Supplemental Material for the article "Semi-analytical computation of Laplacian Green functions in three-dimensional domains with disconnected spherical boundaries"

I. Technical derivations

I.1. Newton's potential

We use the Laplace expansion for the Newton's potential [74],

$$\frac{1}{\|\boldsymbol{x}-\boldsymbol{y}\|} = \frac{1}{\|(\boldsymbol{x}-\boldsymbol{x}_i)-\boldsymbol{L}_i\|} = \sum_{n=0}^{\infty}\sum_{m=-n}^{n}(-1)^m \frac{r_<^n}{r_>^{n+1}} Y_{(-m)n}(\Theta_i,\Phi_i) Y_{mn}(\theta_i,\phi_i), \quad \text{(S1)}$$

where $\boldsymbol{L}_i = \boldsymbol{y}-\boldsymbol{x}_i$, (L_i,Θ_i,Φ_i) are the spherical coordinates of $\boldsymbol{L}_i$, $r_< = \min(\|\boldsymbol{x}-\boldsymbol{x}_i\|, \|\boldsymbol{L}_i\|)$ and $r_> = \max(\|\boldsymbol{x}-\boldsymbol{x}_i\|, \|\boldsymbol{L}_i\|)$. For $r_i < L_i$, one has $r_< = r_i$ and $r_> = L_i$ so that

$$\frac{1}{\|\boldsymbol{x}-\boldsymbol{y}\|} = \sum_{n=0}^{\infty}\sum_{m=-n}^{n}(-1)^m \psi^-_{(-m)n}(L_i,\Theta_i,\Phi_i)\,\psi^+_{mn}(r_i,\theta_i,\phi_i), \quad \text{(S2)}$$

from which Eq. (25) follows. If $\boldsymbol{x}_i = 0$, then this formula is reduced to

$$\mathcal{G}(\boldsymbol{x},\boldsymbol{y}) = \frac{1}{4\pi}\sum_{n=0}^{\infty} P_n\left(\frac{(\boldsymbol{x}\cdot\boldsymbol{y})}{\|\boldsymbol{x}\|\,\|\boldsymbol{y}\|}\right)\frac{\min\{\|\boldsymbol{x}\|,\|\boldsymbol{y}\|\}^n}{\max\{\|\boldsymbol{x}\|,\|\boldsymbol{y}\|\}^{n+1}}\,. \quad \text{(S3)}$$

In the opposite case $r_i > L_i$, one has $r_> = r_i$ and $r_< = L_i$ so that

$$\frac{1}{\|\boldsymbol{x}-\boldsymbol{y}\|} = \sum_{n=0}^{\infty}\sum_{m=-n}^{n}(-1)^m \psi^+_{(-m)n}(L_i,\Theta_i,\Phi_i)\,\psi^-_{mn}(r_i,\theta_i,\phi_i), \quad \text{(S4)}$$

from which Eq. (59) follows.

I.2. Derivation of the harmonic measure density

Taking the derivative of Eq. (25) with respect to r_i, one finds

$$\left(\frac{\partial \mathcal{G}(\boldsymbol{x};\boldsymbol{y})}{\partial \boldsymbol{n_x}}\right)\bigg|_{\boldsymbol{x}\in\partial\Omega_i} = -\sum_{n,m} n V^i_{mn}\psi^-_{mn}(1,\theta_i,\phi_i). \quad \text{(S5)}$$

Similarly, the derivative of Eq. (24) with respect to r_i yields

$$\begin{aligned}
\left(\frac{\partial g(\boldsymbol{x},\boldsymbol{y})}{\partial \boldsymbol{n_x}}\right)\bigg|_{\partial\Omega_i} &= \left(\frac{\partial g_i(r_i,\theta_i,\phi_i;\boldsymbol{y})}{\partial \boldsymbol{n_x}}\right)\bigg|_{\partial\Omega_i} + \sum_{j=1,j\neq i}^{N}\left(\frac{\partial}{\partial \boldsymbol{n_x}} g_j(r_j,\theta_j,\phi_j;\boldsymbol{y})\right)\bigg|_{\partial\Omega_i} \\
&= \frac{\partial}{\partial \boldsymbol{n_x}}\sum_{n,m}\left\{A^i_{mn}\psi^-_{mn}(r_i,\theta_i,\phi_i) + \left(\sum_{j=1,j\neq i}^{N}\sum_{l,k}A^j_{kl}U^{(-j,+i)}_{klmn}\right)\psi^+_{mn}(r_i,\theta_i,\phi_i)\right\}\bigg|_{\partial\Omega_i} \\
&= \frac{1}{R_i}\sum_{n,m}\left\{(n+1)A^i_{mn}\psi^-_{mn}(R_i,\theta_i,\phi_i) - n\left(\sum_{j=1,j\neq i}^{N}\sum_{l,k}A^j_{kl}U^{(-j,+i)}_{klmn}\right)\psi^+_{mn}(R_i,\theta_i,\phi_i)\right\} \\
&= \frac{1}{R_i}\sum_{n,m}\left\{(n+1)A^i_{mn} - n\left(\sum_{j=1,j\neq i}^{N}\sum_{l,k}\hat{U}^{ij}_{mnkl}A^j_{kl}\right)\right\}\psi^-_{mn}(R_i,\theta_i,\phi_i),
\end{aligned}$$

that can also be written as

$$\left(\frac{\partial g(\boldsymbol{x},\boldsymbol{y})}{\partial \boldsymbol{n_x}}\right)\Big|_{\partial\Omega_i} = \frac{1}{R_i}\sum_{n,m}\Big\{(2n+1)A^i_{mn} - n\big(\hat{\mathbf{U}}\mathbf{A}\big)^i_{mn}\Big\}\,\psi^-_{mn}(R_i,\theta_i,\phi_i). \tag{S6}$$

Recalling Eq. (31), one gets a simpler form

$$\left(\frac{\partial g(\boldsymbol{x},\boldsymbol{y})}{\partial \boldsymbol{n_x}}\right)\Big|_{\partial\Omega_i} = \frac{1}{R_i}\sum_{n,m}\big[(2n+1)A^i_{mn} - n\hat{V}^i_{mn}\big]\psi^-_{mn}(R_i,\theta_i,\phi_i). \tag{S7}$$

Combining these results, we get Eq. (34) for the harmonic measure density.

I.3. Computation of the flux

The flux of particles onto the ball Ω_i is

$$\begin{aligned} J_i \;&:=\; \int\limits_{\partial\Omega_i} d\boldsymbol{s}\,\left(-D\frac{\partial n}{\partial \boldsymbol{n_y}}\right)\Big|_{\boldsymbol{y}=\boldsymbol{s}} = -n_0 D\int\limits_{\partial\Omega_i} d\boldsymbol{s}\,\left(\frac{\partial P_\infty}{\partial \boldsymbol{n_y}}\right)\Big|_{\boldsymbol{y}=\boldsymbol{s}} \\ &=\; 4\pi n_0 D\sum_{j=1}^N \int\limits_{\partial\Omega_i} d\boldsymbol{s}\,\left(\frac{\partial A^j_{00}}{\partial \boldsymbol{n_y}}\right)\Big|_{\boldsymbol{y}=\boldsymbol{s}}, \end{aligned} \tag{S8}$$

where we used Eqs. (109, 115). According to Eq. (42), the derivative of A^j_{00} can be expressed as a linear combination of the derivatives of $\hat{V}^k_{mn}$. We show that

$$I^{ij}_{mn} := \int\limits_{\partial\Omega_i} d\boldsymbol{s}\,\left(\frac{\partial \hat{V}^j_{mn}}{\partial \boldsymbol{n_y}}\right)\Big|_{\boldsymbol{y}=\boldsymbol{s}} = \delta_{n0}\,\delta_{m0}\,\delta_{ij}\,R_i, \tag{S9}$$

from which Eq. (116) follows. Indeed, for $j=i$, the integral is

$$I^{ii}_{mn} = \int\limits_{\partial\Omega_i} d\boldsymbol{s}\,\frac{(-1)^m}{4\pi}R_i^{2n+1}\left(-\frac{\partial\psi^-_{(-m)n}(r_i,\theta_i,\phi_i)}{\partial r_i}\right)\Big|_{r_i=R_i} = \delta_{n0}\,\delta_{m0}\,R_i. \tag{S10}$$

For $j\neq i$, we use the addition theorem (20b) to get

$$I^{ij}_{mn} = \int\limits_{\partial\Omega_i} d\boldsymbol{s}\,\frac{(-1)^m}{4\pi}R_j^{2n+1}\sum_{l,k}U^{(-j,+i)}_{(-m)nkl}\left(-\frac{\partial\psi^+_{kl}(r_i,\theta_i,\phi_i)}{\partial r_i}\right) = 0. \tag{S11}$$

I.4. Residence time

We use Eqs. (32, 25, 20b) to write the residence time $\mathcal{T}$ in a ball Ω_I of radius R_I centered at $\boldsymbol{x}_I$ as

$$\begin{aligned} \mathcal{T}(\boldsymbol{y}) \;&=\; \frac{1}{D}\int\limits_{\Omega_I} d\boldsymbol{x}\,G(\boldsymbol{x},\boldsymbol{y}) = \frac{1}{D}\int\limits_{\Omega_I} d\boldsymbol{x}\Big\{\sum_{n,m}V^I_{mn}\psi^+_{mn}(r_I,\theta_I,\phi_I) \\ &-\; \sum_{j=1}^N\sum_{n,m}A^j_{mn}\sum_{l,k}U^{(-j,+I)}_{mnkl}\psi^+_{kl}(r_I,\theta_I,\phi_I)\Big\} \\ &=\; \frac{4\pi R_I^3}{3D}\Big\{\frac{1}{4\pi L_I} - \sum_{j=1}^N\sum_{n,m}A^j_{mn}\psi^-_{mn}(L_{Ij},\Theta_{Ij},\Phi_{Ij})\Big\}, \end{aligned} \tag{S12}$$

where $\boldsymbol{L}_{Ij} = \boldsymbol{x}_j - \boldsymbol{x}_I$, $(L_{Ij}, \Theta_{Ij}, \Phi_{Ij})$ are the spherical coordinates of $\boldsymbol{L}_{Ij}$, $L_I = \|\boldsymbol{y} - \boldsymbol{x}_I\|$, and V_{mn}^I is given by Eq. (26) which is modified for the ball Ω_I.

I.5. Integrals over balls

One can compute the integral of $\psi_{mn}^-(r_j, \theta_j, \phi_j)$ over any ball Ω_I (of radius R_I and centered at $\boldsymbol{x}_I$), which is not overlapping with the ball Ω_j. In fact, denoting the local spherical coordinates associated to Ω_I as (r_I, θ_I, ϕ_I), one can use the I→R addition theorem (20b) for $r_I < L_{Ij}$ to write

$$\begin{aligned}\int\limits_{\Omega_I} d\boldsymbol{x}\, \psi_{mn}^-(r_j, \theta_j, \phi_j) &= \sum_{l,k} U_{mnkl}^{(-j,+I)} \int\limits_{\Omega_I} d\boldsymbol{x}\, \psi_{kl}^+(r_I, \theta_I, \phi_I) \\ &= \frac{4\pi R_I^3}{3} U_{mn00}^{(-j,+I)} = \frac{4\pi R_I^3}{3} \psi_{mn}^-(L_{Ij}, \Theta_{Ij}, \Phi_{Ij}), \qquad \text{(S13)}\end{aligned}$$

where $\boldsymbol{L}_{Ij} = \boldsymbol{x}_j - \boldsymbol{x}_I$, $(L_{Ij}, \Theta_{Ij}, \Phi_{Ij})$ are the spherical coordinates of $\boldsymbol{L}_{Ij}$, and the mixed-basis elements are given by Eq. (22b). Similarly, the integral over the sphere $\partial\Omega_I$ reads

$$\int\limits_{\partial\Omega_I} d\boldsymbol{s}\, \psi_{mn}^-(r_j, \theta_j, \phi_j) = 4\pi R_I^2\, \psi_{mn}^-(L_{Ij}, \Theta_{Ij}, \Phi_{Ij}). \qquad \text{(S14)}$$

Now we consider a more complicated situation when $\Omega_j \subset \Omega_I$. We split the integration domain Ω_I into two subsets, $\Omega_I^<$ and $\Omega_I^>$, such that

$$\begin{aligned}\Omega_I^< &= \{\boldsymbol{x} \in \Omega_I \;:\; \|\boldsymbol{x} - \boldsymbol{x}_I\| < L_{Ij}\}, \\ \Omega_I^> &= \{\boldsymbol{x} \in \Omega_I \;:\; \|\boldsymbol{x} - \boldsymbol{x}_I\| > L_{Ij}\}.\end{aligned} \qquad \text{(S15)}$$

In each subset, we can use the appropriate addition theorem to compute the integral. Using Eq. (20b) for $r_I < L_{Ij}$ and Eq. (20c) for $r_I > L_{Ij}$, we have

$$\int\limits_{\Omega_I^<} d\boldsymbol{x}\, \psi_{mn}^-(r_j, \theta_j, \phi_j) = \sum_{l,k} U_{mnkl}^{(-j,+I)} \int\limits_{\Omega_I^<} d\boldsymbol{x}\, \psi_{kl}^+(r_I, \theta_I, \phi_I) = \frac{4\pi}{3} L_{Ij}^3\, U_{mn00}^{(-j,+I)} \qquad \text{(S16)}$$

and

$$\begin{aligned}\int\limits_{\Omega_I^>} d\boldsymbol{x}\, \psi_{mn}^-(r_j, \theta_j, \phi_j) &= \sum_{l=n}^{\infty} \sum_{k=n+m-l}^{m-n+l} U_{mnkl}^{(-j,-I)} \int\limits_{\Omega_I^>} d\boldsymbol{x}\, \psi_{kl}^-(r_I, \theta_I, \phi_I) \qquad \text{(S17)} \\ &= \sum_{l=n}^{\infty} \sum_{k=n+m-l}^{m-n+l} U_{mnkl}^{(-j,-I)}\, 2\pi \delta_{l0} \delta_{k0} (R_I^2 - L_{Ij}^2) = \delta_{n0} \delta_{m0}\, 2\pi (R_I^2 - L_{Ij}^2),\end{aligned}$$

where we used $U_{0000}^{(-j,-I)} = 1$.

One may also need to compute the integral of $\psi_{mn}^-(r_j, \theta_j, \phi_j)$ over Ω_I without any ball Ω_i:

$$\tilde{\Omega}_I = \Omega_I \backslash \bigcup_{i=1}^{N} \Omega_i. \qquad \text{(S18)}$$

We only consider the case when each ball Ω_i can be either included into Ω_I (i.e., $\Omega_i \subset \Omega_I$), or lie outside Ω_I (i.e., $\Omega_i \cap \Omega_I = \emptyset$). In other words, we do not allow the ball Ω_I to cut any ball Ω_i. In this case, the integral over $\tilde{\Omega}_I$ is simply the integral over Ω_I minus the integrals over each Ω_i. First, we have

$$\int\limits_{\Omega_j} d\boldsymbol{x}\, \psi_{mn}^-(r_j,\theta_j,\phi_j) = \delta_{n0}\,\delta_{m0}\, 2\pi R_J^2 \tag{S19}$$

(although ψ_{mn}^- is singular at $r_j = 0$, this singularity is integrable for $n = 0$ due to the radial weight r^2, whereas the symmetry of the integration domain Ω_j cancels the contribution from other harmonics with $n > 0$). Second, the integral of $\psi_{mn}^-(r_j,\theta_j,\phi_j)$ over Ω_i (with $i \neq j$) is given by Eq. (S13). Combining all these results, we get

$$\int\limits_{\tilde{\Omega}_I} d\boldsymbol{x}\, \psi_{mn}^-(r_j,\theta_j,\phi_j) = 4\pi \biggl\{ \delta_{n0}\delta_{m0}\, \frac{R_I^2 - L_{Ij}^2 - R_J^2}{2} + U_{mn00}^{(-j,+I)} \frac{L_{Ij}^3}{3} - \sum_i \frac{R_i^3}{3}\, U_{mn00}^{(-j,+i)} \biggr\}, \tag{S20}$$

where the last sum is taken over the balls Ω_i (except Ω_j) which are included in Ω_I. This formula allows one to integrate the solution over any ball Ω_I that does not cut balls Ω_i.

Using the addition theorem (20c), one can compute an integral over a large sphere $\partial\Omega_I$ that englobes a ball Ω_j. In fact, since $R_I > L_{Ij}$ because $\Omega_j \subset \Omega_I$, one has

$$\int\limits_{\partial\Omega_I} d\boldsymbol{s}\, \psi_{mn}^-(r_j,\theta_j,\phi_j) = \sum_{l=n}^{\infty} \sum_{k=n+m-l}^{m-n+l} U_{mnkl}^{(-j,-i)} \int\limits_{\partial\Omega_I} d\boldsymbol{s}\, \psi_{kl}^-(r_I,\theta_I,\phi_I) = 4\pi R_I\, \delta_{n0}, \tag{S21}$$

the last equality coming from the rotation symmetry of spherical harmonics Y_{kl} and from the identity $U_{0000}^{(-I,-i)} = 1$. Note that this result depends neither on the location, nor on the radius of the ball Ω_j.

II. Monopole approximation for interior problems

The monopole approximation for the interior problem of finding chemical reaction rates was discussed in [48, 49, 117]. Here, we briefly present its extension for computing the Green function.

For the interior problem, one needs to modify the elements of $\hat{\mathbf{U}}$ and $\hat{\mathbf{V}}$ corresponding to the outer boundary $\partial\Omega_0$:

$$\hat{U}_{0000}^{i0} = R_i \quad (i > 0), \qquad \hat{U}_{0000}^{0j} = \frac{1}{R_0} \quad (j > 0), \qquad \hat{V}_{00}^{0} = \frac{1}{4\pi R_0}. \tag{S22}$$

With this modification, the boundary conditions read

$$(a_i + b_i) A_{00}^i + a_i R_i \sum_{j(\neq i)=1}^{N} L_{ij}^{-1} A_{00}^j + a_i R_i A_{00}^0 \;=\; \frac{a_i R_i}{4\pi L_{i0}} \qquad (i = \overline{1,N}), \tag{S23a}$$

$$a_0 A_{00}^0 + \frac{a_0 - b_0}{R_0} \sum_{j=1}^{N} L_{ij}^{-1} A_{00}^j \;=\; \frac{a_0 - b_0}{4\pi R_0}. \tag{S23b}$$

If $a_0 \neq 0$, one can express A^0_{00} from the last equation and substitute it into the former ones that yields a closed system of linear equations on A^i_{00} for $i = \overline{1,N}$:

$$\left(\frac{a_i + b_i}{R_i} - c_0\right) A^i_{00} + a_i \sum_{j(\neq i)=1}^{N} \left(\frac{1}{L_{ij}} - c_0\right) A^j_{00} = \frac{a_i}{4\pi}\left(\frac{1}{L_{i0}} - c_0\right), \tag{S24}$$

with $c_0 = (a_0 - b_0)/R_0$.

Finally, if $a_0 = 0$ (i.e., the Neumann boundary condition at the outer boundary), the last relation in Eq. (S23) is reduced to

$$\sum_{j=1}^{N} A^j_{00} = \frac{1}{4\pi}. \tag{S25}$$

In this case, Eqs. (S23) can be written as

$$A^i_{00} + c_i \sum_{j(\neq i)=1}^{N} L^{-1}_{ij} A^j_{00} + c_i A^0_{00} = \frac{c_i}{4\pi L_{i0}} \qquad (i = \overline{1,N}), \tag{S26}$$

with $c_i = a_i R_i/(a_i + b_i)$ (for $i = \overline{1,N}$). Summing these equations over i from 1 to N, one gets

$$\frac{1}{4\pi} + \sum_{i=1}^{N} c_i \sum_{j(\neq i)=1}^{N} L^{-1}_{ij} A^j_{00} + C A^0_{00} = \sum_{i=1}^{N} \frac{c_i}{4\pi L_{i0}}, \tag{S27}$$

where $C = c_1 + \ldots + c_N$. Expressing A^0_{00} from this relation, one gets a closed system of linear equations on A^i_{00} for $i = \overline{1,N}$:

$$A^i_{00} + c_i \sum_{j(\neq i)=1}^{N} L^{-1}_{ij} A^j_{00} + \frac{c_i}{C}\left(\sum_{k=1}^{N} \frac{c_k}{4\pi L_{k0}} - \frac{1}{4\pi} - \sum_{k=1}^{N} c_k \sum_{j(\neq k)=1}^{N} L^{-1}_{kj} A^j_{00}\right) = \frac{c_i}{4\pi L_{i0}}, \tag{S28}$$

or

$$A^i_{00} + c_i \sum_{j(\neq i)=1}^{N} L^{-1}_{ij} A^j_{00} - \frac{c_i}{C} \sum_{j=1}^{N} A^j_{00} \sum_{k(\neq j)=1}^{N} c_k L^{-1}_{kj} = \frac{c_i}{4\pi L_{i0}} - \frac{c_i}{C}\left(\sum_{k=1}^{N} \frac{c_k}{4\pi L_{k0}} - \frac{1}{4\pi}\right), \tag{S29}$$

or

$$A^i_{00}\left(1 - \frac{c_i}{\ell_i}\right) + c_i \sum_{j(\neq i)=1}^{N} A^j_{00}\left(L^{-1}_{ij} - \frac{c_i}{\ell_j}\right) = \frac{c_i}{4\pi}\left(\frac{1}{L_{i0}} + 1 - \frac{1}{C}\sum_{k=1}^{N} \frac{c_k}{L_{k0}}\right), \tag{S30}$$

where we denoted

$$\ell^{-1}_j = \frac{1}{C} \sum_{k(\neq j)=1}^{N} c_k L^{-1}_{kj}. \tag{S31}$$