

## Supplementary Information for “Non-Equilibrium Interaction Between Catalytic Colloids: Boundary Conditions and Penetration Depth”

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### I. PERTURBATION THEORY FOR THE TWO DROPLETS PROBLEM

Suppose now there are two spherical particles, labeled here by Roman numerals  $I$  and  $II$ , and positioned in points  $\mathbf{r}_I$  and  $\mathbf{r}_{II}$ . We need to find steady state concentration distributions  $c_A^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II})$  and  $c_B^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II})$  through all points  $\mathbf{r}$  in space. The intuition is that when particles are far apart compared at their own sizes,  $|\mathbf{r}_I - \mathbf{r}_{II}| \gg R$ , the solution for the two particles problem should be somehow approximated by the superposition of single particle solutions. To formalize this idea, we first of all define  $\delta c$  for the two-particles and single particle concentration profiles as the quantities that vanish in infinity, according to

$$\delta c_A^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) = c_A(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) - c_A, \quad (1a)$$

$$\delta c_A^{(1)}(\mathbf{r}|\mathbf{r}_I) = c_A(\mathbf{r}|\mathbf{r}_I) - c_A, \quad (1b)$$

$$\delta c_A^{(1)}(\mathbf{r}|\mathbf{r}_{II}) = c_A(\mathbf{r}|\mathbf{r}_{II}) - c_A, \quad (1c)$$

with similar notation also for  $B$ . Upper indices (1) or (2) indicate solution for one or two particles, respectively. And now we define  $\delta\delta c$  encapsulating the idea of superposition; it is actually the difference between exact solution and superposition:

$$\delta c_A^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) = \delta c_A^{(1)}(\mathbf{r}|\mathbf{r}_I) + \delta c_A^{(1)}(\mathbf{r}|\mathbf{r}_{II}) + \delta\delta c_A^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) \quad (2a)$$

$$\delta c_B^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) = \delta c_B^{(1)}(\mathbf{r}|\mathbf{r}_I) + \delta c_B^{(1)}(\mathbf{r}|\mathbf{r}_{II}) + \delta\delta c_B^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) \quad (2b)$$

For now, this is nothing more than just a notation, the definition of  $\delta\delta c$ ; our goal is now to estimate these functions and to claim that they can be neglected. To do so, we derive, rigorously, equations and boundary conditions satisfied by these functions; we will write all of them in a standard way, with left hand side in every case representing a linear function of  $\delta\delta c$ , and right hand side representing inhomogeneity:

1. Diffusion equations for  $A$  and for  $B$ :

$$\nabla^2 \delta\delta c_A^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) = 0, \quad (3a)$$

$$\nabla^2 \delta\delta c_B^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) = 0. \quad (3b)$$

2. Vanishing in infinity:

$$\delta\delta c_A^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) \Big|_{r \rightarrow \infty} = 0, \quad (3c)$$

$$\delta\delta c_B^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) \Big|_{r \rightarrow \infty} = 0 \quad (3d)$$

3. Diffusion influx of  $A$  continuously connects to chemical transformation flux. For notational simplicity we introduce here rate catalytical rate constants  $k_{AB} = (1/\tau)e^{\beta(\varepsilon_A - \varepsilon^\ddagger)}$  and  $k_{BA} = (1/\tau)e^{\beta(\varepsilon_B - \varepsilon^\ddagger)}$ . This flux continuity condition must be satisfied in every point on the surface of both particles; for brevity, we write this condition only for one particle, particle  $II$ , where we specify an arbitrary point  $\mathbf{r} = \mathbf{r}_{II} + \mathbf{R}$  by a vector  $\mathbf{R}$  with absolute value  $R$ :

$$\begin{aligned} D_A \nabla_{\perp} \delta\delta c_A^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}} - \\ - k_{AB} \delta\delta c_A^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}} + \\ + k_{BA} \delta\delta c_B^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}} = \\ = -D_A \nabla_{\perp} \delta c_A^{(1)}(\mathbf{r}|\mathbf{r}_I) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}} + \\ + k_{AB} \delta c_A^{(1)}(\mathbf{r}|\mathbf{r}_I) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}} + \\ - k_{BA} \delta c_B^{(1)}(\mathbf{r}|\mathbf{r}_I) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}} \end{aligned} \quad (3e)$$

There is also a similar condition for particle  $I$  which we do not write for brevity.

4. Similarly to the above, diffusion outflux of  $B$  continuously connects to chemical transformation flux.

Again for particle  $II$  we have:

$$\begin{aligned}
& D_B \nabla_{\perp} \delta \delta c_B^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}} - \\
& \quad k_{AB} \delta \delta c_A^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}} + \\
& \quad - k_{BA} \delta \delta c_B^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II}) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}} = \\
& = -D_B \nabla_{\perp} \delta c_B^{(1)}(\mathbf{r}|\mathbf{r}_I) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}} + \\
& \quad k_{AB} \delta c_A^{(1)}(\mathbf{r}|\mathbf{r}_I) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}} + \\
& \quad - k_{BA} \delta c_B^{(1)}(\mathbf{r}|\mathbf{r}_I) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}}
\end{aligned} \tag{3f}$$

Equations (3b) through (3f) represent a complete set determining  $\delta \delta c_A^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II})$  and  $\delta \delta c_B^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II})$ . Inhomogeneity in these equations is present only in boundary conditions (3e, 3f), it comes from  $\delta c_A^{(1)}(\mathbf{r}|\mathbf{r}_I) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}}$  and  $\delta c_B^{(1)}(\mathbf{r}|\mathbf{r}_I) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}}$  – the tails of concentration profiles created by particle  $I$  in the region of particle  $II$ . As long as particles are relatively far apart compared at their sizes,  $|\mathbf{r}_I - \mathbf{r}_{II}| \gg R$ , for the vicinity of particle  $II$  we should write

$$\begin{aligned}
\delta c_A^{(1)}(\mathbf{r}|\mathbf{r}_I) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}} & \simeq \delta c_A^{(1)}(\mathbf{r}_{II}|\mathbf{r}_I) + \\
& + \mathbf{R} \cdot \nabla \delta c_A^{(1)}(\mathbf{r}_{II}|\mathbf{r}_I),
\end{aligned} \tag{4}$$

and similarly for  $\delta c_B^{(1)}(\mathbf{r}|\mathbf{r}_I) \Big|_{\mathbf{r}=\mathbf{r}_{II}+\mathbf{R}}$ ,  $\delta c_A^{(1)}(\mathbf{r}|\mathbf{r}_{II}) \Big|_{\mathbf{r}=\mathbf{r}_I+\mathbf{R}}$ , and  $\delta c_B^{(1)}(\mathbf{r}|\mathbf{r}_{II}) \Big|_{\mathbf{r}=\mathbf{r}_I+\mathbf{R}}$ . We should plug this in the boundary conditions (3e, 3f). The inhomogeneous right hand sides of these boundary conditions then become sums of two terms each, one proportional to the value of concentration created by the second particle in the center of the first one (and vice versa),  $\delta c_A^{(1)}(\mathbf{r}_I|\mathbf{r}_{II})$  and  $\delta c_B^{(1)}(\mathbf{r}_I|\mathbf{r}_{II})$ , and another proportional to corresponding gradients,  $\nabla \delta c_A^{(1)}(\mathbf{r}_I|\mathbf{r}_{II})$  etc. Accordingly, we can split the solution for  $\delta \delta c_A^{(2)}(\mathbf{r}|\mathbf{r}_I, \mathbf{r}_{II})$  in the vicinity of particle  $I$  into a sum of two terms, one proportional to concentrations  $\delta c_A^{(1)}(\mathbf{r}_I|\mathbf{r}_{II})$  and  $\delta c_B^{(1)}(\mathbf{r}_I|\mathbf{r}_{II})$ , and another to gradients,  $\nabla \delta c_A^{(1)}(\mathbf{r}_I|\mathbf{r}_{II})$  and  $\nabla \delta c_B^{(1)}(\mathbf{r}_I|\mathbf{r}_{II})$ . The former solution is spherically symmetric around particle  $I$  and, therefore, contributes nothing to the force exerted on this particle. The latter solution is proportional to gradient and, therefore, its contribution to the force decays with distance as  $1/r^3$  and should be neglected as such.

Thus, we have justified the idea that every particle is driven, to the first approximation, by the concentration gradient generated by the other particle. “Interference” effect does exist, as the concentration field created by one sphere is affected by the other sphere, but it becomes relevant only in the sub-leading term with respect to  $r/R \ll 1$  and it is neglected in this work.