Diffusion-related problems in physics and biology

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DIFFUSION OF A PAIR OF PARTICLES

Let us consider the motion of an isolated pair of reactants. Let us indicate with D_i and $\boldsymbol{x}_i(t)$ the diffusion constant and the position vector of the particles $i = 1, 2$ in the chosen reference frame. The diffusive motion of the pair is described by the equation

$$\frac{\partial P(\boldsymbol{x}_1, \boldsymbol{x}_2, t)}{\partial t} = D_1 \nabla_1^2 \rho(\boldsymbol{x}_1, \boldsymbol{x}_2, t) + D_2 \nabla_2^2 P(\boldsymbol{x}_1, \boldsymbol{x}_2, t) \tag{1}$$

which can be obtained in the usual manner by requiring probability conservation in the form of a continuity equation involving the probability currents $\boldsymbol{J}_i = -D_i \boldsymbol{\nabla}_i \rho(\boldsymbol{x}_1, \boldsymbol{x}_2, t)$

$$\frac{\partial P(\boldsymbol{x}_1, \boldsymbol{x}_2, t)}{\partial t} + \boldsymbol{\nabla}_1 \cdot \boldsymbol{J}_1(\boldsymbol{x}_1, \boldsymbol{x}_2, t) + \boldsymbol{\nabla}_2 \cdot \boldsymbol{J}_2(\boldsymbol{x}_1, \boldsymbol{x}_2, t) = 0 \tag{2}$$

The diffusion equation (1) becomes separable upon performing the following change of variables

$$\begin{cases} \boldsymbol{r} = \boldsymbol{x}_1 - \boldsymbol{x}_2 \\ \boldsymbol{R} = \sqrt{\dfrac{D_2}{D_1}}\, \boldsymbol{x}_1 + \sqrt{\dfrac{D_1}{D_2}}\, \boldsymbol{x}_2 \end{cases} \tag{3}$$

where the coordinate $\boldsymbol{R}$ describes the *diffusional* centre of mass, while $\boldsymbol{r}$ is the relative pair separation. This yields

$$\frac{\partial P'(\boldsymbol{R}, \boldsymbol{r}, t)}{\partial t} = D \left(\nabla_R^2 + \nabla_r^2 \right) P'(\boldsymbol{R}, \boldsymbol{r}, t) \tag{4}$$

where $D = D_1 + D_2$ is the coefficient of relative diffusion. Equation (4) is separable and it admits a solution in the form

$$P'(\boldsymbol{R}, \boldsymbol{r}, t) = p(\boldsymbol{R}, t) \rho(\boldsymbol{r}, t) \tag{5}$$

The unphysical diffusion of the centre of mass can be neglected, while the diffusional motion of the two particles can be fully described by following the time evolution along the relative separation $\boldsymbol{r}$. Therefore, without loss of generality we can take $p(\boldsymbol{R}, t) = 1$. Accordingly, the pair dynamics is described by the following equation

$$\frac{\partial \rho(\boldsymbol{r}, t)}{\partial t} = D \nabla^2 \rho(\boldsymbol{r}, t) \tag{6}$$

where we have omitted for brevity the r subscript in the Laplacian operator.

Alternatively, one can perform the simpler change of variables

$$(\boldsymbol{x}_1, \boldsymbol{x}_2) \quad \longrightarrow \quad (\boldsymbol{r} = \boldsymbol{x}_1 - \boldsymbol{x}_2, \boldsymbol{x}_2) \tag{7}$$

which amounts to shifting to the frame of reference attached to particle 2. In this case the diffusion equation becomes

$$\frac{\partial P(\boldsymbol{x}_1, \boldsymbol{x}_1 - \boldsymbol{r}, t)}{\partial t} = D \nabla_r^2 P(\boldsymbol{x}_1, \boldsymbol{x}_1 - \boldsymbol{r}, t) \tag{8}$$

which also reduces to equation (6) with

$$\rho(\boldsymbol{r}, t) = \int P(\boldsymbol{x}_1, \boldsymbol{x}_1 - \boldsymbol{r}, t)\, d^3\boldsymbol{x}_1 \tag{9}$$

The Smoluchowski equation

Equation (6), valid for non-interacting particles, can be easily[1] generalized to the case of particles interacting through a 2-body potential $V(\boldsymbol{r})$. The external force associated with the potential, $\boldsymbol{F} = -\boldsymbol{\nabla} V(\boldsymbol{r})$, causes the particles to drift apart at equilibrium with a relative velocity

$$\boldsymbol{v} = -\frac{\boldsymbol{\nabla} V(\boldsymbol{r})}{\gamma} \tag{10}$$

where γ is the damping coefficient of the fluid where the diffusive motion takes place ($[\gamma]$ = mass $\times$ time^{-1}). The total probability current including the current associated with the external force $\boldsymbol{J}_{F} = \rho \boldsymbol{v}$ is thus

$$\boldsymbol{J}(\boldsymbol{r},t) = -D\,\boldsymbol{\nabla}\rho(\boldsymbol{r},t) - \rho\,\frac{\boldsymbol{\nabla} V(\boldsymbol{r})}{\gamma} \tag{11}$$

At equilibrium $\boldsymbol{J} = 0$ and $\rho(\boldsymbol{r},t) \propto \exp[-\beta V(\boldsymbol{r},t)]$, wich implies Einstein's relation

$$D = \frac{k_B T}{\gamma} \tag{12}$$

The above relation is in fact a simple expression of the fluctuation-dissipation theorem. As a consequence, the total current can be rewritten as

$$\boldsymbol{J}(\boldsymbol{r},t) = -D\left[\boldsymbol{\nabla}\rho(\boldsymbol{r},t) + \beta\rho\,\boldsymbol{\nabla} V(\boldsymbol{r})\right] \tag{13}$$

Inserting the above expression in the continuity equation expressing conservation of probability associated with the radial current [2] $\boldsymbol{J}_r = \boldsymbol{J}_1 - \boldsymbol{J}_2 = -D\boldsymbol{\nabla}_r\rho(\boldsymbol{r},t)$

$$\frac{\partial\rho(\boldsymbol{r},t)}{\partial t} + \boldsymbol{\nabla}_r\cdot\boldsymbol{J}_r = 0 \tag{14}$$

yields the so-called Smoluchowski equation

$$\frac{\partial\rho(\boldsymbol{r},t)}{\partial t} = D\,\boldsymbol{\nabla}\cdot\left[\boldsymbol{\nabla}\rho(\boldsymbol{r},t) + \beta\rho\,\boldsymbol{\nabla} V(\boldsymbol{r})\right] \tag{15}$$

that generalizes the diffusion equation to the presence of a pair-wise interaction potential.

It is interesting to note that the total current (13) can be recast in a slightly different form. We note that

$$\boldsymbol{\nabla}\rho = \beta\rho\,\boldsymbol{\nabla}\left[\beta^{-1}\log\left(\rho\Lambda^{-3}\right)\right] = \beta\rho\,\boldsymbol{\nabla}\mu \tag{16}$$

We recognize the equilibrium chemical potential of the perfect (i.e. non-interacting) ideal (i.e. classical) gas $\mu = \beta^{-1}\log[\rho\Lambda^{-3}]$ whose density is $\rho(\boldsymbol{r},t)$,

$$\mu(\boldsymbol{r},t) = \frac{\delta F[\rho(\boldsymbol{r},t)]}{\delta\rho} \tag{17}$$

where $\delta F/\delta\rho$ denotes the functional derivative of the equilibrium free energy. $\Lambda = \sqrt{2\pi\hbar/mk_B T}$ is De Broglie's wavelength [3]. Formally, equation (16) specifies the chemical potential as a function of time and space. By inserting expression (16) in equation (13) we get

$$\begin{aligned}
\boldsymbol{J}(\boldsymbol{r},t) &= -\beta\,D\rho(\boldsymbol{r},t)\,\boldsymbol{\nabla}[\mu(\boldsymbol{r},t) + V(\boldsymbol{r})] \\
&= -\beta\,D(\boldsymbol{r},t)\,\boldsymbol{\nabla}[\mu(\boldsymbol{r},t) - \mu_{\rm ext}(\boldsymbol{r},t)] \\
&= -\beta\,D\rho(\boldsymbol{r},t)\boldsymbol{\nabla}\left[\frac{\delta F_{\rm tot}[\rho(\boldsymbol{r},t)]}{\delta\rho}\right]
\end{aligned} \tag{18}$$

The above expression shows that an external potential can be interpreted as a shift in the chemical potential. The external potential can be identified as minus the externally fixed chemical potential $\mu_{\rm ext}$. Note the appearance of the *total* free energy

$$F_{\rm tot} = F[\rho(\boldsymbol{r},t)] - \int \mu_{\rm ext}(\boldsymbol{r},t)\rho(\boldsymbol{r},t)\, d^3\boldsymbol{r} \tag{19}$$

In equilibrium, the equation of state

$$\frac{\delta F[\rho(\boldsymbol{r}]}{\delta\rho} = \mu_{\rm ext}(\boldsymbol{r}) \tag{20}$$

is satisfied, and the current $\boldsymbol{J}$ is zero.

For other applications, it is instructive to cast Smoluchowski's equation in another form. To this end, we note that the total current (13) can be rewritten as

$$\boldsymbol{J}(\boldsymbol{r},t) = -De^{-\beta V}\boldsymbol{\nabla}\left(\rho(\boldsymbol{r},t)e^{\beta V}\right) \tag{21}$$

so that the Smoluchowski equation takes the form

$$\frac{\partial\rho(\boldsymbol{r},t)}{\partial t} = D\,\boldsymbol{\nabla}\cdot\left[e^{-\beta V}\boldsymbol{\nabla}\left(\rho(\boldsymbol{r},t)e^{\beta V}\right)\right] \tag{22}$$

PAIR ANNIHILATION AND THE SURVIVAL PROBABILITY

Let us imagine that a pair of particles spherical particles of radius $R/2$ is suddenly formed at $t=0$ at a separation $|\boldsymbol{r}(0)| = r_0$ and is constrained to diffuse in space. We are interested in studying the recombination process. Two useful quantities can be introduced, the pair lifetime distribution $\mathcal{P}(\tau|r_0)$, where τ is the time it takes to the two particles to come to contact at the distance R for the first time, and the pair survival probability $S(t|r_0)$, which is nothing but the cumulative distribution of the density $\mathcal{P}$

$$S(t|r_0) = \int_t^\infty \mathcal{P}(\tau|r_0)\, d\tau \tag{23}$$

which shows that

$$\mathcal{P}(t|r_0) = -\frac{dS(t|r_0)}{dt} \tag{24}$$

The recombination probability is defined as

$$Q(t|r_0) = \int_0^t \mathcal{P}(\tau|r_0)\, d\tau \tag{25}$$

which corresponds to the normalization

$$S(t|r_0) + Q(t|r_0) = 1 \tag{26}$$

indicating that either the two particles survive isolated or recombine.

The Green function for the pair recombination problem

The survival probability $S(t|r_0)$ can be calculated by solving the following boundary value problem

$$\begin{cases} \dfrac{\partial \mathcal{G}(\boldsymbol{r},t|\boldsymbol{r}_0,t_0)}{\partial t} = D\nabla^2 \mathcal{G}(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) + \dfrac{\delta(r-r_0)\delta(t-t_0)}{4\pi r^2} \\ \mathcal{G}(\boldsymbol{r},t|\boldsymbol{r}_0,t_0)|_{r=R} = 0 \\ \lim_{r\to\infty} \mathcal{G}(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) < \infty \end{cases} \tag{27}$$

The function $\mathcal{G}(r,t|r_0,t_0)$ is the Green function of the pair diffusion problem. It only depends on the magnitude of the relative separation and has no angular dependencies. The two (one-dimensional) delta functions correspond to the initial condition of sudden generation of the pair at time t_0 at a separation r_0. In the following, we shall take $t_0 = 0$ for simplicity. The boundary condition at $r = R$ corresponds to the recombination event.

The survival probability is the sum of all the probabilities that the pair separation lies between $\boldsymbol{r}$ and $\boldsymbol{r} + d^3\boldsymbol{r}$, that is

$$S(t|r_0) = \int \mathcal{G}(r,t|r_0,0)\, d^3\boldsymbol{r} \tag{28}$$

Let us now solve equation (27) and calculate the survival probability. For simplicity, we let $t \to Dt$. By taking the Laplace transform of equation (27), we get

$$s\bar{\mathcal{G}} - \frac{\delta(r-r_0)}{4\pi r^2} = \frac{2}{r}\frac{\partial \bar{\mathcal{G}}}{\partial r} + \frac{\partial^2 \bar{\mathcal{G}}}{\partial r^2} \tag{29}$$

where

$$\bar{\mathcal{G}}(r,s|r_0,0) = \int_0^\infty e^{-st}\mathcal{G}(r,t|r_0,0)\, dt \tag{30}$$

We look for solutions in the form

$$\bar{\mathcal{G}}(r,s|r_0,0) = \frac{f(r,s)}{r}$$

By inserting this ansatz in equation (30), the equation is transformed to

$$f''(r,s) - sf(r,s) = -\frac{\delta(r-r_0)}{4\pi r} \tag{31}$$

The general solutions of the homogenous equation are

$$f(r,s) = Ae^{-\sqrt{s}\,r} + Be^{\sqrt{s}\,r}$$

Therefore, the appropriate solution satisfying the boundary condition at infinity is

$$f(r,s) = \frac{Ae^{-\sqrt{s}\,r}}{r} \tag{32}$$

In order to find a particular integral of equation (31), we take the (one-dimensional) Fourier transform

$$(k^2 + s)\tilde{f} = \frac{1}{2(2\pi)^{3/2}}\frac{e^{ikr_0}}{r_0} \tag{33}$$

where

$$\tilde{f}(k,s) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{ikr} f(r,s)\, dr \tag{34}$$

From standard inverse Fourier tables, we get

$$f(r,s) = \frac{e^{-\sqrt{s}|r-r_0|}}{8\pi\, r_0 \sqrt{s}} \tag{35}$$

so that the general solution of equation (29) is

$$\bar{\mathcal{G}}(r,s|r_0,0) = \frac{Ae^{-\sqrt{s}\, r}}{r} + \frac{e^{-\sqrt{s}|r-r_0|}}{8\pi r\, r_0 \sqrt{s}} \tag{36}$$

Imposing the absorbing boundary condition at $r = R$ allows to fix the constant A

$$A = -\frac{1}{8\pi r_0} e^{-\sqrt{s}(r_0 - 2R)}$$

which gives

$$\bar{\mathcal{G}}(r,s|r_0,0) = \frac{1}{8\pi r\, r_0 \sqrt{s}} \left[e^{-\sqrt{s}\,|r-r_0|} - e^{-\sqrt{s}(r+r_0-2R)} \right] \tag{37}$$

The Laplace transform can be inverted through the usual Bromwich closed contour including the branching point around the pole at $s = 0$. The result is

$$\mathcal{G}(r,t|r_0,0) = \frac{1}{8\pi r\, r_0 \sqrt{\pi D t}} \left[e^{-(r-r_0)^2/4Dt} - e^{-(r+r_0-2R)^2/4Dt} \right] \tag{38}$$

The survival probability can now be calculated through eq. (28). The result is

$$S(t|r_0) = 1 - \frac{R}{r_0} \operatorname{erfc}\left(\frac{r_0 - R}{2\sqrt{Dt}} \right) \tag{39}$$

where $\operatorname{erfc}(x)$ the complementary error function

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-x^2}\, dx \tag{40}$$

The corresponding recombination probability is

$$Q(t|r_0) = 1 - S(t|r_0) = \frac{R}{r_0} \operatorname{erfc}\left(\frac{r_0 - R}{2\sqrt{Dt}} \right) \tag{41}$$

The stationary values of the survival and recombination probabilities are

$$\begin{aligned} S(r_0) &= \lim_{t\to\infty} S(t|r_0) = 1 - \frac{R}{r_0} \\ Q(r_0) &= \lim_{t\to\infty} Q(t|r_0) = \frac{R}{r_0} \end{aligned} \tag{42}$$

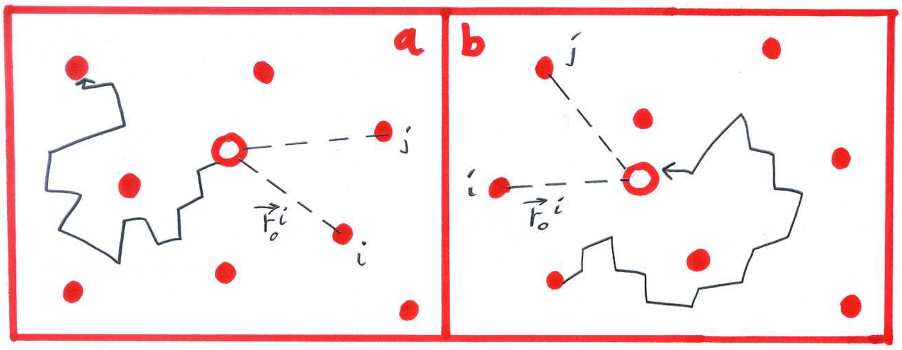

FIG. 1: Schematic illustration of the (a) trapping and (b) target problems. Traps are represented as filled circles and particles by empty circles.

DIFFUSION IN MANY-BODY SYSTEMS: THE TRAPPING AND TARGET PROBLEMS

We have studied the recombination of an isolated pair of particles that diffuse in a fluid. We can now turn to the problem of particle recombination in a many-particle system. Let us consider a system composed of two kind of particles, say A (diffusion coefficient D_A) and B (diffusion coefficient D_B). Without loss of generality we assume that both particles have the same radius $R/2$ so that the encounter distance is R. All particles are assumed as non-interacting. We arbitrarily assign to the particles of type B the character of *traps* (sometimes also called quenchers [4]), while we still refer to particles of type A as the *particles*. Two conceptually distinct scenarios arise as limiting cases

1. **Trapping, $D_B = 0$.** A single particle diffuses amidst a stationary configuration of traps and gets absorbed (it recombines) at the first trap site encountered. This scenario is illustrated schematically in Fig. 1 (a).

2. **Target, $D_A = 0$.** Many traps diffuse in the presence of a single stationary particle (the target) until the first trap hits the target. This scenario is illustrated schematically in Fig. 1 (a).

This problem admits a simple solution only if some assumptions are made. Let us imagine that the particles of kind A are sufficiently diluted so that one can concentrate on a single A particle surrounded by many B particles, say N of them. The $N+1$-body Smoluchowski equation is then

$$\frac{\partial P(\boldsymbol{x}_A, \boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)}{\partial t} = \left(D_A \nabla_A^2 + D_B \sum_{i=1}^{N} \nabla_i^2 \right) P(\boldsymbol{x}_A, \boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) \tag{43}$$

where $\boldsymbol{x}_A$ and the $\boldsymbol{x}_i$'s are the position vectors of the A particle and of the N particles of type B, respectively, in the laboratory frame. the The next step is to change to the reference frame of the A particle

$$\boldsymbol{r}_i = \boldsymbol{x}_i - \boldsymbol{x}_A, \quad i = 1, 2, \ldots, N$$

By doing this, one has

$$\nabla_A^2 = \sum_{i=1}^{N} \nabla_{r_i}^2 + \sum_{i \neq j = 1}^{N} \boldsymbol{\nabla}_{r_i} \cdot \boldsymbol{\nabla}_{r_j}$$

and the N-body Smoluchowski equation (43) becomes

$$\begin{aligned}\frac{\partial \rho(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N, t)}{\partial t} &= (D_A + D_B) \sum_{i=1}^{N} \nabla^2_{r_i} \rho(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N, t) \\ &+ D_A \sum_{i \neq j = 1}^{N} \boldsymbol{\nabla}_{r_i} \cdot \boldsymbol{\nabla}_{r_j} \rho(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N, t)\end{aligned} \tag{44}$$

where

$$\rho(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N, t) = \int P(\boldsymbol{x}_A, \boldsymbol{r}_1 + \boldsymbol{x}_A, \boldsymbol{r}_2 + \boldsymbol{x}_A, \ldots, \boldsymbol{r}_N + \boldsymbol{x}_A)\, d^3\boldsymbol{x}_A$$

We see that, so long as the A particle also diffuses ($D_A \neq 0$) the equation contains cross-terms that make it non-separable. Separability is recovered only in the case $N = 1$ (single pair), as we have already shown [see equation (8)], or for static A particles ($D_A = 0$). Therefore, the full N-body problem can be reduced to an equivalent two-body problem only under the following two assumptions

1. One species must be much more diluted than the other, so that the N-body problem can be reduced to study the fate of a single particle surrounded by many particles of the other species.

2. The diffusion coefficient of the highly diluted species should be much smaller than that of the other species.

Therefore, a tractable problem might be the quenching of large and highly diluted photo-excited particles by (smaller) highly mobile and non-interacting quenchers.

Note that equation (44) also makes clear why the target and trapping problem are not equivalent, as one may naively imagine. One has N particles of one type and a single particle of another type. What equation (44) is telling you is that considering the single particle as static and the others as moving or viceversa are not equivalent problems.

The survival probability

We turn now to calculating the survival probability for the N-body problem in the *target* configuration. Let $\rho_B = N/V$ be the density of traps. Let us denote with $S_1(t|\boldsymbol{r}_0)$ the survival probability of the particle A (taken as static) in the presence of a *single* diffusing trap initially at $\boldsymbol{r}(t = 0) = \boldsymbol{r}_0$. This is the definition of a target problem, but could be equally considered as a trapping problem, as the two are obviously exactly the same for an isolated pair. The single-pair survival probability $S_1(t|\boldsymbol{r}_0)$ and its complement, the pair recombination probability $Q_1(t|\boldsymbol{r}_0) = 1 - S_1(t|\boldsymbol{r}_0)$ have been calculated above,

$$\begin{aligned} S_1(t|\boldsymbol{r}_0) &= 1 - \left(\frac{R}{r_0}\right) \mathrm{erfc}\left[\frac{r_0 - R}{2\sqrt{Dt}}\right] \\ Q_1(t|\boldsymbol{r}_0) &= \left(\frac{R}{r_0}\right) \mathrm{erfc}\left[\frac{r_0 - R}{2\sqrt{Dt}}\right] \end{aligned} \tag{45}$$

Since the traps are non-interacting, one can neglect correlations between them. Hence, the survival probability $S_N(t)$ of an A target in the presence of N diffusing traps initially in the configuration

$\{\boldsymbol{r}_i(0) = \boldsymbol{x}_i, i = 1, 2, \ldots, N\}$, is given by

$$S_N(t) = \prod_{i=1}^{N} S_1(t|\boldsymbol{x}_i) \tag{46}$$

The survival probability is then the average of the function (46) over many realizations of the trap initial configurations

$$\begin{aligned} S(t) &= \langle S_N(t)\rangle = \lim_{N,V\to\infty} \frac{1}{V^N} \int \prod_{i=1}^{N} S_1(t|\boldsymbol{x}_i)\, d^3\boldsymbol{x}_i \qquad (47)\\ &= \lim_{N,V\to\infty} \left[1 - \frac{\rho_B}{N} \int Q_1(t|\boldsymbol{x}_i)\, d^3\boldsymbol{x}_i\right]^N \\ &= \exp\left[-\rho_B \int Q_1(t|\boldsymbol{x}_i)\, d^3\boldsymbol{x}_i\right] \end{aligned}$$

where the limit is performed in the usual way as to keep the density $\rho_B = N/V$ finite. The integral in the last equation is easily calculated, which finally gives the Smoluchowski survival probability

$$S(t) = \exp\left[-k_S t \left(1 + \frac{2R}{\sqrt{\pi D t}}\right)\right] \tag{48}$$

The encounter rate

The encounter rate κ can be easily calculated from the N-body survival probability. This describes the probability per unit time of an $A - B$ encounter in both the trapping and target problems under the above-stated hypotheses. One should be careful in recognizing that when traps are interacting, many-body effects are expected to have different consequences in the target and trapping problems. In general, one has

$$\kappa = \frac{1}{\langle\tau\rangle} = \left[\int_0^\infty \tau\, \mathcal{P}(\tau)\, d\tau\right]^{-1} \tag{49}$$

where $\langle\tau\rangle$ is the average lifetime of an $A - B$ pair and $\mathcal{P}(t)$ is the lifetime density distribution. In general, one has

$$\mathcal{P}(t) = -\frac{dS(t)}{dt}$$

(see eq. (24)). Therefore, an integration by parts in eq. (49) with the boundary condition $\lim_{t\to\infty} S(t) = 0$ leads to

$$\kappa = \left[\int_0^\infty S(t)\, dt\right]^{-1} \tag{50}$$

which allows one to calculate the encounter rate (or, equivalently, the average lifetime of a pair) from the knowledge of the N-body survival probability. Note that the lifetime of an *isolated* pair is not well defined! If an attempt is made to use equation (50) with the survival probability of an isolated pair (45), one gets a diverging lifetime. This is a consequence of the fact that for an isolated pair initially at a distance r_0 an encounter (recombination) does not take place with probability one, as $\lim_{t\to\infty} Q_1(t|r_0) = R/r_0 < 1$. This is not the case in the N-body problem, where an encounter always occurs and

$$\lim_{t\to\infty} Q(t) = \lim_{t\to\infty} 1 - S(t) = 1$$

Encounter rate in the stationary 2-body problems

Before proceeding to calculate the encounter rate from equation (50) with the survival probability (48), it is instructive to calculate κ from the time-independent problem. As we shall see, this calculation, reported in all graduate textbooks covering diffusion-limited reactions does not provide the correct result. The argument goes as following.

Under the same hypotheses as the ones stated above, one can solve the N-body encounter problem by focussing on the fate of a single particle (the highly diluted ones) surrounded by many other particles, equally taken as non-interacting among them. In this case, we have seen that the N-body diffusion equation becomes separable and thus it seems legitimate to reduce the full problem to a two-body problem. We have seen that the appropriate diffusion equation for this problem is

$$\frac{\partial \rho(\boldsymbol{r},t)}{\partial t} = D\nabla^2 \rho(\boldsymbol{r},t)$$

where $D = D_A + D_B$ and $\boldsymbol{r}$ is the relative coordinate. The idea is that the encounter rate can be computed by solving the following stationary boundary-value problem

$$\begin{aligned} &\nabla^2 \rho(\boldsymbol{r}) = 0 \\ &\rho(|\boldsymbol{r}| = R) = 0 \\ &\lim_{r\to\infty} \rho(\boldsymbol{r},t) = \rho_B \end{aligned} \tag{51}$$

The encounter is treated as an absorbing boundary condition (a sink) at the contact distance R. Moreover, far from the encounter distance, the density of the B particles should be the bulk density. In this framework, the encounter rate is nothing but the stationary density flux across any closed surface around the sink. By virtue of the spherical symmetry of the problem one then has

$$\kappa = \int_{\mathcal{S}_r} \boldsymbol{J}\cdot\hat{\boldsymbol{n}}\, dS = 4\pi D r^2 \left.\frac{\partial \rho}{\partial r}\right|_{r=R} \tag{52}$$

where $\mathcal{S}_r$ is a sphere of radius r and center at the origin (the sink) and $\boldsymbol{J}(r) = -D\boldsymbol{\nabla}\rho(r)$ is the (relative) density current. The solution of the boundary problem (51) is easily found to be

$$\rho(r) = \rho_B \left(1 - \frac{R}{r}\right) \tag{53}$$

which gives

$$\kappa = k_S \stackrel{\text{def}}{=} 4\pi D R \rho_B \tag{54}$$

The above expression is widely known as the *Smoluchowski encounter rate* and predicts a linear dependence of the rate with the concentration of B particles.

Now the interesting part. The encounter rate under the (seemingly) same hypotheses as the above simple calculation can be computed from the N-body survival probability by making use of equation (50). By doing so, one gets

$$\kappa = \frac{k_{\rm S}}{1 - e^{k_{\rm S}\tau}\sqrt{\pi k_{\rm S}\tau}\,\mathrm{erfc}(\sqrt{k_{\rm S}\tau})} \tag{55}$$

where $\tau = R^2/\pi D$. If we introduce the packing fraction ϕ

$$\phi = \frac{4\pi}{3}\left(\frac{R}{2}\right)^3 \rho_B \tag{56}$$

it is not difficult to realize that

$$k_{\rm S}\tau = 4R^3\rho_B = \frac{24\,\phi}{\pi}$$

This leads to

$$\frac{\kappa}{k_{\rm S}} = \frac{1}{1 - e^{\sqrt{24\,\phi/\pi}}\sqrt{24\,\phi}\,\mathrm{erfc}(\sqrt{24\,\phi/\pi})} = 1 + \sqrt{24\,\phi} + 24\,\phi\left(1 - \frac{2}{\pi}\right) + \mathcal{O}\left(\phi^{3/2}\right) \tag{57}$$

Hence, we see that, since the N-body survival probability is not a pure exponentially decreasing function of time, the steady-state rate κ does not simply equal the Smoluchowski rate k_S. Rather, it is an increasing function of the trap concentration ϕ. The amazing thing is that the literature is full of pieces of work where this fact is not recognized, and the expansion (57) is (re)derived in many ways with the aim of describing many-body effects! As a side remark, we observe that the Smoluchowski rate would be recovered from equation (50) only if the N-body survival probability were a simple exponential, $S(t) = \exp[-k_S t]$.

SPECTRAL TREATMENT OF THE TRAPPING PROBLEM

The trapping problem is a much more general problem than described above. In general, let us consider a particle that diffuses in a confined volume Ω also hosting a static configuration of traps of arbitrary shape. This is schematically drawn in Fig. 2. The union of the trap surfaces can be considered as the pore (external) surface and that is where particles diffusing within the pore get absorbed. Let $\partial\Omega$ represent the pore surface. The trapping problem can be cast in the form of the following boundary-value problem

$$\begin{aligned} \frac{\partial\rho}{\partial t} &= D\nabla^2\rho + \rho_0\delta(t) \\ \rho|_{\partial\Omega} &= 0 \end{aligned} \tag{58}$$

The initial condition, enforced through the Dirac delta function $\delta(t)$, is $\rho(\boldsymbol{r}, t = 0) = \rho_0$. Let us indicate with ϕ_n the orthonormal eigenfunctions [5] of the Laplacian operator satisfying the boundary conditions in (58),

$$\nabla^2\phi_n = -\lambda_n\phi_n, \qquad \rho|_{\partial\Omega} = 0 \tag{59}$$

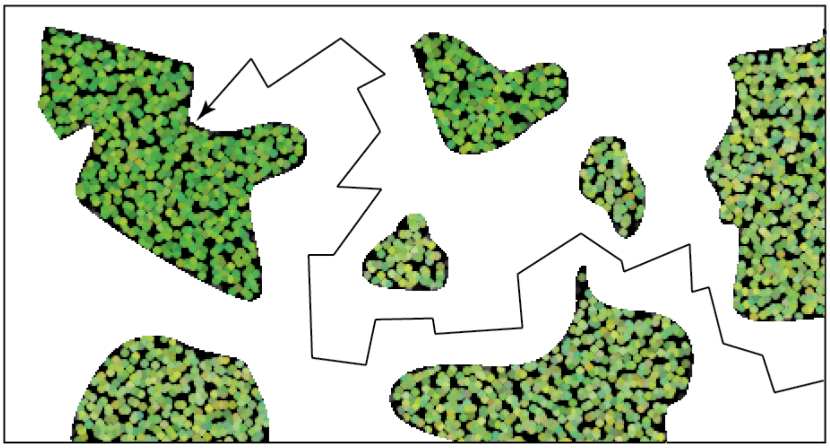

FIG. 2: Schematic illustration of a particle diffusing within a pore Ω (white space) and getting trapped at the pore surface $\partial\Omega$. The traps (colored objects) are characterized by absorbing surfaces (the pore surface).

Then solutions of the boundary-value problem (58) can be expressed as linear combinations of the basis eigenfunctions

$$\rho(\boldsymbol{r},t) = \rho_0 \sum_n a_n e^{-t/\tau_n} \phi_n(\boldsymbol{r}) \tag{60}$$

where $\tau_n = 1/D\lambda_n$.

At long times the largest relaxation time τ_1 dominates. It is important to stress that the the principal (largest) relaxation time is determined by the timescale associated with diffusion within the largest pores in the system.

The initial condition and the normal mode expansion (66) imply that

$$\sum_{n=1}^{\infty} a_n \phi_n(\boldsymbol{r}) = 1 \tag{61}$$

The orthonormality condition for the eigenfunctions $\{\phi_n\}$ reads

$$\frac{1}{\Omega}\int_\Omega \phi_n(\boldsymbol{r})\phi_m(\boldsymbol{r})\, d^3\boldsymbol{r} = \delta_{nm} \tag{62}$$

Comparison with the normalization condition (61) gives the explicit expression for the expansion coefficients a_n

$$a_n = \frac{1}{\Omega}\int_\Omega \phi_n(\boldsymbol{r})\, d^3\boldsymbol{r} \tag{63}$$

The normal modes also form a complete basis. To show this, let us take the square of equation (61) and integrate over the trap-free volume

$$\sum_{n=1}^{\infty}\sum_{m=1}^{\infty} a_n a_m \frac{1}{\Omega}\int_\Omega \phi_n(\boldsymbol{r})\phi_m(\boldsymbol{r})\, d^3\boldsymbol{r} = \frac{1}{\Omega}\int_\Omega d^3\boldsymbol{r}$$

From equation (62) one has

$$\sum_{n=1}^{\infty} a_n^2 = 1 \tag{64}$$

We observe, in passing, that for an arbitrary initial condition $\rho(\boldsymbol{r}, t = 0) = q(\boldsymbol{r})$, one has

$$b_n = \frac{1}{\Omega} \int_\Omega q(\boldsymbol{r})\phi_n(\boldsymbol{r})\, d^3\boldsymbol{r} \tag{65}$$

which corresponds to an expansion of the type (the coefficient b_n have now the dimension of a concentration)

$$\rho(\boldsymbol{r}, t) = \sum_{n=1}^{\infty} b_n e^{-t/\tau_n} \phi_n(\boldsymbol{r}) \tag{66}$$

The survival probability $S(t)$ for a walker diffusing in the trap-free region is defined as

$$S(t) = \frac{1}{\Omega} \int_\Omega \frac{\rho(\boldsymbol{r}, t)}{\rho_0}\, d^3\boldsymbol{r} \tag{67}$$

By using the normal mode expansion (61), we obtain

$$S(t) = \sum_{n=1}^{\infty} a_n^2 e^{-t/\tau_n} \tag{68}$$

The mean survival time τ is given by (see also equation (50))

$$\langle \tau \rangle = \int_0^\infty S(t)\, dt = \sum_{n=1}^{\infty} a_n^2 \tau_n \tag{69}$$

In the thermodynamic limit, $\Omega, V \to \infty$ with $\Omega/V = \phi$ (volume fraction of the trap-free region), ergodicity enables us to equate ensemble and volume averages of some stochastic function $f(\boldsymbol{r})$. So that

$$\langle f \rangle = \lim_{V\to\infty} \frac{1}{V} \int_\Omega f(\boldsymbol{r})\, d^3\boldsymbol{r} \tag{70}$$

Accordingly, equations (62) and (63) become, respectively

$$\frac{1}{\phi} \langle \phi_n \psi_n \rangle = \delta_{nm} \tag{71}$$

and

$$a_n = \frac{1}{\phi} \langle \psi_n \rangle \tag{72}$$

An important theorem [6] states that

For random porous media of arbitrary microstructure of porosity ϕ (volume fraction occupied by the trap-free region), the mean survival time is bounded from above and below in terms of the principal relaxation time τ_1 as follows

$$a_1^2 \tau_1 \le \langle \tau \rangle \le \tau_1$$

where

$$a_1 = \frac{1}{\phi} \langle \psi_1 \rangle$$

Survival probability in a single spherical pore

Let us consider the trapping problem inside a single spherical cavity. The Laplacian eigenfunctions are solutions of the following equation

$$r^2\phi_n'' + 2r\phi_n' + (\lambda_n r)^2\phi_n = 0 \tag{73}$$

The solutions are linear combinations of the two spherical Bessel function of order zero

$$\phi_n(r) = A\left[\frac{\sin\lambda_n r}{\lambda_n r}\right] - B\left[\frac{\cos\lambda_n r}{\lambda_n r}\right] \tag{74}$$

where A and B are constants to be determined through the boundary conditions. In the limit $r \to 0$ we must require that $\phi_n < \infty$, which means $B = 0$. Moreover, at the (interior) spherical surface $r = R$ we have to enforce absorbing boundary conditions $\phi_n(R) = 0$. This means that

$$\lambda_n = \frac{n\,\pi}{R} \quad n = 1, 2, \ldots$$

The normalization conditions fixes the other arbitrary constant ($\Omega = 4\pi R^3/3$)

$$\frac{1}{\Omega}\int_\Omega \phi_n(r)\, d^3\boldsymbol{r} = 1 \Longrightarrow A = \sqrt{\frac{2}{3}}n\,\pi$$

Thus, the expansion coefficients a_n can be calculated through equation (63). The result is

$$a_n = \frac{(-1)^{n+1}\sqrt{6}}{n\,\pi}$$

so that the survival probability can be finally computed by means of equation (69). We get

$$S(t) = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{e^{-t/\tau_n}}{n^2} \tag{75}$$

with

$$\tau_n = \frac{R^2}{\pi^2 n^2 D} \tag{76}$$

The largest relaxation time determining the tail of the survival probability is thus $\tau_1 = R^2/\pi^2 D$. The average lifetime is given by

$$\langle\tau\rangle = \int_0^\infty S(t)\, dt = \frac{6R^2}{\pi^4 D}\sum_{n=1}^{\infty}\frac{1}{n^4} = \frac{R^2}{15\pi^4 D}$$

a classical result.

THE TRAPPING PROBLEM ON A GRAPH

Let us consider a walker diffusing on a graph containing N nodes. The graph is uniquely specified by the connectivity matrix

$$c_{ij} = \begin{cases} 1 & \text{if a link exists between nodes } i \text{ and } j \\ 0 & \text{otherwise} \end{cases}$$

The connectivity of the i-th site is thus defined as

$$k_i = \sum_{j=1}^{N} c_{ij}$$

This means that from a given site m the walker jumps with a given rate (probability per unit time) $w_{m\to j}$ to one of the k_m sites that share a link with it. This process is described by the following master equation

$$\frac{dP_m(t)}{dt} = \sum_{j=1}^{N} c_{jm} w_{j\to m} P_j(t) - \left(\sum_{j\neq m=1}^{N} c_{jm} w_{m\to j} \right) P_m(t) \tag{77}$$

where $P_m(t)$ is the probability that the walker be at site (node) m at time t.

As in the trapping problem in the continuum, we imagine that certain sites are labeled (once for all) as traps and act as sinks for the walker. We want to estimate the average lifetime of the walker and the its survival probability as a function of time. For that we shall restrict to random (Erdös-Rény) graphs, that is graphs where all nodes are connected with the same fixed probability p, or random regular graphs (constant connectivity is also enforced). We note that the average lifetime can also be computed (we shall maybe do it later) as a mean-first passage time, which is not difficult to compute for diffusion on a graph).

Let us imagine to label the n nodes $i_1, i_2, \ldots, i_n$ as traps. From each trap there are k_{i_p}, $p = 1, 2, \ldots, n$ links emanating towards its neighboring nodes. The total number of links emanating from all traps is thus

$$K_n = \sum_{p=1}^{n} k_{i_p}$$

The probability q that the walker during its diffusive motion hop on one of these K_n links (being thus absorbed) is proportional to the corresponding fraction

$$q = A \frac{K_n}{N\langle k\rangle}$$

where

$$\langle k\rangle = \frac{1}{N} \sum_{i=1}^{N} k_i$$

is the average connectivity of the graph. Let us consider a certain number of walkers n_w, that do not see each other in their diffusive motion in the graph. Their density at time t is $\rho(t) = n_w(t)/N$. In the absence of the traps, the master equation (77) conserves the number of walkers, $\rho = const.$. In the presence of the n traps, the density of walkers will decrease exponentially according to

$$\frac{d\rho}{dt} = -q\rho$$

that is

$$S(t) = \frac{\rho(t)}{\rho(0)} = \exp\left[-\frac{AK_n}{N\langle k\rangle}\, t \right] \tag{78}$$

This should be regarded as a partial answer, as the total number of links emanating from the traps K_n is not specified.

The above expression for the survival probability is valid under the hypothesis that the fraction of links connecting traps among them is negligible. This amounts to require that all links emanating from a trap connect to a non-trap node. The fraction of non-trap nodes is

$$\frac{N-n}{N}$$

In a random graph links exist independently of one another. Then the probability that all K_n links extend to non-trap nodes is

$$\left(\frac{N-n}{N}\right)^{K_n} = \left(1-\frac{n}{N}\right)^{K_n} \approx 1-\frac{n^2\langle k\rangle}{N}$$

where we have used $\langle K_n\rangle \approx n\langle k\rangle$. This is $\mathcal{O}(1)$ if the following condition is respected

$$n \ll \sqrt{\frac{N}{\langle k\rangle}} \tag{79}$$

This is also the condition for the expression (78) to hold. Let us see how to calculate $S(t)$ in the two above mentioned cases.

Random regular graphs

In a random regular graph $k_i = k$. Thus

$$K_n = \sum_{p=1}^{n} k_{i_p} = nk$$

Hence

$$S(t) = e^{-Act}$$

where $c = n/N$ is the trap concentration.

Erdös-Rény graphs

In a random graph the probability distribution of connectivity is Poisson

$$P(k) = \frac{\langle k\rangle^k e^{-\langle k\rangle}}{k!} \tag{80}$$

Single trap In this case K_n is nothing but the connectivity of the trap. Therefore, the global survival probability will be given by averaging the single-K_n survival probability over the distribution (80), that is

$$\begin{aligned} S(t) &= \sum_{k=1}^{\infty} \frac{\langle k\rangle^k e^{-\langle k\rangle}}{k!} \exp\left[-\frac{Ak}{N\langle k\rangle}\,t\right] \\ &\simeq \exp\left[-\langle k\rangle\left(1-e^{-At/N\langle k\rangle}\right)\right] \end{aligned} \tag{81}$$

The above sum starts from $k = 1$ as we consider that there are no traps on isolated nodes. This amounts to neglect $P_0 = e^{-\langle k\rangle}$, which is reasonable if $\langle k\rangle$ is large enough.

Many traps The sum of n Poisson variables is still a Poisson variable, with average given by n times the single one. This means that

$$P(K_n) = \frac{[n\langle k\rangle]^k e^{-n\langle k\rangle}}{k!} \tag{82}$$

By following the same line of reasoning as for the single-trap case, we have

$$\begin{aligned} S(t) &= \sum_{k=n}^{\infty} \frac{[n\langle k\rangle]^k e^{-n\langle k\rangle}}{k!} \exp\left[-\frac{Ak}{N\langle k\rangle}\,t\right] \\ &\simeq \exp\left[-n\langle k\rangle\left(1 - e^{-At/N\langle k\rangle}\right)\right] \end{aligned} \tag{83}$$

The sum starts at $k = n$ as this is the lowest possible value for K_n, corresponding to only one link per trap. We note that

1. For $t \ll N\langle k\rangle$ one recover the regular random graph result, $S(t) \propto \exp[-Act]$.
2. For later times, the survival probability does not depend on the trap concentration only (as at early times). Rather, it depends on n and N separately. This is because at long times the configurations with small values of K_n contribute the most, and these scale as n. However, the probability that a particle falls on a trap still scale as the total number of links, that is $\simeq N\langle k\rangle$.

   As a further demonstration of this feature, one can calculate the average lifetime $\langle\tau\rangle$ from

   $$\langle\tau\rangle = \int_0^{\infty} S(t)\,dt$$

   The result is

   $$\langle\tau\rangle = \frac{1}{A\,n\langle k\rangle c} + \gamma + \log[n\langle k\rangle] + \mathcal{O}\left(\frac{1}{N}\right)$$

   where γ is the Eulero-Mascheroni constant.

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[1] This is actually the major part of one of the famous papers by Albert Einstein published in the *annus mirabilis 1905*
[2] The quoted expression corresponds to our choice $p = 1$.
[3] Note that we could have chosen an arbitrary length to make the argument of the logarithm non-dimensional.
[4] This terminology arises from the study of fluorescence quenching experiments, where one type of particles are excited by laser pulses, while the other kind of particles is able to quench them to the ground state upon encounter at the contact distance R
[5] That a complete set of orthonormal eigenfunctions of the Laplacian operator with Dirichlet-type boundary conditions on $\partial\Omega$ exist is guaranteed by the powerful ...... theorem.
[6] See S. Torquato, Random Heterogeneous Materials, Springer, section 13.7.2.