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Supporting Material

How subdiffusion changes the kinetics of binding to a surface

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Derivation of the fractional diffusion equation with reactive boundary condition (Eqs. (5) and (7) in the main text)

To describe the particle exchange with the reactive boundary we establish a system of master equations, each of which describes the probability to find a particle at a given site. Let $A_i(t)$ be the probability that the particle is at a bulk site $i = 1, 2, \ldots$. Similarly, let $\mathcal{A}_0(t)$ be the probability that the particle is at the exchange site $i = 0$. Our notation is meant as a reminder of the difference between a bulk site and the exchange site: namely, a particle at a bulk site only jumps whereas a particle at the exchange site either jumps or binds. We write

$$\frac{d}{dt}A_i(t) = I_i^+(t) - I_i^-(t), \tag{S1a}$$

$$\frac{d}{dt}\mathcal{A}_0(t) = I_0^+(t) - I_0^-(t) - \kappa\mathcal{A}_0(t) + j_{\text{release}}(t). \tag{S1b}$$

Here $I_i^{\pm}(t)$ are the gain and loss at site i due to jumping from and to adjacent sites $i \pm 1$, and $\kappa\mathcal{A}_0(t)$ is the loss at site 0 due to binding, see also below. Although we do not require exact knowledge of $j_{\text{release}}(t)$, it must be chosen such that probability is conserved.

If a particle jumps from site i at time t, then it must have been there to begin with or arrived there at some time t' $(0 < t' < t)$. We have

$$I_i^-(t) = \psi(t)A_i(0) + \int_0^t \psi(t-t')I_i^+(t')dt', \tag{S2a}$$

$$I_0^-(t) = \psi_\kappa(t)\mathcal{A}_0(0) + \int_0^t \psi_\kappa(t-t')\left[I_0^+(t') + j_{\text{release}}(t')\right]dt'. \tag{S2b}$$

The first term in each of Eqs. (S2) corresponds to a particle, initially at site i, that jumps away at time t. Let us denote the Laplace transform of a function $f(t)$ by explicit dependence on the argument:

$$f(u) \equiv \int_0^\infty f(t)e^{-ut}\,dt. \tag{S3}$$

Then the Laplace transforms of Eqs. (S1) are

$$uA_i(u) - A_i(t=0) = I_i^+(u) - I_i^-(u), \tag{S4a}$$

$$u\mathcal{A}(u)_0 - \mathcal{A}_0(t=0) = I_0^+(u) - I_0^-(u) - \kappa\mathcal{A}_0(u) + j_{\text{release}}(u), \tag{S4b}$$

due to the differentiation theorem of the Laplace transformation, $\mathcal{L}\left\{\frac{d}{dt}f(t)\right\} = uf(u) - f(t=0)$. Likewise, by virtue of the convolution theorem, the Laplace transforms of Eqs. (S2) read

$$I_i^-(u) = \psi(u)A_i(0) + \psi(u)I_i^+(u), \tag{S5a}$$

$$I_0^-(u) = \psi_\kappa(u)\mathcal{A}_0(0) + \psi_\kappa(u)\left[I_0^+(u) + j_{\text{release}}(u)\right]. \tag{S5b}$$

Note that, by the definition (Eq. (4) in the main text), we have $\psi_\kappa(u) = \psi(u+\kappa)$. Solving the former equations for $I_i^+(u)$ and substituting this expression into the latter equations, we find the solution for the I_i^- as Laplace convolutions

$$I_i^-(t) = \int_0^t \Phi(t-t')A_i(t')dt', \tag{S6a}$$

$$I_0^-(t) = \int_0^t \Phi_\kappa(t-t')\mathcal{A}_0(t')dt', \tag{S6b}$$

after transforming back to the time domain. The kernel $\Phi(t)$ is defined by its Laplace transform

$$\Phi(u) = \frac{u\psi(u)}{1-\psi(u)}; \tag{S7}$$

and we have $\Phi_\kappa(u) = \Phi(u+\kappa)$. Assuming that the particle is equally likely to jump in either direction, the gain is

$$I_i^+(t) = I_{i-1}^-(t)/2 + I_{i+1}^-(t)/2, \tag{S8a}$$

$$I_0^+(t) = I_0^-(t)/2 + I_1^-(t)/2. \tag{S8b}$$

Note that the particle returns to the exchange site if it attempts to jump toward the boundary from that site (an unsuccessful binding attempt) while the actual adsorption process is defined in Eq. (S1b) by the term $\kappa\mathcal{A}_0(t)$. This definition will let us take a consistent continuum limit.

For convenience, we now introduce a transformation to the new time-dependent quantity $A_0(t)$ by

$$\int_0^t \Phi(t-t')A_0(t')dt' \equiv \int_0^t \Phi_\kappa(t-t')\mathcal{A}_0(t')dt', \tag{S9}$$

which corresponds to $A_0(u) = \Phi_\kappa(u)\mathcal{A}_0(u)/\Phi(u)$. This allows us to write

$$\frac{dA_i(t)}{dt} = \int_0^t \Phi(t-t')\frac{A_{i-1}(t') - 2A_i(t') + A_{i+1}(t')}{2}\,dt' \tag{S10}$$

for $i \geq 1$ and therefore puts the probability to be at the exchange site on equal footing with the probabilities at the bulk sites by compensating the temporal change with the rate κ. Taking $A(x = ai, t) = A_i(t)/a$ with the lattice spacing a, we obtain

$$\frac{\partial A(x,t)}{\partial t} = \frac{a^2}{2}\int_0^t \Phi(t-t')\frac{\partial^2 A(x,t')}{\partial x^2}dt' \tag{S11}$$

in the continuum limit $a \to 0$. Since $u\tau \ll 1$ in the long time limit and we infer the relation $\psi(u) \sim 1 - (u\tau)^\alpha$ by use of Tauberian theorems [1, 2], we have

$$\Phi(u) \sim u^{1-\alpha}\tau^{-\alpha} \tag{S12}$$

to leading order. With the Laplace pair $u^{-\alpha} \leftrightarrow t^{\alpha-1}/\Gamma(\alpha)$, we can perform the Laplace inversion of Eq. (S11) using the fractional Riemann-Liouville operator [3, 4]

$$ {}_0D_t^{1-\alpha} A(x,t) = \frac{1}{\Gamma(\alpha)} \frac{\partial}{\partial t} \int_0^t \frac{A(x,t')}{(t-t')^{1-\alpha}} dt'. \tag{S13} $$

Namely, together with the anomalous diffusion coefficient $K_\alpha = a^2/[2\tau^\alpha]$, we find that Eq. (S11) is equivalent to the fractional diffusion equation

$$ \frac{\partial A(x,t)}{\partial t} = K_\alpha \, {}_0D_t^{1-\alpha} \frac{\partial^2 A(x,t)}{\partial x^2} \tag{S14} $$

for $x > 0$ [3, 4]. Similarly, Eq. (S1b) can be recast into the form

$$ \frac{d\mathcal{A}_0(t)}{dt} + \kappa \int_0^t (\Phi_\kappa^{-1}\Phi)(t-t') A_0(t') dt' - j_{\text{release}}(t) = \int_0^t \Phi(t-t') \frac{A_1(t') - A_0(t')}{2} dt', \tag{S15} $$

where $(\Phi_\kappa^{-1}\Phi)(t)$ is defined via the inverse Laplace transform of the ratio $\Phi(u)/\Phi_\kappa(u)$. In the continuum limit, we recover the following expression

$$ -\delta(t)\mathcal{A}_0(0) + \int_0^t \Psi(t-t') A(0,t') dt' - j_{\text{release}}(t) = \frac{a^2}{2} \int_0^t \Phi(t-t') \left. \frac{\partial A(x,t')}{\partial x} \right|_{x=0} dt' \tag{S16} $$

with

$$ \Psi(u) = a(u+\kappa) \frac{\Phi(u)}{\Phi_\kappa(u)}. \tag{S17} $$

The value of $\mathcal{A}_0(0)$ is 1 if the particle is initially at the exchange site and 0 otherwise (see below). The reaction rate for binding at the boundary is, self-consistently,

$$ j_{\text{react}}(t) = a\kappa \int_0^t (\Phi_\kappa^{-1}\Phi)(t-t') A(0,t') dt'. \tag{S18} $$

The right-hand side of Eq. (S16) represents the flux into $x = 0$ from positive x. We expand Eq. (S16) at $u = 0$ in the Laplace domain (note that $u \ll \kappa$), producing the sought for reactive boundary condition

$$ K_\alpha \, {}_0D_t^{-\alpha} \left. \frac{\partial A(x,t)}{\partial x} \right|_{x=0} = -\mathcal{A}_0(0) + k \, {}_0D_t^{-\alpha} A(0,t) - \int_0^t j_{\text{release}}(t') dt'. \tag{S19} $$

The parameter

$$ k = 2\kappa K_\alpha / [a\Phi_\kappa(u=0)] \sim a\kappa^\alpha \tag{S20} $$

because $\kappa\tau \to 0$. We held K_α and k constant in the above derivation, which implies that

$$ \tau \simeq a^{2/\alpha} \quad \text{and} \quad \kappa \simeq a^{-1/\alpha}. \tag{S21} $$

Eqs. (S14) and (S19) are quoted as Eqs. (5) and (7) in the main text.

References

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[2] Hughes, B. D. 1995. Random Walks and Random Environments, Volume 1:Random Walks. (Oxford, UK: Oxford University Press).

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[4] Metzler, R., and J. Klafter. 2004. The restaurant at the end of the random walk: Recent developments in the description of anomalous transport by fractional dynamics. J. Phys. A *37*, R161-R208.