(\lambda+\kappa^2)} \quad (22)$$

4 The heat kernel

To obtain the heat kernel corresponding to the equation (12) we use (33) to obtain $K(x,y,t)=$

$$\frac{1}{2\pi i}\lim_{T\to\infty}\int_{\gamma-iT}^{\gamma+iT}e^{-\lambda t}(R(\lambda,x,y)-R_N(\lambda,x,y))d\lambda+\int_{\gamma-iT}^{\gamma+iT}e^{-\lambda t}R_N(\lambda,x,y)d\lambda \quad (23)$$

We now recall that the second term above is just the heat kernel of the *Neumann* problem. This can be expanded in eigenfunctions:

$$K_N(x,y,t)=\frac{1}{2\pi i}\lim_{T\to\infty}\int_{\gamma-iT}^{\gamma+iT}e^{-\lambda t}R_N(\lambda,x,y)d\lambda$$
$$=1+\frac{1}{2}\sum_{k=1}^{\infty}e^{-k^2\pi^2 t}cos(k\pi x)\cos(k\pi y) \quad (24)$$

Then we calculate the residues of $(R-R_N)e^{-\lambda t}$ using (22). The residue at the pole $\lambda=-\kappa^2$ due to the second term in (22) is

$$\frac{\kappa\cosh(\kappa/2)\cosh(\kappa(x-1/2))}{2\sinh(\kappa/2)}e^{\kappa^2 t} \quad (25)$$

Let us now evaluate the other poles of (22). The poles of the first term (the coefficients of $\sin(\lambda^{1/2}(x-1/2))$ are originated by two sources: Since $\sin(\lambda^{1/2}/2)/Det(\lambda)$ has no singularity at $\lambda=(2m\pi)^2$, the only singularity due to $Det(\lambda)$ are the roots of (16), i.e at $\lambda=\lambda_m$. The residue Theorem at this singularities yield

$$\frac{\kappa^2 A(\lambda_m,y)(\sqrt{\lambda_m}+\kappa^2/\sqrt{\lambda_m})}{2\sqrt{\lambda_m}Det'(\lambda_m)}\sin\left(\frac{\sqrt{\lambda_m}(1-2x)}{2}\right)e^{-\lambda_m t}\ . \tag{26}$$

where $A(\lambda,y)$ as given in (18). However, the first term of (22) contains also the poles at $\lambda=(2k+1)\pi$ due to the singularity of $A(\cdot,y)$ at these points. A direct calculation implies that the residue at these poles are precisely

$$-\frac{1}{2}\cos((2k+1)x)\cos((2k+1)y)e^{-4k^2\pi^2 t} \tag{27}$$

which eliminate the sum of odd indices in the Neumann heat kernel (24).

The second term in (22) also contain poles at $\lambda=(2k\pi)^2$, $k\in\mathbb{N}\cup\{0\}$. The sum of the resides is

$$\kappa^2\sum_{k=1}^{\infty}\frac{\cos(2k\pi x)e^{-4k^2\pi^2 t}}{2k\pi(4k^2\pi^2+\kappa^2)}-1\ . \tag{28}$$

Summarizing (25-28) in (23), using (24) and taking into account (11) we obtain

$$\begin{aligned}K(x,y,t)=&\frac{\kappa\cosh(\kappa/2)\cosh(\kappa(x-1/2))}{2\sinh(\kappa/2)}\\&+\sum_{k=1}^{\infty}\frac{\kappa^2 A(\lambda_k,y)(\sqrt{\lambda_k}+\kappa^2/\sqrt{\lambda_k})}{2\sqrt{\lambda_k}Det'(\lambda_k)}\sin\left(\frac{\sqrt{\lambda_k}(1-2x)}{2}\right)e^{-(\lambda_k+\kappa^2)t}\\&+\frac{1}{2}\sum_{k=1}^{\infty}\cos(2k\pi x)\left(\cos(2k\pi y)+\frac{1}{k\pi(4k^2\pi^2+\kappa^2)}\right)e^{-(4k^2\pi^2+\kappa^2)t}\end{aligned} \tag{29}$$

Corollary 4.1. *The real eigenfunctions of the* adjoint *operator $\mathcal{L}_0^\dagger$ under boundary conditions $\mathcal{D}$ (12) are:*

- $\mu_k:\quad \phi_k^{(1)}(y)=\cos(2k\pi y)+\frac{1}{k\pi(4k^2\pi^2+\kappa^2)}.\ k\in\mathbb{N}.$
- $\lambda_k:\quad \phi_k^{(2)}(y)=A(\lambda_k,y),\ \ k\in\mathbb{N}.$
- $\lambda_0=-\kappa^2$*:* $\quad\phi^{(0)}(y)=1.$

5 Conclusions

The leading term in the eigenfunctions expansions of the PNP equation (1, 5) is the stationary term proportional to $\cosh(\kappa(x-1/2))$. The other modes decay exponentially. Out of these decaying mode, the leading one decays as $\exp(-(\lambda_1+\kappa^2)t)$ where $\lambda_1 \in (0,\pi^2)$. In general, the decaying modes correspond to two sets: μ_n decay as $\exp(-(4n^2\pi^2+\kappa^2)t)$, and λ_n decay as $\exp(-(\lambda_n+\kappa^2)t)$ where $\lambda_n \in (4(n-1)^2\pi^2, (2n-1)^2\pi^2)$.

The heat kernel associated with the operator $\mathcal{L}_0 := d^2/dx^2$ on the domain $\mathcal{D}$ satisfying the boundary conditions (5) is given by (8). The operator $\mathcal{L}_0$ itself, acting on a function $h \in \mathcal{D}$, takes the form of a formal series of the eigenstates $\psi_n^{(1,2)}$ and ψ_0:

$$\begin{aligned}\mathcal{L}_0 h(x) = \frac{\partial}{\partial t}K|_{t=0} * h = \\ \frac{\kappa^3\cosh(\kappa/2)}{2\sinh(\kappa/2)} < \phi_0, h > \psi_0(x) \\ -\sum_{n=1}^{\infty}\lambda_n \frac{\kappa^2(\sqrt{\lambda_n}+\kappa^2/\sqrt{\lambda_n})}{2\sqrt{\lambda_n}Det'(\lambda_n)} < \phi_n^{(1)}, h > \psi_n^{(1)}(x) \\ -2n^2\pi^2\sum_{n=1}^{\infty} < \phi_n^{(2)}, h > \psi_n^{(2)}(x) \quad (30)\end{aligned}$$

where $< \phi, h >:= \int_0^1 h(y)\phi(y)dy$. An interesting conclusion concerns the adjoint of the operator $\mathcal{L}_0^\dagger$. Its heat kernel $K^\dagger$ is obtained by swapping x and y in K, namely $K^\dagger(x,y,t) = K(y,x,t)$. Thus

$$\begin{aligned}\mathcal{L}_0^\dagger h(x) = \frac{\kappa^3\cosh(\kappa/2)}{2\sinh(\kappa/2)} < \psi_0, h > \phi_0(x) \\ -\sum_{n=1}^{\infty}\lambda_n \frac{\kappa^2(\sqrt{\lambda_n}+\kappa^2/\sqrt{\lambda_n})}{2\sqrt{\lambda_n}Det'(\lambda_n)} < \psi_n^{(1)}, h > \phi_n^{(1)}(x) \\ -2n^2\pi^2\sum_{n=1}^{\infty} < \psi_n^{(2)}, h > \phi_n^{(2)}(x) \quad (31)\end{aligned}$$

The associated eigenfunctions, given by $\phi_k^{(1)}(y) = \cos(2k\pi y) + \frac{1}{k\pi(4k^2\pi^2+\kappa^2)}$ and $\phi_k^{(2)}(y) = A(\lambda_k, y)$ are not trigonometric functions. In particular we *cannot* identify $\mathcal{L}_0^\dagger$ with d^2/dx^2 on a certain domain $\mathcal{D}^\dagger$, as we did for $\mathcal{L}_0$.

Open question: *Find an explicit expression for the generator to the adjoint operator $\mathcal{L}_0^\dagger$ and its domain $\mathcal{D}^\dagger$.*

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A Appendix

A.1 From resulvent to heat kernel

From the resolvent to the heat kernel Let $U(\lambda, x)$ be a solution of

$$U_{xx} + \lambda U + f = 0 \tag{32}$$

satisfying a well posed boundary conditions, where $\lambda \in \mathbb{C}$. Then

$$U(\lambda, x) = \int_0^1 R(\lambda, x, y) f(y) dy$$

where R is the Resolvent:

$$\frac{\partial^2 R}{\partial x^2} + \lambda R + \delta_{x-y} = 0$$

Suppose U is analytic, as function of λ, in the half plane $Re(\lambda) \leq \gamma$ for some $\gamma \in \mathbb{R}$. Then

$$u(x,t) = \frac{1}{2\pi i} \lim_{T\to\infty} \int_{\gamma - iT}^{\gamma + iT} e^{-\lambda t} U(\lambda, x) d\lambda \tag{33}$$

is the solution of (12). Indeed

$$u_t = -\frac{1}{2\pi i} \lim_{T\to\infty} \int_{\gamma - iT}^{\gamma + iT} \lambda e^{-\lambda t} U(\lambda, x) d\lambda$$

while, by (32),

$$u_{xx} = \frac{1}{2\pi i} \lim_{T\to\infty} \int_{\gamma - iT}^{\gamma + iT} e^{-\lambda t} U_{xx}(\lambda, x) d\lambda = \frac{1}{2\pi i} \lim_{T\to\infty} \int_{\gamma - iT}^{\gamma + iT} e^{-\lambda t} [-f - \lambda U(\lambda, x)] d\lambda$$

$$= u_t - f(x) \frac{1}{2\pi i} \lim_{T\to\infty} \int_{\gamma - iT}^{\gamma + iT} e^{-\lambda t} d\lambda \ ,$$

while

$$\frac{1}{2\pi i}\lim_{T\to\infty}\int_{\gamma-iT}^{\gamma+iT} e^{-\lambda t}d\lambda = \frac{1}{\pi}e^{-\gamma t}\lim_{T\to\infty}\frac{\sin(tT)}{t} = e^{-\gamma t}\delta_{t=0} = \delta_{t=0}$$

as a distribution.

The heat kernel can, then, be written as

$$K(x,y,t) = \frac{1}{2\pi i}\lim_{T\to\infty}\int_{\gamma-iT}^{\gamma+iT} e^{-\lambda t}R(\lambda,x,y)d\lambda \tag{34}$$

where $t \geq 0$ *and* $x, y \in [0,1]^2$.

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