

# Supplementary Information: Adsorption Kinetics in Open Nanopores as a Source of Low-Frequency Noise

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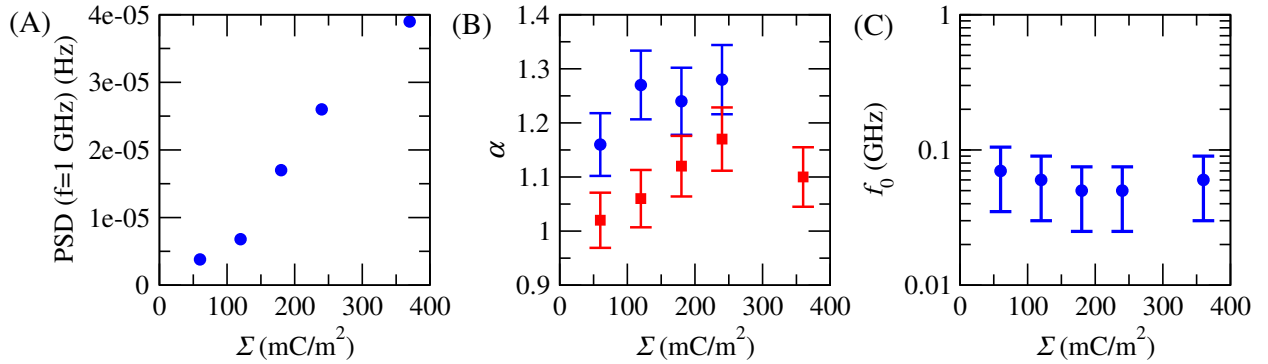


Figure S1: **(A)** Value of the PSD of the number of free particle at  $f = 1 \text{ GHz}$  as a function of the surface charge  $\Sigma$ , for a nanopore of radius  $R_n = 1 \text{ nm}$ , length  $L_n = 1 \text{ nm}$ , connected to half spherical reservoirs of radius  $H_n = 10 \text{ nm}$ , desorption frequency  $\lambda = 100 \text{ GHz}$ , and bulk salt concentration  $c_s = 20 \text{ mM}$ . **(B)** Exponent of the PSD of  $N_F$  (disks) and  $N_B$  (squares) as a function of the surface charge  $\Sigma$ . **(C)** Low frequency cut-off as a function of the surface charge  $\Sigma$ .

# Model

## Infinite cylinder

Let us consider  $N$  particles in an infinite cylindrical pore of radius  $R_c$  (Fig. 2 A of the main text). Each particle undergoes consecutive surface adsorption and desorption events, we introduce a binary adsorption state variable  $n_A^i(t)$  for each particle  $i = 1 \dots N$  that is  $n_A^i(t)=1$  when the particle is adsorbed and  $n_A^i(t)=0$  when the particle is desorbed. The number of adsorbed particles at any time  $t$  follows as

$$N_A(t) = \sum_{i=1}^N n_A^i(t). \quad (\text{S1})$$

The auto-correlation function of  $N_A(t)$  writes

$$\langle N_A(0)N_A(t) \rangle = \sum_{i,j=1}^N \langle n_A^i(0)n_A^j(t) \rangle. \quad (\text{S2})$$

If the particles are uncorrelated among each other, one can write:

$$\langle N_A(0)N_A(t) \rangle = \sum_{i \neq j}^N \langle n_A^i(0) \rangle \langle n_A^j(t) \rangle + \sum_{i=1}^N \langle n_A^i(0)n_A^i(t) \rangle. \quad (\text{S3})$$

Defining the probability for a particle to be adsorbed as  $p_A = \langle n_A^i(0) \rangle = \langle n_A^j(t) \rangle$ , we can rewrite the auto-correlation function as

$$\langle N_A(0)N_A(t) \rangle = N^2 p_A^2 + N p_A C_{AA}(t) - N p_A^2, \quad (\text{S4})$$

where the single-particle correlation function

$$C_{AA}(t) = \langle n_A(0)n_A(t) \rangle / \langle n_A(0) \rangle, \quad (\text{S5})$$

is the only non-trivial quantity to calculate. It denotes the conditional probability that a particle is adsorbed at time  $t$  given that it was adsorbed at time  $t = 0$ , and can be written as

$$C_{AA}(t) = \sum_{n=0}^{\infty} \left[ \int_0^{\infty} dt_e Q(t_e) \prod_{m=1}^n \left[ \int_0^{\infty} dt_m P(t_m) \int_0^{\infty} dt'_m J_c(t'_m) \right] \times \delta \left( t_e + \sum_{k=1}^n (t_k + t'_k) - t \right) \right], \quad (\text{S6})$$

where the outer sum counts the number of desorption and re-adsorption events. The distribution  $P(t)$  is the probability for an adsorbed particle to desorb from the surface at time  $t$ . We assume an exponential

desorption distribution  $P(t) = \lambda e^{-\lambda t}$ , with  $\lambda$  in inverse time unit. Then it's Laplace transform writes

$$\tilde{P}(\omega) = \frac{\lambda}{\lambda + \omega}. \quad (\text{S7})$$

$Q(t)$  is the survival distribution. It corresponds to the probability for a particle to be adsorbed over the time span from  $t=0$  to  $t$  and is given by  $Q(t) = \int_t^\infty dt' P(t')$ . In our case, it writes  $Q(t) = e^{-\lambda t}$  and it's Laplace transform is

$$\tilde{Q}(\omega) = \frac{1}{\lambda + \omega}. \quad (\text{S8})$$

Finally, the first-return distribution  $J_c(t)$  is the probability for a particle that has been desorbed at time zero to return to the cylinder surface for the first time at  $t$ . Note the different physical units of the distributions,  $P(t)$  and  $J_c(t)$  have units of inverse time,  $Q(t)$  is unitless, and the probability  $C_{AA}(t)$  is unitless because of the delta function. By means of Laplace transformation the correlation function factorizes into a geometric sum as

$$\tilde{C}_{AA}(\omega) = \sum_{n=0}^{\infty} \left( \tilde{Q}(\omega) \left[ \tilde{P}(\omega) \tilde{J}_c(\omega) \right]^n \right) = \frac{\tilde{Q}(\omega)}{1 - \tilde{P}(\omega) \tilde{J}_c(\omega)}, \quad (\text{S9})$$

where  $\tilde{J}_c(\omega)$  is the Laplace transform of  $J_c(t)$ .

### Green function

Here we calculate the first return distribution  $\tilde{J}_c(\omega)$  for an infinite cylinder of radius  $R_c$ . The radially symmetric Green function for a particle to be at time  $t$  at a radius  $r$  when starting at a radius  $r_0$  obeys the radial diffusion equation in cylindrical coordinates

$$\partial_t \mathcal{G}_c(r, t | r_0) = D \nabla^2 \mathcal{G}_c(r, t | r_0), \quad (\text{S10})$$

where  $D$  denotes the diffusion constant and  $\nabla^2 = r^{-1} \partial_r r \partial_r$ . We assumed that  $\mathcal{G}_c(r, t | r_0)$  is independent of both  $z$  and  $\theta$ . Performing a Laplace transform with respect to the time, we have

$$(\omega - D \nabla^2) \tilde{\mathcal{G}}_c(r, \omega | r_0) = \frac{\delta(r - r_0)}{2\pi r}, \quad (\text{S11})$$

where we used the initial condition  $\mathcal{G}_c(r, t = 0 | r_0) = \delta(r - r_0)/2\pi r$ . Using the rescaled radial coordinate  $\tilde{r} = r \sqrt{\omega/D}$ , Eq. (S11) can be brought into the canonical form of a Bessel differential equation

$$\frac{\tilde{r}}{2\pi D} \delta(\tilde{r} - \tilde{r}_0) = \tilde{r}^2 \tilde{\mathcal{G}}_c(\tilde{r}, \omega | r_0) - \tilde{r} \partial_{\tilde{r}} \tilde{\mathcal{G}}_c(\tilde{r}, \omega | r_0) - \tilde{r}^2 \partial_{\tilde{r}}^2 \tilde{\mathcal{G}}_c(\tilde{r}, \omega | r_0). \quad (\text{S12})$$

The general solution is

$$\tilde{\mathcal{G}}_c(\tilde{r}, \omega | \tilde{r}_0) = \begin{cases} a_c I_0(\tilde{r}) & \text{for } \tilde{r} < \tilde{r}_0 \text{ and} \\ b_c I_0(\tilde{r}) + c_c K_0(\tilde{r}) & \text{for } \tilde{r} > \tilde{r}_0, \end{cases} \quad (\text{S13})$$

where  $I_0(x)$  and  $K_0(x)$  are modified Bessel functions. The coefficients  $a_c$ ,  $b_c$ ,  $c_c$  are determined by the following three boundary conditions:

- **(BC1)** continuity at  $\tilde{r} = \tilde{r}_0$ :

$$a_c I_0(\tilde{r}_0) = b_c I_0(\tilde{r}_0) + c_c K_0(\tilde{r}_0), \quad (\text{S14})$$

- **(BC2)** initial condition Eq. (S12):

$$\frac{1}{2\pi D \tilde{r}_0} = a_c I_1(\tilde{r}_0) - b_c I_1(\tilde{r}_0) + c_c K_1(\tilde{r}_0), \quad (\text{S15})$$

where  $\partial_x I_0(x) = I_1(x)$  and  $\partial_x K_0(x) = -K_1(x)$ ,

- **(BC3)** a surface reaction boundary condition at  $r = R_c$  which in unrescaled units reads

$$\tilde{j}(\tilde{r}, \omega | \tilde{r}_0) \big|_{r=R_c} = -D \partial_R \tilde{\mathcal{G}}_c(\tilde{R}_c, \omega | \tilde{r}_0) = k \tilde{\mathcal{G}}_c(\tilde{R}_c, \omega | \tilde{r}_0), \quad (\text{S16})$$

and reflects that the particle boundary flux  $\tilde{j}(\tilde{R}_c, \omega | r_0)$  is proportional to the particle boundary density times a phenomenological rate constant  $k$  (m/s). In rescaled radial units and using  $k = \tilde{k} \sqrt{\omega D}$  this condition reads

$$\partial_{\tilde{R}} \tilde{\mathcal{G}}_c(\tilde{R}_c, \omega | \tilde{r}_0) = -\tilde{k} \tilde{\mathcal{G}}_c(\tilde{R}_c, \omega | \tilde{r}_0), \quad (\text{S17})$$

which explicitly yields

$$b_c I_1(\tilde{R}_c) - c_c K_1(\tilde{R}_c) = -\tilde{k} [b_c I_0(\tilde{r}_0) + c_c K_0(\tilde{r}_0)]. \quad (\text{S18})$$

Introducing rescaled coefficients  $\tilde{a}_c = 2\pi D \tilde{r}_0 a_c$  (and similarly for  $b_c$  and  $c_c$ ) we arrive at the final boundary conditions

$$\tilde{a}_c I_0(\tilde{r}_0) = \tilde{b}_c I_0(\tilde{r}_0) + \tilde{c}_c K_0(\tilde{r}_0), \quad (\text{S19})$$

$$1 = \tilde{a}_c I_1(\tilde{r}_0) - \tilde{b}_c I_1(\tilde{r}_0) + \tilde{c}_c K_1(\tilde{r}_0), \quad (\text{S20})$$

$$\tilde{b}_c I_1(\tilde{R}_c) - \tilde{c}_c K_1(\tilde{R}_c) = -\tilde{k} [\tilde{b}_c I_0(\tilde{R}_c) + \tilde{c}_c K_0(\tilde{R}_c)]. \quad (\text{S21})$$

The solutions for  $\tilde{b}_c$  and  $\tilde{c}_c$  read

$$\tilde{c}_c = \frac{I_0(\tilde{r}_0)}{K_0(\tilde{r}_0)I_1(\tilde{r}_0) + K_1(\tilde{r}_0)I_0(\tilde{r}_0)} \quad \text{and} \quad \tilde{b}_c = \tilde{c}_c \left( \frac{K_1(\tilde{R}_c) - \tilde{k}K_0(\tilde{R}_c)}{I_1(\tilde{R}_c) + \tilde{k}I_0(\tilde{R}_c)} \right), \quad (\text{S22})$$

which leads to

$$\tilde{\mathcal{G}}_c(\tilde{r}, \omega | \tilde{r}_0) = \frac{1}{2\pi D \tilde{r}_0} \left[ \left( \frac{K_1(\tilde{R}_c) - \tilde{k}K_0(\tilde{R}_c)}{I_1(\tilde{R}_c) + \tilde{k}I_0(\tilde{R}_c)} \right) I_0(\tilde{r}) + K_0(\tilde{r}) \right] \frac{I_0(\tilde{r}_0)}{K_0(\tilde{r}_0)I_1(\tilde{r}_0) + K_1(\tilde{r}_0)I_0(\tilde{r}_0)}. \quad (\text{S23})$$

### First return distribution in infinite cylinder

The local flux at the cylinder surface can be calculated from the Green function as (Eq. (S16))

$$\tilde{j}(\tilde{R}_c, \omega | \tilde{r}_0) = -D \left. \frac{\partial \tilde{\mathcal{G}}_c(\tilde{r}, \omega | \tilde{r}_0)}{\partial r} \right|_{r=\tilde{R}_c} = k \tilde{\mathcal{G}}_c(\tilde{R}_c, \omega | \tilde{r}_0). \quad (\text{S24})$$

Finally we define the unitless first return distribution by considering all trajectories starting from the surface of the cylinder,

$$\tilde{J}_c(\omega) = 2\pi \tilde{R}_c \tilde{j}(\tilde{R}_c, \omega | \tilde{R}_c) = \frac{\tilde{k}I_0(\tilde{R}_c)}{I_1(\tilde{R}_c) + \tilde{k}I_0(\tilde{R}_c)}. \quad (\text{S25})$$

## Sphere

### Green function

We consider the radially symmetric Green function between two concentric spheres with radii  $R$  and  $H > R$  (Fig. 3 A of the main text) for a particle to be at time  $t$  at a radius  $r$  when starting at a radius  $r_0$ . It obeys the radial diffusion equation in spherical coordinates

$$\partial_t \mathcal{G}_s(r, t|r_0) = D \Delta_r \mathcal{G}_s(r, t|r_0) = D \frac{1}{r^2} \partial_r r^2 \partial_r \mathcal{G}_s(r, t|r_0), \quad (\text{S26})$$

where  $D$  denotes the diffusion constant. The Laplace transformed equation reads

$$\omega \tilde{\mathcal{G}}_s(r, \omega|r_0) - \frac{\delta(r - r_0)}{4\pi r_0^2} = D \frac{1}{r^2} \partial_r r^2 \partial_r \tilde{\mathcal{G}}_s(r, \omega|r_0) = \frac{2D}{r} \partial_r \tilde{\mathcal{G}}_s(r, \omega|r_0) + D \partial_r^2 \tilde{\mathcal{G}}_s(r, \omega|r_0), \quad (\text{S27})$$

where we used the initial condition

$$\mathcal{G}_s(r, t = 0|r_0) = \frac{\delta(r - r_0)}{4\pi r^2}. \quad (\text{S28})$$

The general solution reads

$$\tilde{\mathcal{G}}_s(r, \omega|r_0) = \begin{cases} (a_s e^{-\gamma r} + b_s e^{\gamma r})/r & \text{for } R < r_0 < r < H \text{ and} \\ (c_s e^{-\gamma r} + d_s e^{\gamma r})/r & \text{for } R < r < r_0 < H, \end{cases} \quad (\text{S29})$$

and  $\gamma = \sqrt{\omega/D}$ . The coefficients  $a_s, b_s, c_s, d_s$  are determined by the following four boundary conditions:

- **(BC1)** continuity at  $r = r_0$

$$a_s e^{-\gamma r_0} + b_s e^{\gamma r_0} = c_s e^{-\gamma r_0} + d_s e^{\gamma r_0}, \quad (\text{S30})$$

- **(BC2)** the initial condition Eq. S27 which can be written as

$$-\frac{1}{4\pi D r_0^2} = -a_s e^{-\gamma r_0} \left( \frac{\gamma}{r_0} + \frac{1}{r_0^2} \right) + b_s e^{\gamma r_0} \left( \frac{\gamma}{r_0} - \frac{1}{r_0^2} \right) + c_s e^{-\gamma r_0} \left( \frac{\gamma}{r_0} + \frac{1}{r_0^2} \right) - d_s e^{\gamma r_0} \left( \frac{\gamma}{r_0} - \frac{1}{r_0^2} \right), \quad (\text{S31})$$

- **(BC3)** the surface reaction boundary condition at the outer sphere  $r = H$  which reads

$$\tilde{j}(H, \omega|r_0) = -D \partial_H \tilde{\mathcal{G}}(H, \omega|r_0) = K_H \tilde{\mathcal{G}}(H, \omega|r_0), \quad (\text{S32})$$

defining a phenomenological absorption rate constant  $K_H$ . It can be rewritten as

$$-D \left[ -a_s e^{-\gamma H} \left( \frac{\gamma}{H} + \frac{1}{H^2} \right) + b_s e^{\gamma H} \left( \frac{\gamma}{H} - \frac{1}{H^2} \right) \right] = K_H [a_s e^{-\gamma H}/H + b_s e^{\gamma H}/H], \quad (\text{S33})$$

- **(BC4)** the surface reaction boundary condition at the inner sphere  $r = R$  which reads

$$\tilde{j}(R, \omega|r_0) = D \partial_R \tilde{\mathcal{G}}_s(R, \omega|r_0) = K_R \tilde{\mathcal{G}}_s(R, \omega|r_0), \quad (\text{S34})$$

defining a phenomenological absorption rate constant  $K_R$ . It can be rewritten as

$$D \left[ -c_s e^{-\gamma R} \left( \frac{\gamma}{R} + \frac{1}{R^2} \right) + d_s e^{\gamma R} \left( \frac{\gamma}{R} - \frac{1}{R^2} \right) \right] = K_R [c_s e^{-\gamma R}/R + d_s e^{\gamma R}/R]. \quad (\text{S35})$$

Using the rescaled radial coordinates  $\tilde{r} = r\gamma$ ,  $\tilde{H} = H\gamma$  and  $\tilde{R} = R\gamma$ , the four conditions can be rewritten as

$$(a_s - c_s) e^{-\tilde{r}_0} = (d_s - b_s) e^{\tilde{r}_0}, \quad (\text{S36})$$

$$\frac{1}{4\pi D} = e^{-\tilde{r}_0} (a_s - c_s) (\tilde{r}_0 + 1) + e^{\tilde{r}_0} (d_s - b_s) (\tilde{r}_0 - 1), \quad (\text{S37})$$

$$a_s e^{-\tilde{H}} (\tilde{H} + 1) - b_s e^{\tilde{H}} (\tilde{H} - 1) = \tilde{K}_H \tilde{H} (a_s e^{-\tilde{H}} + b_s e^{\tilde{H}}), \quad (\text{S38})$$

$$-c_s e^{-\tilde{R}} (\tilde{R} + 1) + d_s e^{\tilde{R}} (\tilde{R} - 1) = \tilde{K}_R \tilde{R} (c_s e^{-\tilde{R}} + d_s e^{\tilde{R}}), \quad (\text{S39})$$

where we defined  $\tilde{K}_H = K_H/(D\gamma)$  and  $\tilde{K}_R = K_R/(D\gamma)$ . The solutions for  $a_s$ ,  $b_s$ ,  $c_s$  and  $d_s$  read

$$a_s = \frac{W_1 e^{\tilde{r}_0} - e^{-\tilde{r}_0}}{8\pi \tilde{r}_0 D (W_1 + W_2)}, \quad b_s = W_2 a_s, \quad c_s = -\frac{W_2 e^{\tilde{r}_0} + e^{-\tilde{r}_0}}{8\pi \tilde{r}_0 D (W_1 + W_2)} \quad \text{and} \quad d_s = -W_1 c_s, \quad (\text{S40})$$

where we defined the auxiliary expressions

$$W_1 = e^{-2\tilde{R}} \frac{\tilde{R} + 1 + \tilde{R}\tilde{k}}{1 - \tilde{R} + \tilde{R}\tilde{k}} \quad \text{and} \quad W_2 = e^{-2\tilde{H}} \frac{\tilde{H} + 1 - \tilde{H}\tilde{K}_H}{\tilde{H} - 1 + \tilde{H}\tilde{K}_H}. \quad (\text{S41})$$

### Single sphere of radius $R_s$

To obtain the first-return rate distribution to a sphere  $R_s$  from the inside we use our result Eq. (S32) for the flux at the outer sphere  $H$ . At the end of this section, we will put  $R = 0$  and associate the outer sphere radius  $H$  with  $R_s$ . The total flux onto the sphere at  $H$  when starting from a point  $r_0 < H$  inside the outer sphere reads

$$\tilde{j}_s(\omega|r_0) = 4\pi H^2 \tilde{j}(H, \omega|r_0) = 4\pi \tilde{K}_H D \tilde{H} (a_s e^{-\tilde{H}} + b_s e^{\tilde{H}}), \quad (\text{S42})$$

which using the explicit results for  $a_s$  and  $b_s$  can be rewritten as

$$\tilde{J}_s(\omega|r_0) = \frac{\tilde{K}_H \tilde{H} e^{\tilde{r}_0 - \tilde{H}} (W_1 - e^{-2\tilde{r}_0}) (W_2 e^{2\tilde{H}} + 1)}{2\tilde{r}_0 (W_1 + W_2)}. \quad (\text{S43})$$

Choosing the source point as  $r_0 = H$ , we obtain the first return rate distribution

$$\tilde{J}_s(\omega) = \frac{\tilde{K}_H (W_1 - e^{-2\tilde{H}}) (W_2 e^{2\tilde{H}} + 1)}{2(W_1 + W_2)}. \quad (\text{S44})$$

Now we put  $R = 0$ , which means that  $W_1 = 1$ , and replace the remaining radius variable  $\tilde{H}$  by  $\tilde{R}_s$  as well as  $\tilde{K}_H$  by  $\tilde{k}$ . We obtain the unitless first return distribution for a single sphere of radius  $R_s$

$$\tilde{J}_s(\omega) = \frac{\tilde{k} \tilde{R}_s (1 - e^{-2\tilde{R}_s})}{\tilde{R}_s - 1 + \tilde{k} \tilde{R}_s + e^{-2\tilde{R}_s} (\tilde{R}_s + 1 - \tilde{k} \tilde{R}_s)}. \quad (\text{S45})$$

#### Concentric spheres of respective radius $R_{\text{cs}}$ and $H_{\text{cs}}$ with $H_{\text{cs}} > R_{\text{cs}}$

In order to match the notations used in the main text, we now rewrite the inner radius as  $R_{\text{cs}}$  and the outer radius as  $H_{\text{cs}}$  where ‘cs’ stands for concentric spheres. From Eq. (S34) the total flux onto the inner sphere at  $R_{\text{cs}}$  when starting from a point  $r_0 > R_{\text{cs}}$  outside the inner sphere reads

$$\tilde{J}_{\text{cs}}(\omega|r_0) = 4\pi R_{\text{cs}}^2 \tilde{j}(R_{\text{cs}}, \omega|r_0) = 4\pi \tilde{k} D \tilde{R}_{\text{cs}} (c_s e^{-\tilde{R}_{\text{cs}}} + d_s e^{\tilde{R}_{\text{cs}}}), \quad (\text{S46})$$

where we replaced  $\tilde{K}_R$  by  $\tilde{k}$ . Using the explicit results for  $c_s$  and  $d_s$ , it can be rewritten as

$$\tilde{J}_{\text{cs}}(\omega|r_0) = \frac{\tilde{k} \tilde{R}_{\text{cs}} e^{\tilde{r}_0 - \tilde{R}_{\text{cs}}} (W_2 + e^{-2\tilde{r}_0}) (W_1 e^{2\tilde{R}_{\text{cs}}} - 1)}{2\tilde{r}_0 (W_1 + W_2)}. \quad (\text{S47})$$

Now choosing the source point as  $r_0 = R_{\text{cs}}$  we obtain the first return rate distribution

$$\tilde{J}_{\text{cs}}(\omega) = \frac{\tilde{k} (W_2 + e^{-2\tilde{R}_{\text{cs}}}) (W_1 e^{2\tilde{R}_{\text{cs}}} - 1)}{2(W_1 + W_2)}. \quad (\text{S48})$$

In the limit of large outer sphere  $H_{\text{cs}} \rightarrow \infty$ ,

$$\tilde{J}_{\text{cs}}(\omega) = \frac{\tilde{k} \tilde{R}_{\text{cs}}}{1 + \tilde{R}_{\text{cs}} + \tilde{k} \tilde{R}_{\text{cs}}}, \quad (\text{S49})$$



that can be rewritten in terms of non-rescaled unit as

$$\tilde{J}_{\text{cs}}(\omega) = \left( \frac{D}{kR_{\text{cs}}} + \frac{\sqrt{\omega D}}{k} + 1 \right)^{-1}. \quad (\text{S50})$$

## Adsorbing plates

Let us consider  $N$  particles between two plates separated by  $2R_p$ . Each particle undergoes consecutive surface adsorption and desorption events, we introduce binary adsorption state variables  $n_A^i(t)$  and  $n_B^i(t)$  for each particle  $i = 1 \dots N$  that is  $n_A^i(t) = 1$  when the particle is adsorbed on plate  $A$ ,  $n_B^i(t) = 1$  when the particle is adsorbed on plate  $B$ , and  $n_A^i(t) = n_B^i(t) = 0$  when the particle is desorbed. The number of ions adsorbed at plate  $A$  at time  $t$  follows as

$$N_A(t) = \sum_{i=1}^N n_A^i(t). \quad (\text{S51})$$

The auto-correlation function of  $N_A(t)$  writes

$$\langle N_A(0)N_A(t) \rangle = \sum_{i,j=1}^N \langle n_A^i(0)n_A^j(t) \rangle. \quad (\text{S52})$$

If the particles are uncorrelated among each other, one can write:

$$\langle N_A(0)N_A(t) \rangle = \sum_{i \neq j}^N \langle n_A^i(0) \rangle \langle n_A^j(t) \rangle + \sum_{i=1}^N \langle n_A^i(0)n_A^i(t) \rangle. \quad (\text{S53})$$

Defining the probability for a particle to be adsorbed as  $p_A = \langle n_A^i(0) \rangle = \langle n_A^j(t) \rangle$ , we can rewrite the auto-correlation function as

$$\langle N_A(0)N_A(t) \rangle = N^2 p_A^2 + N p_A C_{AA}(t) - N p_A^2, \quad (\text{S54})$$

where the single-particle correlation function

$$C_{AA}(t) = \langle n_A(0)n_A(t) \rangle / \langle n_A(0) \rangle, \quad (\text{S55})$$

denotes the conditional probability that a particle is adsorbed at time  $t$  given that it was adsorbed at time  $t = 0$ . Let us first work out the correlation function for a single surface  $A$ , i.e., for the situation when surface  $B$  is infinitely far away. The probability for a particle to be adsorbed at plate  $A$  at time  $t$  given that it is adsorbed at plate  $A$  at time  $t = 0$  is given by

$$C_{AA}(t) = \sum_{n=0}^{\infty} \left[ \int_0^{\infty} dt_e Q_A(t_e) \prod_{m=1}^n \left[ \int_0^{\infty} dt_m P_A(t_m) \int_0^{\infty} dt'_m J_{AA}(t'_m) \right] \times \delta \left( t_e + \sum_{k=1}^n (t_k + t'_k) - t \right) \right], \quad (\text{S56})$$

where the outer sum counts the number of desorption and re-adsorption events. The distribution  $P_A(t)$  is the probability for an adsorbed ion to desorb from the surface at time  $t$ . We assume an exponential desorption distribution  $P_A(t) = \lambda e^{-\lambda t}$ , with  $\lambda$  in inverse time unit. Then it's Laplace transform  $P_A(\omega) = \int_0^\infty \exp(-\omega t) P_A(t) dt$  writes

$$\tilde{P}_A(\omega) = \frac{\lambda}{\lambda + \omega}. \quad (\text{S57})$$

The probability for a particle to be absorbed at  $t$  is given by the survival distribution  $Q_A(t)$ . It corresponds to the probability for a particle to be adsorbed over the time span from  $t = 0$  to  $t$  and is given by  $Q_A(t) = \int_t^\infty dt' P_A(t')$ . In our case, it writes  $Q_A(t) = e^{-\lambda t}$  and it's Laplace transform is

$$\tilde{Q}_A(\omega) = \frac{1}{\lambda + \omega}. \quad (\text{S58})$$

Finally, the first-return distribution  $J_{AA}(t)$  is the probability for a particle to desorb at time zero and to return to plate  $A$  for the first time at  $t$ . By means of Laplace transformation the correlation function factorizes into a geometric sum as

$$\tilde{C}_{AA}(\omega) = \sum_{n=0}^{\infty} \left( \tilde{Q}_A(\omega) \left[ \tilde{P}_A(\omega) \tilde{J}_{AA}(\omega) \right]^n \right) = \frac{\tilde{Q}_A(\omega)}{1 - \tilde{P}_A(\omega) \tilde{J}_{AA}(\omega)}. \quad (\text{S59})$$

In the presence of a second plate  $B$  at finite separation  $2R_p$ , a particle can desorb from plate  $A$  and return to plate  $A$  without touching plate  $B$  or it can adsorb onto plate  $B$ . It is useful to do a resummation of re-adsorption events onto plate  $A$  without ever adsorbing onto plate  $B$  according to

$$\tilde{C}_{AA}^*(\omega) = \frac{1}{1 - \tilde{P}_A(\omega) \tilde{J}_{AA}(\omega)}, \quad (\text{S60})$$

which counts for an arbitrary number of re-adsorption events onto plate  $A$  and can be viewed as a renormalized first return probability onto plate  $A$ . The expression for plate  $B$  looks similarly

$$\tilde{C}_{BB}^*(\omega) = \frac{1}{1 - \tilde{P}_B(\omega) \tilde{J}_{BB}(\omega)}. \quad (\text{S61})$$

The autocorrelation function at plate  $A$  now follows as

$$\tilde{C}_{AA}(\omega) = \frac{\tilde{Q}_A(\omega) \tilde{C}_{AA}^*(\omega)}{1 - \tilde{P}_A(\omega) \tilde{C}_{AA}^*(\omega) \tilde{J}_{AB}(\omega) \tilde{C}_{BB}^*(\omega) \tilde{P}_B(\omega) \tilde{J}_{BA}(\omega)}. \quad (\text{S62})$$

Likewise the autocorrelation function at plate  $B$  follows as

$$\tilde{C}_{BB}(\omega) = \frac{\tilde{Q}_B(\omega)\tilde{C}_{BB}^*(\omega)}{1 - \tilde{P}_B(\omega)\tilde{C}_{BB}^*(\omega)\tilde{J}_{BA}(\omega)\tilde{C}_{AA}^*(\omega)\tilde{P}_A(\omega)\tilde{J}_{AB}(\omega)}, \quad (\text{S63})$$

and the crosscorrelation functions follow as

$$\tilde{C}_{AB}(\omega) = \tilde{C}_{AA}^*(\omega)\tilde{P}_A(\omega)\tilde{J}_{AB}(\omega)\tilde{C}_{BB}(\omega), \quad (\text{S64})$$

$$\tilde{C}_{BA}(\omega) = \tilde{C}_{BB}^*(\omega)\tilde{P}_B(\omega)\tilde{J}_{BA}(\omega)\tilde{C}_{AA}(\omega). \quad (\text{S65})$$

### Green function

The Green function for a particle to be at time  $t$  at position  $z$  when starting at position  $z_0$  at time  $t_0$  obeys the one-dimensional diffusion equation

$$\partial_t \mathcal{G}_p(z, t|z_0) = D \partial_z^2 \mathcal{G}_p(z, t|z_0), \quad (\text{S66})$$

where  $D$  denotes the diffusion constant. The Laplace transformed equation reads

$$(\omega - D \partial_z^2) \tilde{\mathcal{G}}_p(z, \omega|z_0) = \delta(z - z_0), \quad (\text{S67})$$

where we used the initial condition  $\mathcal{G}_p(z, t=0|z_0) = \delta(z - z_0)$ . The general solution reads

$$\tilde{\mathcal{G}}_p(z, \omega|z_0) = \begin{cases} a_p e^{-\gamma z} + b_p e^{\gamma z} & \text{for } 0 < z < z_0 < 2R_p \text{ and} \\ c_p e^{-\gamma z} + d_p e^{\gamma z} & \text{for } 0 < z_0 < z < 2R_p, \end{cases} \quad (\text{S68})$$

where  $\gamma = \sqrt{\omega/D}$ . The coefficients  $a_p, b_p, c_p, d_p$  are determined by the following four boundary conditions:

- **(BC1)** the continuity at  $z = z_0$ ,

$$a_p e^{-\gamma z_0} + b_p e^{\gamma z_0} = c_p e^{-\gamma z_0} + d_p e^{\gamma z_0}, \quad (\text{S69})$$

- **(BC2)** the initial condition

$$\frac{-1}{\gamma D} = a_p e^{-\gamma z_0} - b_p e^{\gamma z_0} - c_p e^{-\gamma z_0} + d_p e^{\gamma z_0}, \quad (\text{S70})$$

- **(BC3)** the surface reaction boundary condition at the surface  $A$ , in  $z = 0$ , which reads

$$\tilde{j}(z, \omega|z_0)|_{z=0} = +D\partial_z \tilde{\mathcal{G}}(0, \omega|z_0)|_{z=0} = K_A \tilde{\mathcal{G}}(0, \omega|z_0), \quad (\text{S71})$$

and leads to

$$-D\gamma(a_p - b_p) = K_A(a_p + b_p), \quad (\text{S72})$$

- **(BC4)** the surface reaction boundary condition at  $z = 2R_p$  which reads

$$\tilde{j}(z, \omega|z_0)|_{z=2R_p} = -D\partial_z \tilde{\mathcal{G}}(2R_p, \omega|z_0)|_{z=2R_p} = K_B \tilde{\mathcal{G}}(2R_p, \omega|z_0), \quad (\text{S73})$$

and leads to

$$D\gamma(c_p e^{-\gamma 2R_p} - d_p e^{\gamma 2R_p}) = K_B(c_p e^{-\gamma 2R_p} + d_p e^{\gamma 2R_p}). \quad (\text{S74})$$

Using the rescaled coordinate  $\tilde{z} = z\sqrt{\omega/D}$  and  $K_A = \tilde{K}_A\sqrt{\omega D}$ , this lead to

$$\tilde{a}_p e^{-\tilde{z}_0} + \tilde{b}_p e^{\tilde{z}_0} = \tilde{c}_p e^{-\tilde{z}_0} + \tilde{d}_p e^{\tilde{z}_0}, \quad (\text{S75})$$

$$1 = -\tilde{a}_p e^{-\tilde{z}_0} + \tilde{b}_p e^{\tilde{z}_0} + \tilde{c}_p e^{-\tilde{z}_0} - \tilde{d}_p e^{\tilde{z}_0}, \quad (\text{S76})$$

$$-\tilde{a}_p + \tilde{b}_p = \tilde{K}_A [\tilde{a}_p + \tilde{b}_p], \quad (\text{S77})$$

$$\tilde{c}_p e^{-2\tilde{R}_p} - d_p e^{2\tilde{R}_p} = \tilde{K}_B [c_p e^{-2\tilde{R}_p} + d_p e^{2\tilde{R}_p}]. \quad (\text{S78})$$

Defining the auxiliary expression

$$W_0 = \left( \frac{1 + \tilde{K}_B}{1 - \tilde{K}_B} \right) \left( \frac{1 + \tilde{K}_A}{1 - \tilde{K}_A} \right) e^{4\tilde{R}_p} - 1, \quad (\text{S79})$$

we obtain

$$\tilde{a}_p = \frac{e^{\tilde{z}_0}}{2W_0} \left[ 1 + \left( \frac{1 + \tilde{K}_B}{1 - \tilde{K}_B} \right) e^{4\tilde{R}_p - 2\tilde{z}_0} \right], \quad (\text{S80})$$

$$\tilde{b}_p = \tilde{a}_p \left( \frac{1 + \tilde{K}_A}{1 - \tilde{K}_A} \right), \quad (\text{S81})$$

$$\tilde{c}_p = \tilde{d}_p \left( \frac{1 + \tilde{K}_B}{1 - \tilde{K}_B} \right) \exp(4\tilde{R}_p), \quad (\text{S82})$$

$$\tilde{d}_p = \tilde{a}_p \left( \frac{1 + \tilde{K}_A}{1 - \tilde{K}_A} \right) - e^{-\tilde{z}_0}/2. \quad (\text{S83})$$

### First return distribution for a planar system

The local flux at the bottom surface  $A$  in  $z = 0$  can be calculated from the Green function as

$$\tilde{j}(0, \omega|z_0) = D \left. \frac{\partial \tilde{\mathcal{G}}_p(z, \omega|z_0)}{\partial z} \right|_{z=0} = K_A \tilde{\mathcal{G}}_p(0, \omega|z_0). \quad (\text{S84})$$

In order to match the situation and notations of the main text, we fix  $K_A = K_B = k$ . We define the first return distribution by considering all trajectories starting from the surface  $A$  in  $z = 0$ ,

$$\tilde{J}_{AA}(\omega) = \tilde{j}(0, \omega|0) = \frac{\tilde{k} \left( 1 - \tilde{k} + (1 + \tilde{k})e^{4\tilde{R}_c} \right)}{e^{4\tilde{R}_c} (1 + \tilde{k})^2 - (1 - \tilde{k})^2}, \quad (\text{S85})$$

and  $\tilde{J}_{BB}(\omega) = \tilde{J}_{AA}(\omega)$ . For the distribution to leave from surface  $B$  and to adsorb to surface  $A$  we obtain

$$\tilde{J}_{BA}(\omega) = \frac{2\tilde{k}e^{2\tilde{R}_c}}{e^{4\tilde{R}_c} (1 + \tilde{k})^2 - (1 - \tilde{k})^2}. \quad (\text{S86})$$