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Irreversible bimolecular reactions with inertia: from the trapping to the target setting at finite densities

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Abstract

We investigate numerically pseudo-first-order irreversible bimolecular reactions of the type $A + B \rightarrow B$ between hard spheres undergoing event-driven Brownian dynamics. We study the encounter rate and the survival probability of A particles as functions of the packing fraction ϕ in the trapping (a single particle diffusing among static non-overlapping traps) and target (many traps diffusing in the presence of a single static target particle) settings, as well as in the case of diffusing traps and particles (full mobility). We show that, since inertial effects are accounted for in our simulation protocol, the standard Smoluchowski theory of coagulation of non-interacting colloids is recovered only at times greater than a characteristic time Δt , marking the transition from the under-damped to the over-damped regime. We show that the survival probability $S(t)$ decays exponentially during this first stage, with a rate $1/\tau_0 \propto \phi$. Furthermore, we work out a simple analytical expression that is able to capture to an excellent extent the numerical results for $t < \Delta t$ at low and intermediate densities. Moreover, we demonstrate that the time constant of the asymptotic exponential decay of $S(t)$ for diffusing traps and particles is k_S^{-1} , where $k_S = 4\pi(D_A + D_B)R\rho$ is the Smoluchowski rate.

Detailed analyses of the effective decay exponent $\beta = d[\log(-\log S(t))]/d(\log t)$ and of the steady-state encounter rate reveal that the full mobility and trapping problem are characterized by very similar kinetics, rather different from the target problem. Our results do not allow one to ascertain whether the prediction $S(t) \propto \exp(-at^{3/2})$ ($a = \text{const.}$) as $t \rightarrow \infty$ for the trapping problem in 3D is indeed recovered. In fact, at high density, $S(t)$ is dominated by short encounter times, which makes it exceedingly hard to record the events corresponding to the exploration of large, trap-free regions. As a consequence, at high densities the steady-state rate simply tends to $1/\tau_0$. Finally, we work out an analytical formula for the rate that shows a remarkable agreement with the numerics up $\phi = 0.4$.

(Some figures may appear in colour only in the online journal)

1. Introduction

The encounter dynamics of two species, say particles (A) and traps (B), provides a theoretical framework for describing

many processes in physics and biology, from bimolecular reactions in chemical and biochemical kinetics [1], to search strategies connected to issues in population dynamics of living agents [2, 3]. Often, first the (molecular) components

need to encounter diffusively, the specific (chemical) reaction taking place subsequently within the so-called encounter complex [1]. In many contexts, such as in a liquid environment, the latter part of the process is typically much quicker, which makes the overall process diffusion-limited.

Despite the first quantitative account of such processes in the context of chemical kinetics dating back one century to Smoluchowski's theory of coagulation of colloids [4], many important questions still remain unanswered. In particular, things get rather complicated at high densities, that is, in crowded conditions [5–9], a situation which is highly relevant in many domains in biology and chemistry, such as association, folding and stability of proteins [10, 11] and bimolecular reactions in solution [12–16], including enzyme kinetics [17], but also in the dynamics of active agents [2].

In some contexts, inertial effects should also be taken into account in the dynamics of the reacting species. Despite some work having been done to assess the role of inertial effects on diffusion-guided reactions [18–26], how these get modulated at high densities and how this in turn shapes the rate remains largely unknown. It is important to stress that inertial effects and, more generally, ballistic-to-diffusive transitions are important in many contexts. In viscoelastic solids, for example, diffusion can be accompanied by structural relaxation [27], making inertial effects of practical relevance. Recently, the effect of mass on particle diffusion in the chemical reaction of muonium with oxygen in aqueous solution has been studied by electron spin exchange [28]. Inertial effects are also of relevance in the coagulation of aerosol particles [29] and in the dynamics of solvate ions at very short time scales [30]. It is interesting to observe that deviations from diffusive behaviors are observed in many other contexts where crowding effects are important, such as the diffusion and encounter dynamics of protozoa [2] and, more generally, the motion involved in animal search strategies [3].

Smoluchowski's theory maps bimolecular encounters between uncharged reactants in a fluid to an effective two-body relative diffusion problem that can be solved exactly. However, despite the widely held belief that low density is the only hypothesis underlying such a reduction, Szabo was the first to show that the situation is much subtler than that. In fact, even at low density, only if one of the two partners is immobilized, i.e. its diffusion constant vanishes, and much more diluted than the other, does the low-density hypothesis allow one to map the full N -body problem to an effective two-body one [31]. Needless to say, the situation is indeed exceedingly hard even at low densities if both species are diffusing [32]. To summarize, a single immobilized A particle surrounded by a low-density fluid of B particles is the minimum set of requirements allowing one to map the full problem onto one of relative diffusion of an A – B pair. So much at vanishing densities.

A moment's thought should be enough to convince oneself that the above conditions raise an additional subtle, yet important question, when the density is increased. How will finite-density effects affect the encounter rate if (i) the density of the B fluid is allowed to increase while the A particle

is fixed (the so-called target problem, also known as the Scavenger reaction [33]), (ii) the B traps are held immobilized at increasing density while the single A particle is now allowed to diffuse (the so-called trapping problem)? Intuition would suggest a certain specularity, at least at low trap densities. In this regime, both problems should be reducible to the same effective two-body problem. But is this intuitive specularity going to hold at finite density? To raise the bet further, what happens if the B trap density is increased in the case where both species are diffusing? In this paper we shall focus on the above questions through event-driven Brownian dynamics (EDBD) simulations of a hard-sphere fluid [34]. It should be emphasized that the trapping problem studied in this work refers to static configurations of non-overlapping spherical traps. Although our focus is on the concentration dependence of the A – B encounter rate in the three cases, we will discuss the behavior of the survival probability of A in the presence of a single trap B beforehand.

The paper is organized as follows. In section 1.1, we outline in some detail Smoluchowski's theory of diffusion-limited irreversible bimolecular encounters. First, in section 1.1.1 we report the standard calculation of the encounter rate from the stationary problem of relative pair diffusion. In section 1.1.2, we work out the calculation of the encounter rate from the survival probability. We dwell on these calculations for two reasons. First, because this is instrumental to a proper definition of the questions that we address in this paper. Second, because this information is available in the literature in a somewhat fragmented fashion. Hence, we also take advantage of this to provide a critical recollection of this important piece of theoretical knowledge. In section 2, we describe our simulations and discuss our main results. First, we describe how the survival probability changes as a function of the trap density in the target, trapping and intermediate setting. We show that the initial decay of the survival probability corresponds to the initial ballistic stage of the particle relative displacements. Beyond the ballistic–diffusive cross-over time, the survival probability is well described, at low and intermediate packing fractions, by the standard Smoluchowski theory. Furthermore, we work out a simple theory which shows an excellent agreement with the simulations in the ballistic regime at low and intermediate densities. Finally, in the last section we summarize the main results of this study.

1.1. Diffusion-limited bimolecular reactions: the trapping and target scenarios

Let us consider a system composed of two kinds of particles in a given fluid, say A and B , with diffusion coefficients and bulk densities D_A, D_B and ρ_A, ρ_B , respectively. All particles are assumed as non-interacting. We arbitrarily assign to the particles of type B the character of traps (sometimes also called quenchers⁵), while we still refer to particles of type A as the particles.

⁵ This terminology arises from the study of fluorescence quenching experiments, where one type of particles are excited by laser pulses, while the other particles are able to quench them to the ground state upon encounter at the contact distance R .

Our goal is to determine the rate of A – B encounters as a function of the densities. In order to simplify the problem, we assume that the particles A and B have the same radius $R/2$ (so that the encounter distance is R). The full problem is exceedingly hard to treat analytically. However, as it was first recognized by Smoluchowski in 1917 [4], one can reduce it to the effective two-body problem of relative diffusion of a single A – B pair under certain hypotheses. However, as already noted by Szabo [31], the commonly accepted hypothesis of high dilution, namely $\rho_A, \rho_B \ll 1$, is not enough. The first step towards the equivalent two-body problem is that one species be much more diluted than the other. Yet, not even this is enough.

To see this, 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 reads

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

where \mathbf{x}_A and the \mathbf{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 next step is to change to the reference frame of the A particle $\mathbf{r}_i = \mathbf{x}_i - \mathbf{x}_A$, $i = 1, 2, \dots, N$. By doing this, the Smoluchowski equation (1) becomes

$$\frac{\partial \rho(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t)}{\partial t} = (D_A + D_B) \sum_{i=1}^N \nabla_{r_i}^2 \rho(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t) + D_A \sum_{i \neq j=1}^N \nabla_{r_i} \cdot \nabla_{r_j} \rho(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t) \quad (2)$$

where $\rho(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t) = \int P(\mathbf{x}_A, \mathbf{r}_1 + \mathbf{x}_A, \mathbf{r}_2 + \mathbf{x}_A, \dots, \mathbf{r}_N + \mathbf{x}_A) d^3 \mathbf{x}_A$. 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), or for static A particles ($D_A = 0$). To summarize, the full N -body problem can be reduced to an equivalent two-body problem only under the following two assumptions.

- (i) One species must be much more diluted than the other, so that the full problem can be reduced to study the fate of a single particle surrounded by many particles of the other species.
- (ii) The diffusion coefficient of the highly diluted species should be much smaller than that of the other species (from N -body to two-body).

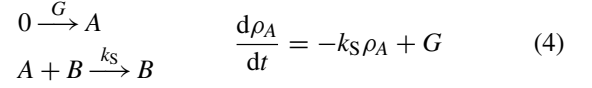
1.1.1. The encounter rate from the stationary problem.

Under the two above hypotheses, one can reduce the full problem to a two-body problem. In this case, the appropriate

equation simply reads

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = D \nabla^2 \rho(\mathbf{r}, t) \quad (3)$$

where $D = D_A + D_B$ is the relative diffusion coefficient and \mathbf{r} is the relative coordinate. The encounter problem can now be reformulated as the stationary state of the reactions



where particles A are created with rate G within a sea of B particles and disappear (i.e. they encounter a B mate) with rate k_S .

The usual way the encounter rate is calculated is by solving the following stationary boundary-value problem

$$\nabla^2 \rho(\mathbf{r}) = 0 \quad \begin{cases} \rho(|\mathbf{r}| = R) = 0 \\ \lim_{|\mathbf{r}| \rightarrow \infty} \rho(\mathbf{r}) = \rho_B. \end{cases} \quad (5)$$

The encounter is treated as an absorbing boundary condition (a sink) at the contact distance R . Moreover, the stationary solution of equation (4) is conveniently replaced by the condition of constant bulk density of the B particles far from the encounter distance. In this framework, k_S 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

$$\kappa = \int_{\mathcal{S}_r} \mathbf{J} \cdot \hat{\mathbf{n}} dS = 4\pi D r^2 \frac{\partial \rho}{\partial r} \quad (6)$$

where \mathcal{S}_r is a sphere of radius r and center at the origin (the sink) and $\mathbf{J} = -D \vec{\nabla} \rho$ is the (relative) density current. The solution of the boundary problem (5) is easily found to be

$$\rho(r) = \rho_B \left(1 - \frac{R}{r} \right) \quad (7)$$

which gives

$$k_S = 4\pi D R \rho_B. \quad (8)$$

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.

1.1.2. The encounter rate from the time-dependent problem.

Formula (8), despite being widely known and quoted as the result of Smoluchowski theory, is actually not what Smoluchowski predicted in 1917. In this section, we will develop the rest of the theoretical tools necessary for interpreting our numerical results.

The starting point is the computation of the survival and encounter⁶ probabilities for an isolated A – B pair initially at a distance r_0 , respectively $S_1(t|r_0)$ and $Q_1(t|r_0) = 1 -$

⁶ This would be the so-called recombination probability for a geminate pair of two oppositely charged particles.

$S_1(t|r_0)$. $S_1(t|r_0)$ can be calculated by solving the following boundary-value problem

$$\begin{aligned} \frac{\partial \mathcal{G}(\mathbf{r}, t|r_0, t_0)}{\partial t} &= D\nabla^2 \mathcal{G}(\mathbf{r}, t|r_0, t_0) + \frac{\delta(r-r_0)\delta(t-t_0)}{4\pi r^2} \\ \mathcal{G}(\mathbf{r}, t|r_0, t_0)|_{r=R} &= 0 \\ \lim_{r \rightarrow \infty} \mathcal{G}(\mathbf{r}, t|r_0, t_0) &< \infty \end{aligned} \quad (9)$$

where $\mathcal{G}(\mathbf{r}, t|r_0, t_0)$ is the Green function of the pair diffusion problem. 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 \mathbf{r} and $\mathbf{r} + d^3\mathbf{r}$, that is

$$S_1(t|r_0) = \int \mathcal{G}(\mathbf{r}, t|r_0, 0) d^3\mathbf{r}. \quad (10)$$

The solution of the boundary problem (9) is a standard text-book calculation (see for example [1]). The result is

$$\begin{aligned} \mathcal{G}(\mathbf{r}, t|r_0, 0) &= \frac{1}{8\pi r r_0 \sqrt{\pi D t}} \\ &\times [e^{-(r-r_0)^2/4Dt} - e^{-(r+r_0-2R)^2/4Dt}]. \end{aligned} \quad (11)$$

Equation (10) then yields

$$S_1(t|r_0) = 1 - \frac{R}{r_0} \operatorname{erfc}\left(\frac{r_0 - R}{2\sqrt{Dt}}\right) \quad (12)$$

where $\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-x^2} dx$ is the complementary error function. It should be noted that $\lim_{t \rightarrow \infty} S_1(t|r_0) = 1 - R/r_0 \neq 0$, i.e. the pair has a finite asymptotic probability of not recombining at all.

We wish now to compute the survival probability $S(t)$ of an A target in the presence of N diffusing traps B , initially in the configuration $\{\mathbf{r}_0^i = \mathbf{x}_i, i = 1, 2, \dots, N\}$. Since the traps are non-interacting, one can neglect correlations among them. Hence,

$$S(t|\mathbf{x}) = \prod_{i=1}^N S_1(t|\mathbf{x}_i). \quad (13)$$

The survival probability is then the average of the function (13) over many realizations of the initial configurations of the traps

$$\begin{aligned} S(t) &= \langle S(t|\mathbf{x}) \rangle = \lim_{N, V \rightarrow \infty} \frac{1}{V^N} \int \prod_{i=1}^N S_1(t|\mathbf{x}_i) d^3\mathbf{x}_i \\ &= \lim_{N, V \rightarrow \infty} \left[1 - \frac{\rho_B}{N} \int \mathcal{Q}_1(t|\mathbf{x}_i) d^3\mathbf{x}_i \right]^N \\ &= \exp \left[-\rho_B \int \mathcal{Q}_1(t|\mathbf{x}_i) d^3\mathbf{x}_i \right] \end{aligned} \quad (14)$$

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

Smoluchowski survival probability

$$S(t) = \exp \left[-k_S t \left(1 + \frac{2R}{\sqrt{\pi D t}} \right) \right] \quad (15)$$

where $k_S = 4\pi D R \rho_B$ is the Smoluchowski rate (8).

The encounter rate (or, equivalently, the average lifetime) of a pair can be computed from the knowledge of the N -body survival probability. One simply has

$$\kappa = \frac{1}{\langle \tau \rangle} = \left[\int_0^\infty \tau \mathcal{P}(\tau) d\tau \right]^{-1} = \left[\int_0^\infty S(t) dt \right]^{-1} \quad (16)$$

where $\langle \tau \rangle$ is the average lifetime of an A - B pair and $\mathcal{P}(t)$ is the lifetime density distribution. The last passage follows from the observation that the survival probability is nothing but the cumulative distribution of the density \mathcal{P} , i.e. $S(t) = \int_t^\infty \mathcal{P}(\tau) d\tau$. Note that the lifetime of an isolated pair is not well defined. If an attempt is made to use equation (16) with the single-pair survival probability (12), 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. This is not the case in the N -body problem, where an encounter always occurs, that is, $\lim_{t \rightarrow \infty} S(t) = 0$.

Proceeding on to calculate the encounter rate from the survival probability (15), one finally obtains

$$\kappa = \frac{k_S}{1 - e^{k_S \tau} \sqrt{\pi k_S \tau} \operatorname{erfc}(\sqrt{k_S \tau})} \quad (17)$$

where $\tau = R^2/\pi D$. Furthermore, one has $k_S \tau = 4R^3 \rho_B = 24\phi/\pi$, which leads to

$$\begin{aligned} \frac{\kappa}{k_S} &= \frac{1}{1 - e^{24\phi/\pi} \sqrt{24\phi/\pi} \operatorname{erfc}(\sqrt{24\phi/\pi})} \\ &= 1 + \sqrt{24\phi} + 24\phi \left(1 - \frac{2}{\pi} \right) + \mathcal{O}(\phi^{3/2}). \end{aligned} \quad (18)$$

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 a nonlinear function of the trap concentration ϕ .

It is interesting to note that the $\propto \sqrt{\phi}$ correction has been derived by many authors in many ways as the lowest-order finite-density correction [35, 36], while it also naturally appears in the above standard derivation, which is performed under the assumption of infinite dilution. The reason for this is, to our knowledge, still unknown.

The above setting is known as the target problem, as one is considering many B traps diffusing in the presence of a single stationary ($D_A = 0$) or at least slowly diffusing ($D_A \ll D_B$) A particle (the target) until the first trap hits it (see figure 1). Intuitively, as the full problem has been reduced to studying the relative diffusion of an isolated pair, one may think that the above theoretical framework should equally describe the opposite situation, namely a single A particle diffusing amidst a stationary configuration of B traps and getting absorbed at the first trap site encountered. This scenario is known as the trapping problem (figure 1).

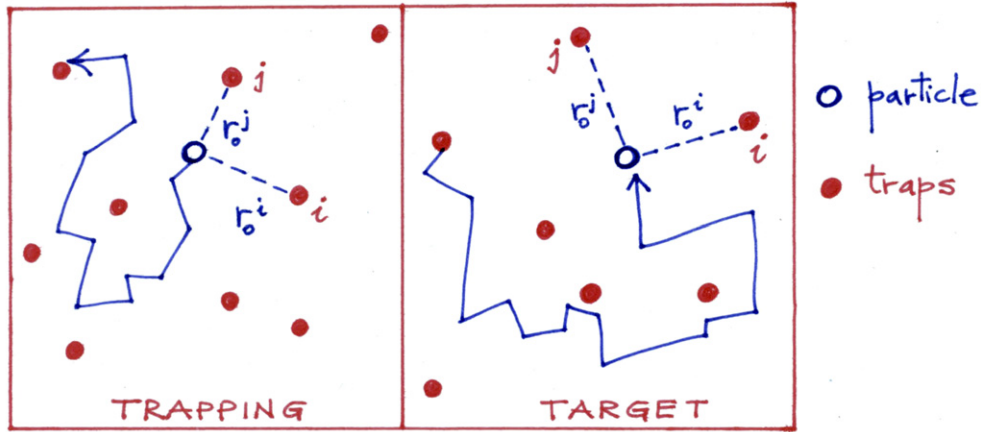


Figure 1. Schematic illustration of the trapping and target problems. The initial configuration of traps is indicated by the relative position vectors $\{r_0^i\}$.

However, equation (2) makes it clear that the target ($D_A = 0$) and trapping ($D_B = 0$) problems are by no means equivalent⁷. Of course, the two problems will indeed become equivalent in the case of infinite dilution of both species, as the relative diffusion of an isolated pair is then recovered exactly—for a single $A-B$ pair it does not obviously make any difference which partner is considered as immobilized, if any. However, if finite-density effects of the B fluid are the subject of investigation, the trapping and target settings are no longer expected to describe the same physical process, even if they can still be thought of implementations of the $A + B \rightarrow B$ reaction. Even more interestingly, as already remarked by Szabo *et al* [32], the case where both $D_A \neq 0$ and $D_B \neq 0$ provides yet another physical instance of the same reaction.

The important question then arises to characterize the encounter dynamics of the target, intermediate ($D_A \neq 0, D_B \neq 0$) and trapping problems as the concentration ρ_B is increased. This is one of the main purposes of the present work.

2. Numerical simulations

In order to provide an answer to the above questions, we simulated a fluid of $N = 1000$ identical hard spheres of radius $R/2$ in a box of volume V with periodic boundary conditions at fixed packing fraction $\phi = \pi NR^3/(6V)$. Particles have mass $m = 1$ and the simulations were carried out at a temperature $T = 1$. According to the above specifications, within each simulation we may have two types of particles, namely particles A and traps B , each particle in the system belonging either to the A or B class. The number of particles and traps are N_A and $N_B = N - N_A$, respectively. Particles can be immobile or mobile. The latter ones wander around according to event-driven Brownian dynamics (EDBD), i.e. their velocities are periodically reset, sampling from a Gaussian distribution, with a time interval equal to Δt . During the interval between two successive velocity rescaling operations, as described in [34], the system evolves according to Newtonian dynamics.

⁷ Even if the coordinate system in equation (2) is admittedly not the smartest possible choice for the trapping problem.

In EDBD the translational diffusion coefficient D in the infinite-dilution limit is

$$D = \frac{k_B T \Delta t}{2m} \quad (19)$$

where k_B is the Boltzmann constant and m is the mass of the particles. In all simulations we set $\Delta t = 0.05$, so that the diffusive regime in the infinite-dilution limit sets in for times $\gg 0.05$. The EDBD protocol is very efficient and, as an additional benefit, it allows one to explore inertial effects, as it reproduces an under-damped Langevin dynamics at times shorter than Δt [26]. This feature makes our numerical protocol particularly intriguing in view of studying crowding effects in the encounter dynamics. In fact, it is reasonable to imagine that at high densities inertial effects should become detectable as the average collision time decreases approaching Δt .

In section 2.1 we describe in detail the three different simulation protocols which we adopted for the target ($D_A = 0$), trapping ($D_B = 0$) and full-mobility ($D_A = D_B$) cases.

2.1. Target case

In a ‘target simulation’ we set $N_A = 1$ and the single particle is immobile, while traps are mobile. Let \mathcal{B} denote the ensemble of $N - 1$ traps. The simulation proceeds according to the following scheme.

- (i) Randomize the system for a time $\tau_{\text{rand}} = 1.0$. During this step all N particles are mobile and undergo Brownian motion according to EDBD.
- (ii) Set the velocity of particle p to 0, so that it is now immobile and has the label A . The remaining N_B traps are mobile and undergo Brownian motion according to EDBD. If a trap $t \in \mathcal{B}$ and the immobile A particle collide (encounter), we record the survival time, i.e. the time elapsed from the beginning of the present step.
- (iii) Re-label the immobile particle p as a mobile trap $\in \mathcal{B}$ and choose randomly a trap n different from t and p . Make the trap n the new immobile particle, i.e. $p = n$ is the new A particle.
- (iv) Go to step (i).

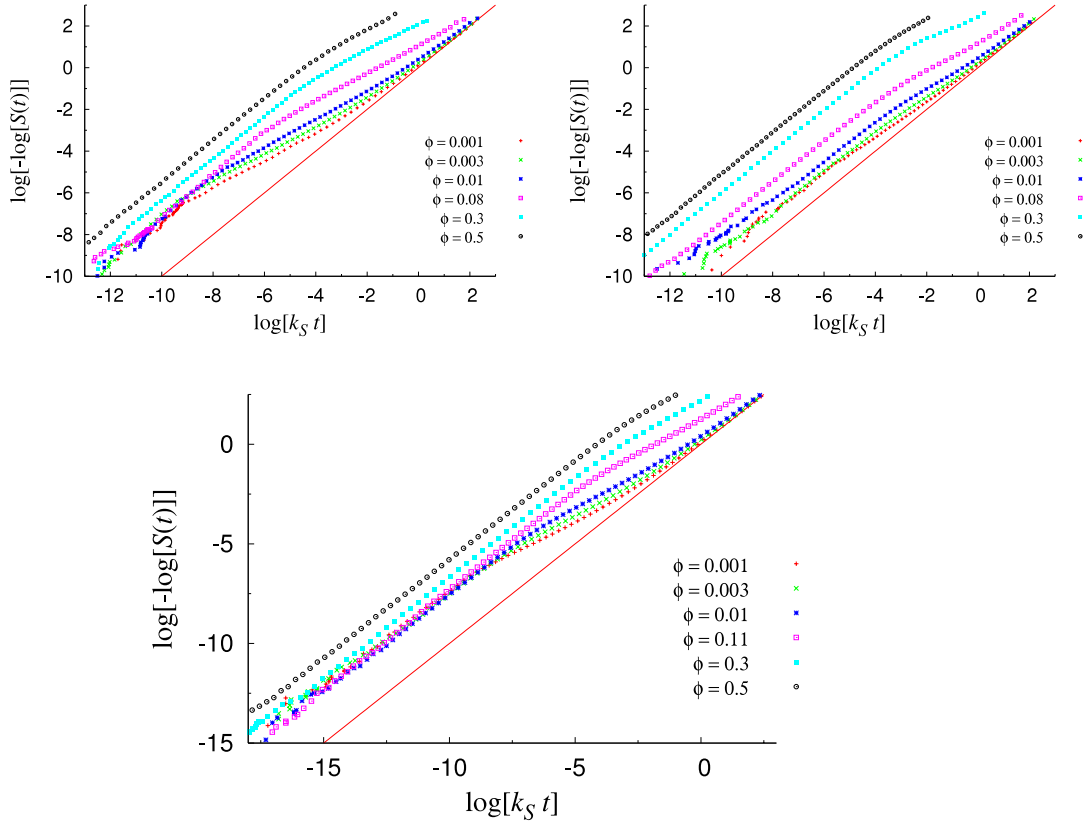


Figure 2. Survival probability versus time for the trapping (top left), target (top right) and $D_A = D_B$ case (bottom) at different packing fractions. Time is expressed in non-dimensional time units $k_S t$, where k_S is the Smoluchowski rate (8). In the above representation, the long-time limit of the Smoluchowski survival probability (15) is a straight line with slope one (red solid lines). The function $\log(x)$ denotes Neperian logarithm throughout this paper.

2.2. Trapping case

In a ‘trapping simulation’ we set $N_B = N - 1$, all these traps being immobile and randomly distributed, while the remaining A particle is mobile. Let \mathcal{B} denote the ensemble of the $N - 1$ traps. The simulation proceeds according to the following scheme.

- (i) Randomize the system for a time $\tau_{\text{rand}} = 1.0$. During this step all N particles are mobile and undergo Brownian motion according to EDBD.
- (ii) Set the velocity of the N_B traps to 0, so that they are now immobile, while the single particle p is mobile and undergoes Brownian motion according to the EDBD scheme. If an immobile trap $t \in \mathcal{B}$ and the mobile particle p collide (i.e. encounter), we store the survival time, i.e. the time elapsed from the beginning of the present step.
- (iii) Make the mobile particle p a trap so that $p \in \mathcal{B}$ and choose randomly a trap n different from t and p . Make the trap n the new mobile particle, i.e. $p = n$ is the new A particle.
- (iv) Go to step (i).

2.3. Full-mobility case

In the ‘full-mobility’ case we have $N_B = 0$ and the $N_A = N$ particles are all mobile. The simulation protocol in this case is the following.

- (i) Randomize the system for a time $\tau_{\text{rand}} = 1.0$. During this step all N particles are mobile and undergo Brownian motion according to EDBD.
- (ii) All particles positions evolve according to EDBD. If two particles p_1 and p_2 , which have not collided (i.e. encountered) since the beginning of the current step, encounter, we store the survival time, i.e. the time elapsed from the beginning of the present step to the current collision between p_1 and p_2 . When all N particles have collided, go to step (i).

2.4. Analysis of the survival probability

In figure 2 we show the survival probability versus time extracted from the numerics according to equation (16) for a choice of different packing fractions in the three cases. In our representation, $\log[-\log S(t)]$ versus $\log t$, a pure exponential corresponds to a straight line of slope one, while a stretched exponential $\simeq \exp[-(t/T)^\beta]$ corresponds to a straight line of slope β . Therefore, the Smoluchowski prediction (15) would be detectable as a straight line of slope $1/2$ at early times, crossing over to a straight line of slope one at a characteristic time of the order of $\tau = R^2/\pi D$. The numerics clearly show that this is not what is actually observed. Rather, we observe a cross-over from a first pure exponential, $\exp(-t/\tau_0)$, to the long-term Smoluchowski prediction, $S(t) \simeq \exp(-k_S t)$,

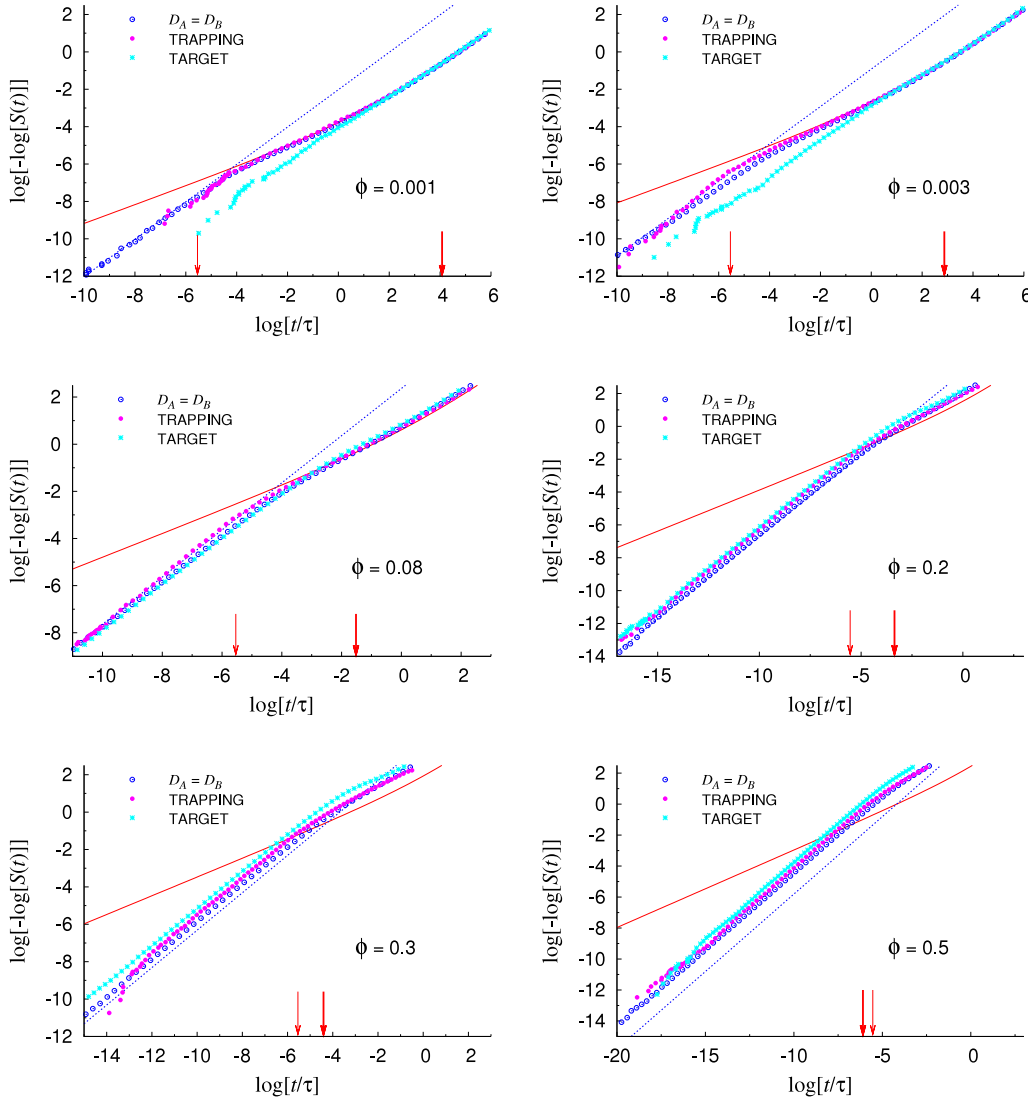


Figure 3. Survival probability for the trapping, intermediate and target problem at different packing fractions. Time is expressed in non-dimensional time units t/τ , with $\tau = R^2/\pi(D_A + D_B)$. The solid line is a plot of the Smoluchowski survival probability (15), the dashed line is a plot of the ballistic survival probability (26). The thin arrows mark the time $t = \Delta t$. The thick arrows mark the time $t = 1/\kappa$, where the rate κ is calculated through formula (16). Times are rescaled by a factor of two for the $D_A = D_B$ case in order to compare with the trapping and target settings.

with $k_S \tau_0 \ll 1$. It seems that, at least for the trapping and full-mobility cases, the time constant of the first exponential decay stage scales as ϕ^{-1} for low and intermediate packing fractions. In the non-dimensional units used in figure 2, this is easily understood from the good collapse of the data for such early trend at different packing fractions $\phi < 0.3$ and recalling that $k_S \propto \phi$. Note that this is certainly the case for the trapping and $D_A = D_B \neq 0$ case, while a different scaling seems to characterize such early exponential stage in the target problem (no collapse using the non-dimensional units $k_S t$). We shall return to this point in more detail later on in the paper.

Remarkably, we see that in the full-mobility case $S(t) \propto \exp(-k_S t)$ as $t \rightarrow \infty$, at least at low and intermediate packing fraction. It is known since the works of Redner and Kang [33] and Bramson and Lebowitz [37, 38] that $S(t) \propto \exp(-at)$ as $t \rightarrow \infty$, with $a = \text{const.} \propto \phi$. Therefore, our results allow us to determine that $a = k_S = 4\pi(D_A + D_B)R\rho$. Note that this

also means that the same scaling is valid at high densities, where it is exceedingly hard to record large encounter times to sample the tails of $S(t)$. Furthermore, our results agree with the accepted theoretical prediction of an exponential tail for the target problems as well [33, 39, 40]. Also in this case we find $S(t) \propto \exp(-k_S t)$ as $t \rightarrow \infty$.

In figure 3 we report the same data as in figure 2 grouped in a different fashion and with a different non-dimensionalization of the time axis. This representation helps make clearer a few facts. First, the time constant of the initial exponential decay is density dependent, as dictated by the different y-axis intercept. Furthermore, the full Smoluchowski prediction (15) is recovered, including a portion of the initial stretched exponential decay $\simeq \exp[-t^{1/2}]$ at a cross-over time of the order of Δt . This conclusion is valid to a good degree of confidence at low and intermediate packing fractions. At

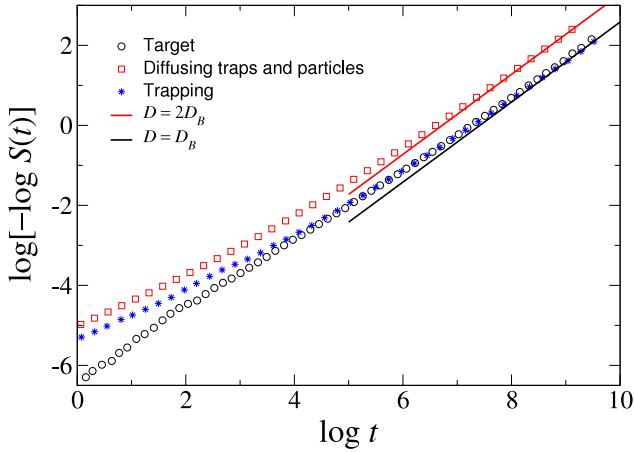


Figure 4. Survival probability versus time at $\phi = 0.001$. The solid lines are plots of the asymptotic decay $S(t) \propto \exp(-k_S t)$ with $k_S = 4\pi DR\rho = 24D\phi/R^2$, where $D = (D_A + D_B)$ is the relative diffusion coefficient, $D = D_B$ (trapping and target problems) and $D = 2D_B$ for diffusing traps and particles.

higher densities, as pointed out above, our data do not allow us to probe the asymptotic tails of $S(t)$.

Finally, it should be observed that our simulations appear to be in contradiction with recent results, reporting that the time constant of the asymptotic exponential decay of $S(t)$ for diffusing traps and particles only depends on the trap diffusion coefficient. This implies that the trapping and full-mobility survival probabilities should coincide asymptotically, in one and two dimensions [41] and also in three dimensions [42]. Figure 4 demonstrates that this is clearly not the case in our simulations, where the asymptotic exponential tail of $S(t)$ clearly depends on the relative diffusion coefficient $D = D_A + D_B$. This point clearly necessitates further investigation in order to assess the reasons for such discrepancies between our results and the analytical estimates in 3D reported in [42].

The situation is even more delicate for the trapping problem, where the predicted scaling is $S(t) \propto \exp(-at^{3/5})$ as $t \rightarrow \infty$ in three dimensions [43]. This prediction, valid for overlapping [44] and non-overlapping [45] traps, is a direct consequence of the existence of arbitrarily large trap-free regions that are explored diffusively by the particle [46]. Our data show a similar scenario in this case as for the trapping problem and for the case where both traps and particles move. This suggests an exponential scaling of the tails also at high density, where many-body effects are known to be responsible for the $\exp(-at^{3/5})$ scaling of the survival probability. This point goes beyond the aims of the present paper, but certainly deserves further accurate numerical investigation.

2.4.1. The effective exponent. A rather instructive way to examine the decay of the survival probability is to calculate the effective exponent β , defined as

$$\beta(t) = \frac{d[\log(-\log S(t))]}{d[\log t]}. \quad (20)$$

A unitary value of β signals a pure exponential law⁸, while a value $\beta < 1$ flags a stretched exponential decay.

⁸ With $\log(\dots)$ we indicate the Neperian logarithm.

The results of these calculations, performed through a super-low-noise Lanczos differentiator [47] are illustrated in figure 5. These calculations reinforce the finding that the trapping setting and the case where both species diffuse bear close resemblances to each other. In particular, both seem to be characterized by rather universal curves for the time dependence of the exponent β . The decay starts off exponentially, as fast encounters follow a ballistic dynamics, as we have seen above. Subsequently, the decay law slows down and asymptotically speeds up again, suggesting the recovery of a pure exponential at $t \simeq \tau = R^2/\pi D$ in all cases. The two cross-over times appear to be independent of density except for the target problem, where a similar dynamics is observed but the asymptotic recovery of a pure exponential decay appears to be ruled by a density-dependent phenomenon. As we have pointed out above, while these results are consistent with theoretical prediction of the tails of $S(t)$ for the trapping scenario and the case where particles and traps both move, they are at odds with the known prediction for the trapping problem in 3D, $\lim_{t \rightarrow \infty} \beta(t) = 3/5$. However, as this is directly connected to the fluctuations of the trap distribution [43], we should investigate the possibility that in our simulations we are limited in the size of trap-free regions and consequently we are under-estimating the weight of such configurations, which are known to determine the long-time tails of $S(t)$. To this end, we have performed simulations by doubling the linear size of our simulation boxes. The effective exponents calculated for the larger systems are shown in figure 6. Our results strongly suggest that finite-size effects do not alter the computation of the effective decay exponent of the survival probability, at least in the trapping setting and for the full-mobility case with $D_A = D_B$. Conversely, the target problem seems to display finite-size effects, even if it is not clear whether these impact or not the asymptotic value of the exponent. All in all, these results further strengthen the idea that trapping and full-mobility scenarios share numerous important features, while the target problem appears to display more idiosyncratic features. It is certainly true that the issue of what is the true asymptotic effective exponent deserves more detailed work beyond our double-size box simulations. This interesting and delicate point will assuredly be the subject of further analysis in the near future.

However, it should be remarked that the debate concerning the asymptotic tails of the survival probability is somewhat immaterial if one is only interested in describing the encounter rate. At large packing fractions, even if the tails of $S(t)$ are rather hard to capture numerically, the overall encounter kinetics is dominated by the first stage of the decay. Consequently, our simulations show that the steady-state rate tends to $1/\tau_0$ as the packing fraction grows beyond about 0.4. We will come back on this in more detail later on in the paper.

To summarize, the first important finding reported so far is that the survival probability in the case of diffusing traps and targets follows the asymptotic law $S(t) \simeq \exp(-k_S t)$, with $k_S = 4\pi(D_A + D_B)R\rho$. The second finding is that the Smoluchowski prediction for the survival probability is inaccurate at low times if inertial effects are considered. Interestingly, deviations from the Smoluchowski theory are

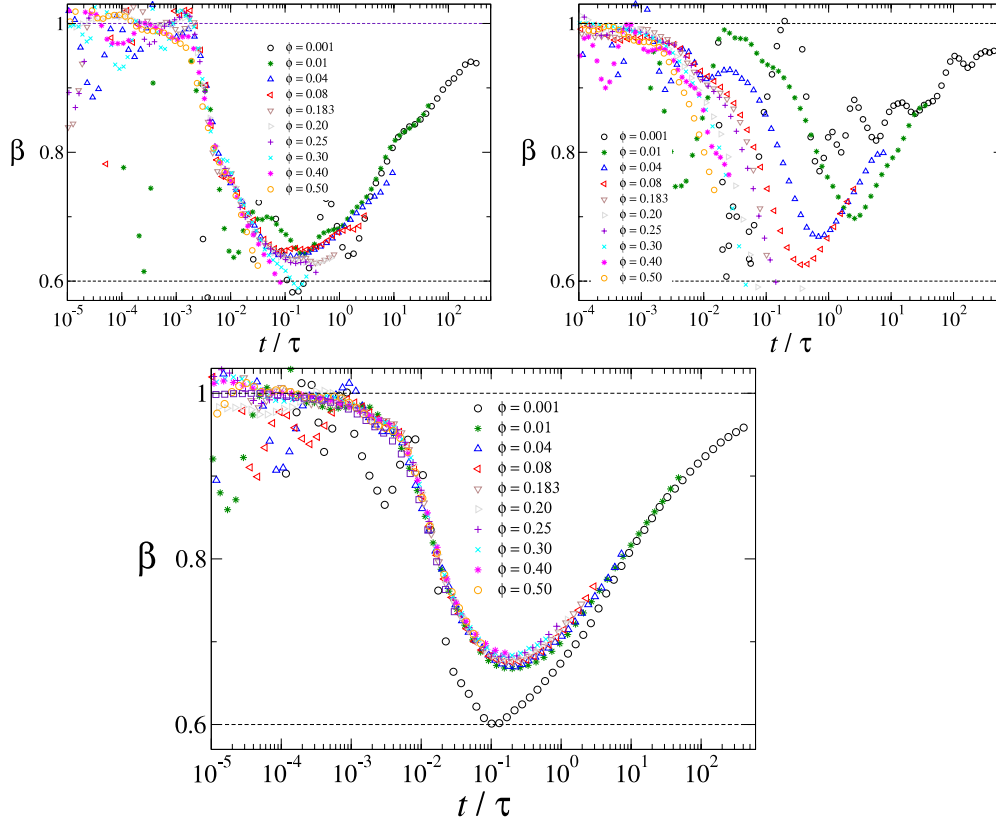


Figure 5. Effective decay exponent (20) of the survival probability versus time for the trapping (top left), target (top right) and $D_A = D_B$ case (bottom) at different packing fractions. Time is expressed in non-dimensional time units t/τ , with $\tau = R^2/\pi(D_A + D_B)$. The asymptotic exponent predicted for the trapping problem $\beta = 3/5$ is marked explicitly.

observed at high density, when the mean free path becomes comparable to the distance over which particle velocities relax to the thermal velocity. In the following, we will show how one can build a simple theory to calculate the survival probability in the ballistic regime.

2.4.2. Inertial effects: ballistic-to-diffusive transition. The first cross-over that we observe in the survival probability is dictated by a density-independent phenomenon, which is regulated by the time scale Δt . As we have proved recently [26], our simulation algorithm is able to reproduce inertial effects, which indeed play a leading role at times $\leq \Delta t$. Therefore, the observed cross-over is the equivalent of the transition from the under-damped regime (Fokker–Planck) to the over-damped (Smoluchowski) regime reported in [26]. In other words, such a cross-over reflects the transition from the ballistic to the diffusive regime, which has already been investigated in the diluted regime in the related context of annihilation reactions [19].

We wish to calculate the survival probability of a particle moving with a randomly oriented constant velocity amidst a static random configuration of traps. Whatever the direction of the velocity, the particle will see a linear distribution of traps, whose density λ is of the order of $\lambda = \rho_B \sigma^2$. Taking the linear cross section σ of the order of one diameter, one then obtains

$$\lambda = \rho_B \pi R^2 = \frac{6\phi}{R}. \quad (21)$$

Consequently, the distribution of distances $P_x(x)$ between consecutive traps along the direction of motion of the particle will be given by

$$P_x(x) = \left(\frac{6\phi}{R}\right) e^{-6\phi(x/R)}. \quad (22)$$

The simplest assumption is that the particle travels on average with the thermal velocity $v_{\text{th}} = \sqrt{\langle v^2 \rangle}$, which in the EDBD scheme is given by (recall that $D_A = k_B T \Delta t / 2m$)

$$v_{\text{th}} = \sqrt{\frac{6D_A}{\Delta t}}. \quad (23)$$

Consequently, we assume that the distribution of velocities $P_v(v)$ is a Dirac delta

$$P_v(v) = \delta(v - v_{\text{th}}). \quad (24)$$

The distribution of the particle lifetimes $t = x/v$, $\mathcal{P}(t)$, can now be computed through a straightforward procedure. Let us consider the joint distribution $P_{xv}(x, v) = P_x(x)P_v(v)$ and let us perform the two-dimensional change of variables $(x, v) \rightarrow (t = x/v, z = v)$. The distribution $\mathcal{P}(t)$ can then be calculated by marginalizing the joint distribution $P_{tz}(t, z)$ with respect to z , namely

$$\mathcal{P}(t) = \int_0^\infty z P_x(zt) P_v(z) dz \quad (25)$$

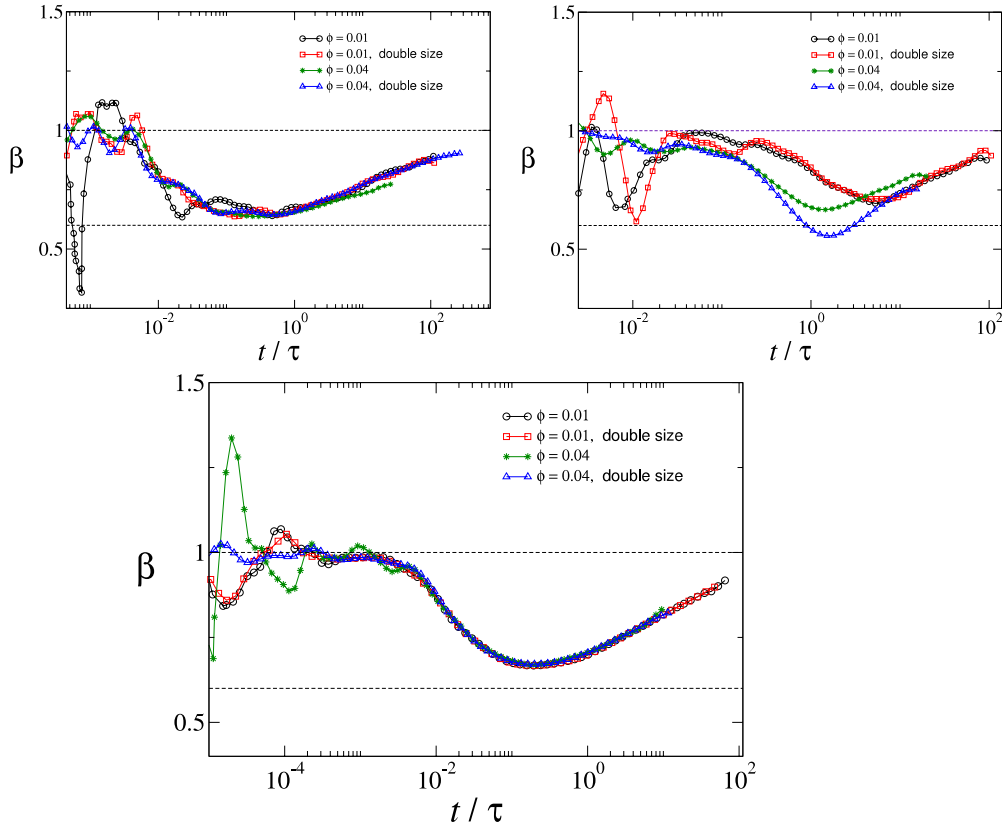


Figure 6. Study of finite-size effects. Effective decay exponent (20) of the survival probability versus time for the trapping (top left), target (top right) and $D_A = D_B$ case (bottom) for two different sizes of the simulation box and two different values of the packing fraction. The number of particles is $N = 8000$ for the large simulation box (two-fold increase of the box side, hence eight-fold increase in volume). Time is expressed in non-dimensional time units t/τ , with $\tau = R^2/\pi(D_A + D_B)$. The asymptotic exponent predicted for the trapping problem $\beta = 3/5$ is marked explicitly.

which is normalized to one, as it can easily be checked by straightforward integration. The required survival probability can finally be computed through equation (16). Recalling expressions (22) and (24), one has

$$\begin{aligned}
 S(t) &= \int_t^\infty d\tau \int_0^\infty z P_x(z\tau) P_v(z) dz \\
 &= \int_0^\infty P_v(v) e^{-6\phi(vt/R)} dv \\
 &= e^{-6\phi(v_{th}t/R)}.
 \end{aligned}
 \tag{26}$$

Hence, we get an exponentially decreasing survival probability for $t \leq \Delta t$, with characteristic decay time given by

$$\tau_0 \stackrel{\text{def}}{=} \frac{1}{6\phi} \left(\frac{R}{v_{th}} \right) = \frac{1}{6\phi} \sqrt{\frac{\pi \tau \Delta t}{6}}
 \tag{27}$$

where we have reintroduced the characteristic diffusive time $\tau = R^2/\pi D_A$ (see again equation (17)). We note that the above result is consistent with the finding of Majumdar and Bray for a ballistic tracer particle with constant velocity in a fluid of diffusing traps [18]. A plot of formula (27) against the initial decay times determined numerically is shown in figure 7. The agreement between our simple theoretical approach and the numerics is excellent for low and intermediate packing fractions. Furthermore, as can be seen

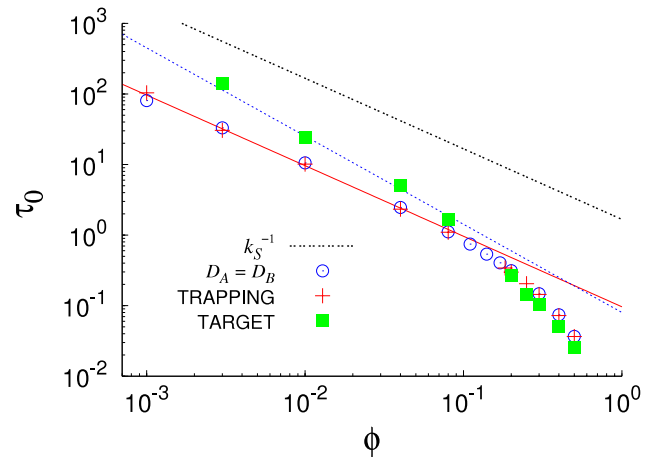


Figure 7. Time constant of the initial exponential decay of the survival probability as a function of the packing fraction (symbols). The solid line is a plot of $\tau_0(\phi)$ as predicted by equation (27), while the dashed line is an inverse-power law of the type $\phi^{-5/4}$. The inverse Smoluchowski rate is also reported for comparison (double dotted line).

from figure 3, the agreement of equation (26) with the survival probability extracted from the numerics is best for the trapping configuration. This is of course expected in view of the nature of the arguments employed in the above calculation.

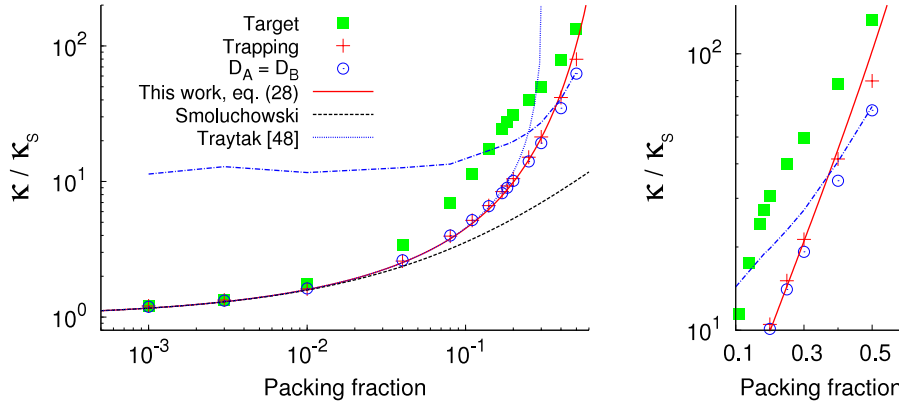


Figure 8. Encounter rate computed from the numerical survival probability according to the prescription (16) normalized by the Smoluchowski rate $k_S = 4\pi(D_A + D_B)R\rho_B$. The solid (red) line is the prediction of the modified Smoluchowski theory, equation (28), the dashed (black) line is the prediction of standard Smoluchowski theory equation (17), while the blue dot-dashed line is the ballistic rate $k_0 = 1/\tau_0$ (same data as in figure 7 for $D_A = D_B$). The right panel shows a close-up of the same plot at the high-density end.

2.5. The encounter rate

The encounter rate is an integrated measure of the encounter dynamics, as is clear from its very definition (16). Therefore, a number of important facts about the encounter dynamics are concealed in a simple plot of the rate, which is the reason we discussed the distinctive features of the survival probability at length earlier.

Figure 8 illustrates the encounter rate as a function of density for the three settings. The first obvious observation is that the rate is a monotonously increasing function of the density up to the highest values of the packing fraction considered in this study. The second, less obvious piece of evidence is that the full-mobility case shows almost no difference with respect to the trapping setting. The rate calculated in the target problem, instead, increases rather faster with density. Remarkably, the rate for the target problem is always greater than that found in the other two cases. This agrees with analytical calculations of the ballistic-to-diffusive transition in the one-dimensional target and trapping problems performed by Berezhkovskii *et al* [21].

Furthermore, as expected, at low density the prediction of the full Smoluchowski theory, equation (17), is found to describe the data to an excellent extent. This is because, despite the fact that Smoluchowski theory is fundamentally incorrect at short times if inertial effects are taken into account, the relative weight of short times in the computation of rate through the integral (16) is negligible. Conversely, at very high densities the observed rate is well approximated by the early-stage ballistic rate $1/\tau_0$, as the short-time portion of the encounter time axis provides the largest contribution to the integral in this regime. The formula worked out by Traytak in 1995 for the trapping problem through an original renormalization group-based approach, $\kappa/k_S = 1 + \sqrt{24\phi}/[1 + (1 - 2/\pi)\sqrt{24\phi}]$ [48], provides a good description beyond the Smoluchowski approximation up to intermediate densities.

In order to find an empirical formula allowing one to interpolate the measured rate up to relatively high densities, where the rate is almost completely dominated by ballistic

events, it is possible to employ an argument present, among other sources, in the 1980 paper by Kayser and Hubbard [45]. The probability of occurrence $p(r)$ of trap-free spherical regions of radius r and volume $v_r = 4\pi r^3/3$ for non-overlapping traps can be obtained from the corresponding probability calculated for totally random (Poisson) traps, $p(r) = \rho \exp(-\rho v_r)$ (ρ being the trap concentration) by simply replacing the trap density with the full equation of state, i.e. $\rho \rightarrow \rho Z(\phi)$, where $Z(\phi)$ is the compressibility factor. This suggests the idea of the replacement $\phi \rightarrow \phi Z(\phi)$ in the rhs of equation (18), which gives

$$\frac{\kappa}{k_S} = \frac{1}{1 - e^{24\phi Z(\phi)/\pi} \sqrt{24\phi Z(\phi)} \operatorname{erfc}(\sqrt{24\phi Z(\phi)/\pi})}. \quad (28)$$

A plot of the empirical formula (28) with $Z(\phi)$ approximated through the Carnahan–Starling (CS) equation of state, $Z(\phi) = (1 + \phi + \phi^2 - \phi^3)/(1 - \phi)^3$ [49], shows an excellent agreement with the numerical data for the trapping and full-mobility problems (see figure 8).

It appears clear that equation (28) provides an excellent approximation up to packing fractions $\phi \geq 0.4$, where the steady-state rate becomes completely dominated by ballistic encounters and therefore $\kappa \approx 1/\tau_0$ (see again figure 8)—despite the CS approximation still being valid beyond $\phi = 0.4$, inertial effects cannot be captured by equation (28) (see also the close-up of the high-density end in figure 8).

3. Conclusions

In this paper we have reported the results of extensive event-driven Brownian dynamics simulations of irreversible bimolecular reactions of the type $A + B \rightarrow B$ between hard spheres in the trapping, target and full-mobility settings. In the first case, a single particle wanders among static configurations of non-overlapping traps, while in the target setting a fluid of moving traps annihilate a static target sphere. The last case is when particles and traps are both mobile. Our algorithm incorporates inertial effects for times below a

characteristic time Δt (set by the user), where the dynamics crosses over from the ballistic to the diffusive regime.

We first analyze the survival probability $S(t)$ of a particle as a function of the density. In the trapping and target problems this is the density of traps, while it is the overall (trap + particle) density in the full-mobility case. We find that the trapping and full-mobility problems are characterized by similar survival probabilities. More precisely, the initial decay stage up to times of the order of Δt is exponential and reflects the short encounter times dominated by ballistic motions. This elucidates why Smoluchowski theory is incorrect at short times if inertial effects are taken into account. We formulate a simple theory valid for the situation of motion at constant velocity among a random configuration of static traps, which is found to interpolate the observed decay times of this first exponential stage to an excellent extent for low and intermediate packing fractions.

An effective exponent analysis reveals that the initial exponential decay slows down at $t > \Delta t$. While this happens in a density-independent fashion for the trapping and full-mobility problems, this cross-over in the target setting is ruled by a clearly density-dependent phenomenon. At a time of the order of $\tau = R^2/\pi D$ (R being the encounter distance, i.e. the particle diameter), the decay of $S(t)$ slowly turns back to purely exponential. However, while this trend is unquestionable for low and intermediate packing fraction (at least up to $\phi \simeq 0.2$), our data do not allow us to conclude whether the same thing happens at higher densities, as long encounter times become exceedingly hard to observe even in extremely long simulations. We note that this finding appears at odds with the classic prediction $S(t) \simeq \exp[-at^{3/5}]$ ($a = \text{const.}$) for the trapping problem in 3D. The reason for this is unknown at the present stage. It is interesting to observe that the approach proposed in [50] could be used to get further insight into this problem.

We then analyze the encounter rate κ in the three settings as a function of the density. The rate κ is calculated as $\kappa = [\int_0^\infty S(t) dt]^{-1}$. The rates are found to increase monotonically with the density (up to the highest volume fraction explored in this study). In accordance with what was found for the survival probability, we find that the trapping and full-mobility settings are characterized by roughly the same rate (once the appropriate diffusion coefficients are taken into account, of course). Instead, the target problem appears to follow a different law. It is shown that the low-density regime corresponds to the classic prediction of the full Smoluchowski theory of colloid coagulation

$$\frac{\kappa}{k_S} = \frac{1}{1 - e^{k_S \tau} \sqrt{\pi k_S \tau} \operatorname{erfc}(\sqrt{k_S \tau})}$$

where $\tau = R^2/\pi D$ and $k_S = 4\pi R D \rho$ is the celebrated Smoluchowski rate. Therefore, even if Smoluchowski theory is fundamentally incorrect at short times when inertial effects are taken into account, this fact is somewhat concealed in the encounter rate (an integrated measure), since the relative weight of short encounter times at low density is negligible.

Remarkably, we find that the substitution $\phi \rightarrow \phi Z(\phi)$, $Z(\phi)$ being the compressibility (we use the Carnahan–

Starling approximation) in the rhs of the above formula allows one to interpolate the trapping and full-mobility problems perfectly. This substitution amounts to replacing the density by the pressure, $\rho \rightarrow P/k_B T$ (i.e. the full equation of state), and has the meaning of restoring the non-overlapping character of the spherical traps [45], as also found in other models of diffusion-limited processes [51, 52].

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