Supplementary data

1. The derivation of the infinitesimal covariance

1.1. The infinitesimal mean

The expression for the infinitesimal mean (and also the infinitesimal variance) can be easily obtained by comparing equations 1 and 3 with equation 5 in the manuscript. However, the stochastic derivation will be presented here for completeness.

Let r_{ij} be the distance separating the two diffusing particles *i* and *j* at time *t*. r_{ij} is the length of the three-dimensional vector \mathbf{r}_{ij} given as

$$\mathbf{r}_{ij}(t) = \left(X_{ij}(t), Y_{ij}(t), Z_{ij}(t)\right)$$
(1)

where X_{ij} , Y_{ij} and Z_{ij} are independent unbounded unbiased Brownian motions with specified diffusion coefficients along the *x*, *y* and *z* axes respectively and

$$U_{ij}(t) = U_j(t) - U_i(t)$$
⁽²⁾

where U_{ij} is X_{ij} , Y_{ij} or Z_{ij} . Since they are Brownian motions, their infinitesimal mean and variance are given as follows (see, for example, references 15–18 for more details)

$$\mu_{U_{ij}} = \lim_{\delta t \downarrow 0} \frac{1}{\delta t} E\left[\left\{\left|\delta U_{ij}\left(t\right)\right|\right\}\right| U_{ij}\left(t\right)\right] = 0$$
(3)

$$\sigma_{U_{ij}}^{2} = \lim_{\delta i \downarrow 0} \frac{1}{\delta t} E\left[\left\{\delta U_{ij}(t)\right\}^{2}\right\} U_{ij}(t) = 2\left(D_{i} + D_{j}\right) = 2D_{ij}$$
(4)

where D_i and D_j are the diffusion coefficients of the particles *i* and *j* respectively, D_{ij} is the relative diffusion coefficient of the particles *i* and *j*, δt is an infinitesimal time increment and

$$\delta U_{ij}(t) = U_{ij}(t + \delta t) - U_{ij}(t)$$
(5).

The vector **r** changes infinitesimally during the time increment δt and becomes **r**+ δ **r** where

$$\delta \mathbf{r}_{ij}(t) = \left(\delta X_{ij}(t), \delta Y_{ij}(t), \delta Z_{ij}(t)\right)$$
(6).

Hence, the desired expression for the infinitesimal mean μ is

$$u\left(r_{ij}\right)\delta t = E\left[\delta r_{ij} \left| r_{ij}\right] = E\left[\left\{\left|\mathbf{r}_{ij} + \delta \mathbf{r}_{ij}\right| - r_{ij}\right\} r_{ij}\right]$$
(7)

and then

$$\mu\left(r_{ij}\right)\delta t = r_{ij} E\left[\left\{\sqrt{1 + \frac{2\mathbf{r}_{ij} \cdot \delta\mathbf{r}_{ij}}{r_{ij}^{2}} + \frac{\delta\mathbf{r}_{ij} \cdot \delta\mathbf{r}_{ij}}{r_{ij}^{2}}} - 1\right\} \middle| r_{ij}\right]$$
(8)

where the following property of the conditional expectation was used

$$E\left[r_{ij} \mid r_{ij}\right] = r_{ij} \tag{9}$$

Expanding the square root as a series gives

$$\mu(\mathbf{r}_{ij})\delta t = \mathbf{r}_{ij} E \left[\frac{\mathbf{r}_{ij} \cdot \delta \mathbf{r}_{ij}}{r_{ij}^{2}} + \frac{1}{2} \frac{\delta \mathbf{r}_{ij} \cdot \delta \mathbf{r}_{ij}}{r_{ij}^{2}} - \frac{1}{8} \left(\frac{2\mathbf{r}_{ij} \cdot \delta \mathbf{r}_{ij}}{r_{ij}^{2}} + \frac{\delta \mathbf{r}_{ij} \cdot \delta \mathbf{r}_{ij}}{r_{ij}^{2}} \right)^{2} + O\left[\left(\delta \mathbf{r}_{ij} \right)^{3} \right] \right]$$
(10)

where the indicator of conditional expectation ($|r_{ij}\rangle$) has been removed for convenience and O is a polynomial function of leading order $(\delta \mathbf{r}_{ij})^3$. The terms containing δr_{ij} of order 3 and higher have zero expectation and so do the first-order terms. Hence

$$\mu(\mathbf{r}_{ij})\delta t = \frac{r_{ij}}{2}E\left[\frac{\delta \mathbf{r}_{ij} \cdot \delta \mathbf{r}_{ij}}{r_{ij}^2} - \left(\frac{\mathbf{r}_{ij} \cdot \delta \mathbf{r}_{ij}}{r_{ij}^2}\right)^2\right]$$
(11).

Finally,

$$\mu\left(r_{ij}\right)\delta t = \frac{r_{ij}}{2} \left[\frac{3 \times 2D_{ij}\delta t}{r_{ij}^2} - \frac{2D_{ij}\delta t}{r_{ij}^2}\right] = \frac{2D_{ij}\delta t}{r_{ij}}$$
(12).

And therefore,

$$\mu\left(r_{ij}\right) = \frac{2D_{ij}}{r_{ij}} \tag{13}.$$

1.2. The infinitesimal variance

The derivation for the infinitesimal variance proceeds similarly and will be briefly presented here. The infinitesimal variance is

$$\sigma^{2}\left(\mathbf{r}_{ij}\right)\delta t = E\left[\left(\delta r_{ij}\right)^{2} \middle| r_{ij}\right] = E\left[\left(\left|\mathbf{r}_{ij} + \delta \mathbf{r}_{ij}\right| - r_{ij}\right)^{2} \middle| r_{ij}\right]$$
(14).

As before, expanding the square root as a power series

$$\sigma^{2}\left(r_{ij}\right)\delta t = r_{ij}^{2}E\left[\left(\frac{\mathbf{r}_{ij}\cdot\delta\mathbf{r}_{ij}}{r_{ij}^{2}} + O\left[\left(\delta\mathbf{r}_{ij}\right)^{2}\right]\right)^{2}\right]$$
(15)

where the indicator ($| r_{ij}$) was dropped for convenience, and so

$$\sigma^{2}\left(\mathbf{r}_{ij}\right)\delta t = r_{ij}^{2}E\left[\left(\frac{\mathbf{r}_{ij}\cdot\delta\mathbf{r}_{ij}}{r_{ij}^{2}}\right)^{2} + O\left[\left(\delta\mathbf{r}_{ij}\right)^{3}\right]\right]$$
(16).

Because the terms of order 3 and higher (as before) have expectation zero, it follows that

$$\sigma^{2}\left(r_{ij}\right)\delta t = r_{ij}^{2}E\left[\left(\frac{\mathbf{r}_{ij}}{r_{ij}^{2}}\right)^{2}\right]$$
(17).

Finally,

$$\sigma^2 \left(r_{ij} \right) = 2D_{ij} \tag{18}$$

1.3. The infinitesimal covariance

Deriving the expression for the infinitesimal covariance of two distances r_{ij} and r_{jl} proceeds in the same way and again the same notations used above will be used here. Starting with the following definition for the covariance

$$\sigma^{2}\left(\mathbf{r}_{ij},\mathbf{r}_{jl}\right)\delta t = E\left[\left\{\left(\left|\mathbf{r}_{ij}+\delta\mathbf{r}_{ij}\right|-\mathbf{r}_{ij}\right)\left|\mathbf{r}_{jl}+\delta\mathbf{r}_{jl}\right|-\mathbf{r}_{jl}\right)\right\}\left|\mathbf{r}_{ij},\mathbf{r}_{jl}\right]$$
(19).

The conditional expectation indicator ($|r_{ij}, r_{jl}$) is ignored from this point on for convenience, and so

$$\sigma^{2}\left(r_{ij}, r_{jl}\right)\delta t = r_{ij}r_{jl}E\left[\left(\frac{\mathbf{r}_{ij}\cdot\delta\mathbf{r}_{ij}}{r_{ij}^{2}} + O\left[\left(\delta\mathbf{r}_{ij}\right)^{2}\right]\right]\left(\frac{\mathbf{r}_{jl}\cdot\delta\mathbf{r}_{jl}}{r_{jl}^{2}} + O\left[\left(\delta\mathbf{r}_{jl}\right)^{2}\right]\right]\right]$$
(20).

If keeping only the terms that have non-zero expectation

$$\sigma^{2}\left(r_{ij}, r_{jl}\right)\delta t = r_{ij}r_{jl}E\left[\frac{\mathbf{r}_{ij}\cdot\delta\mathbf{r}_{ij}}{r_{ij}^{2}}\frac{\mathbf{r}_{jl}\cdot\delta\mathbf{r}_{jl}}{r_{jl}^{2}}\right]$$
(21).

Evaluating the last expression and realizing that the only terms that will contribute to the expectation are the terms containing $(\delta U_i)^2$ where U_i is X_i , Y_i or Z_i gives

$$\sigma^{2}\left(r_{ij}, r_{jl}\right)\delta t = \frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{jl}}{r_{ij} r_{jl}} 2D_{j}\delta t$$
(22),

or

$$\sigma^{2}\left(r_{ij}, r_{jk}\right) = 2D_{j}\cos\left(\mathbf{r}_{ij}, \mathbf{r}_{jl}\right)$$
(23).

2. Bessel bridge (RF simulations)

Because of the non-zero time-step in the RF simulations, it is essential to take into account the possibility that an encounter between two particles may occur during the course of a time step, but that by the sample time the pair may have diffused apart again. This phenomenon leads to a systematic underestimate of reaction probability in the simulation. A correction may be made using what is called a bridging process. Briefly, consider one-dimensional Brownian motion moving from a separation of x to a separation of y during time δt , and passing through a separation of a (the reaction distance of the two particles here) in between. The probability of passing through a, conditional on starting at x and ending at y, is given as follows (see references 9,15–18 in the manuscript for more details)

$$\Pr = 1 - \frac{p_a(x, y, \delta t)}{p(x, y, \delta t)}$$
(24)

where $p_a(x,y,\delta t)$ is the probability density of an absorbed motion (a motion that is killed when it first hits a separation of *a*) and $p(x,y,\delta t)$ is the probability density of reaching the separation *y* starting from *x* during δt in an unbounded diffusion. Both functions are known for a three-dimensional Bessel process, which is the random distance between two diffusing particles, and are given as follows (see references 9, 15–18 in the manuscript)

$$p(x, y, \delta t) = \frac{y}{x\sqrt{4\pi D'\delta t}} \left[e^{-(y-x)^2/4D'\delta t} - e^{-(y+x)^2/4D'\delta t} \right]$$
(25)

$$p_a(x, y, \delta t) = \frac{y}{x\sqrt{4\pi D'\delta t}} \left[e^{-(y-x)^2/4D'\delta t} - e^{-(y+x-2a)^2/4D'\delta t} \right]$$
(26).

where D' is the relative diffusion coefficient. Equation (24) then gives the following bridging condition for a Bessel process

$$\Pr = \frac{e^{-(x-a)(y-a)/D'\delta t} - e^{-xy/D'\delta t}}{1 - e^{-xy/D'\delta t}}$$
(27)

which can be used to calculate the probability that a reaction takes place during the time step δt in the course of Monte Carlo RF simulations, properly conditioned on the initial and final separations.

3. The IRT method

The IRT method to simulate radiation chemical kinetics is based on the approximation of independent pairs, and was first proposed in 1982 (see references 1–4, 9–14, 23–25, 26, 27 in the manuscript for more details). Since the only necessary parameters to obtain the chemical kinetics are the reaction times, the IRT method is built to generate the reaction times without having to monitor the trajectories of the reactants, as done in the RF simulations. Briefly, consider a system of only two neutral particles *i* and *j* separated initially by a distance r_{ij} , the probability W_{ij} that they have reacted by time *t* is given by equation 5 in the manuscript where, as discussed there, the reaction is assumed to be fully diffusion-controlled. Therefore,

$$t = \frac{1}{4D_{ij}} \left[\frac{r_{ij} - a}{\operatorname{erfc}^{-1}(\lambda)} \right]^2 \qquad : \ \lambda = \frac{r_{ij}}{a} W_{ij}$$
(28)

where erfc^{-1} is the inverse of the complementary error function. This is very important because it indicates that if the initial separation of the two particles r_{ij} is known, a reaction time for them can be generated if W_{ij} in the last equation is replaced by a uniformly distributed random number between 0 and 1 (provided the function erfc^{-1} can be computed). If the random number is greater that a/r_{ij} the encounter time is deemed to be infinite, i.e. that pair never encounters. This method is known as the inverse function method for generating non-uniform random numbers [see reference 28 in the manuscript]. The IRT method employs the independent pairs approximation to obtain the reaction times in systems of more than two particles, i.e. a random reaction time for each pair present is generated as described above from its initial separation distance, ignoring the presence of any other particles. It is worth noting that the reaction times that belong to a realizable particle configuration (e.g. they obey triangle inequalities etc.) The reaction times are independent but conditional on the initial distances.

The Monte Carlo IRT simulation generally proceeds as follows: it starts from an initial configuration, which in a model track will typically be a random distribution of some sort but for the purpose of testing can be of a specific geometry. The interparticle separations are then used to generate random reaction times independently using equation (28). Following that, the minimum of the generated times is chosen to be the first reaction time. The next minimum time (limited to the surviving particles) is then chosen to be the next reaction time and so on. The processes terminate either by the reaction of all particles involved or by reaching a maximum time limit used to stop the process. The process is repeated a large number of times (realizations) so that the data become statistically representative and this leads to the reaction rate (or similarly the survival probability).