On-off dissociation dynamics of colloidal doublets

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Abstract – First passage time theory is used to analyze the dissociation behavior of doublets of colloidal particles. The first passage time distribution for particles interacting via a DLVO potential is determined numerically. For strongly attractive particles the distribution becomes broad such that the mean first passage time becomes a poor measure of the dynamics. In spite of this, use can be made of the mean in a matching condition, which allows for reproducing distributions for strongly attractive doublets by a semi-analytical solution for particles interacting only through surface adhesion. The smallest eigenvalue in the analytical solution, which governs the long-time asymptotic behavior of the first passage time distribution, is identified analytically for strongly attractive pairs of particles. In addition, in this limit the distribution is shown to asymptote to an exponential distribution, which means the dissociation process can be simply captured by an on-off model, without sacrificing the effect of the surface chemistry, with a constant probability for dissociation. This probability is simply related to the surface adhesive parameter and the separation distance at which the pair of particles ceases to be considered a doublet.

Introduction. – Dissociation of colloidal clusters, including the redispersion of aggregated colloids [1], detachment of particles from surfaces and other larger particles [2], dispersion of dry solids to form colloidal species [3], is of wide-ranging importance. Some examples where colloidal dissociation plays an important role include drug release from tablet formulations [4] and subsurface transport of contaminants, filtration, bioremediation, water treatment, and erosion [5–8], and there are substantial savings to be made related to transportation and storage by having redispersible polymer latices [9]. However, whereas the initial stage of colloidal aggregation, i.e. the dimerization of initially disperse particles, is well understood [10,11], the same cannot be said for the correspondingly basic step of the reverse process – the dissociation of pairs of colloidal particles.

In this work we are concerned with how the dissociation kinetics depends on the interaction potential between particles within a first passage time description of the dynamics. With particles pairs being trapped initially in a potential well one may expect that the dissociation kinetics should be a sensitive probe of the potential [12]. Here we will show that, for all but the shortest times, the dissociation dynamics of reversibly aggregated doublets can be captured quantitatively by mapping onto a simple system characterized by surface

adhesion, which suggests that the details of the potential are in fact relatively unimportant for this type of process.

First passage time theory. – Following Chan and Halle [12], we focus on dissociation of particle pairs caught in the secondary minimum of a DLVO potential comprising screened Coulomb and non-retarded van der Waals interactions [13]. Redispersion of colloidal aggregates usually proceeds by dilution or dialysis to change the electrolyte and particle concentrations [1]. In this work we envision an experiment in which a reversibly aggregated pair of colloidal particles is placed in a solvent with a prescribed ionic strength at infinite dilution. In other words, the doublet is initially held together by a finite attraction and we then ask for its lifetime. This situation can be modeled by first passage time theory [14], which deals with diffusive motion of particles to a region of space, like a binding site, a boundary, or, as in this case, a particular separation distance beyond which the particles no longer are considered a doublet. For a pair of colloidal particles the appropriate statistical description is furnished by the two-particle Smoluchowski equation, which is simplified by introducing the survival probability $\Sigma(\tau|x)$ and first passage time distribution $\varrho(\tau|x) = -\frac{\partial}{\partial\tau}\Sigma(\tau|x)$ [12,14], where τ is time and x is the initial separation distance made dimensionless with the diameter and relative diffusion coefficient. These describe the probability that a pair of particles, initially at separation x, by time τ remain associated and dissociate for the first time, respectively.

Neglecting hydrodynamic interactions, the survival probability satisfies the following adjoint Smoluchowski equation

$$\frac{\partial}{\partial\tau}\Sigma(\tau|x) \quad = \quad \frac{1}{x^2}e^{\beta u(x)}\frac{\partial}{\partial x}\left(x^2 e^{-\beta u(x)}\frac{\partial\Sigma(\tau|x)}{\partial x}\right) \tag{1}$$

where $u(x)$ is the interaction potential and $\beta = (k_B T)^{-1}$. Numerical solutions of eq. 1 for $\Sigma(\tau|x)$, satisfying a no-flux boundary condition at a short separation x_a and an absorbing boundary condition at a larger separation x_b, are readily generated by implicit finite-difference schemes [2]. Moreover, the mean first passage time can be expressed in closed form as [12,14,15]

$$\bar{\tau} \quad = \quad \int_x^{x_b} dss^{-2}e^{\beta u(s)}\int_{x_a}^{s} dtt^2 e^{-\beta u(t)} \tag{2}$$

but sometimes it is easier to determine $\bar{\tau}$ from the numerical solution to eq. 1 as the first moment of the first passage time distribution, i.e. $\bar{\tau} = \int_0^\infty \tau\varrho(\tau|x)d\tau$.

In fig. 1 first passage time distributions are shown for a series of DLVO potentials corresponding to 1, 2, and 3 mM of monovalent salt. As the salt concentration is increased the range of the repulsive part of the DLVO potential is progressively shortened and the depth of the secondary minimum grows. The first passage time distributions have been determined by starting the particles from an initial separation distance corresponding to the secondary DLVO minimum and the particles are taken to be dissociated when they first reach a separation where the potential is -1 $k_B T$. The first passage time distribution starts from zero at short times, which reflects the fact that particles cannot dissociate instantaneously. It grows to reach a maximum from which it decays as it becomes increasingly likely that particles have had sufficient time to escape from the potential well. As the well depth is made deeper through the addition of salt the distribution becomes broader. For a DLVO minimum of about 14 $k_B T$ the first passage time distribution is stretched over five decades in time. It follows that for such broad distributions the mean first passage time provides an inadequate description of the particle release dynamics [16], though this is often assumed because it affords a simplified analysis [12]. In addition, for deep potentials the initial condition is not particularly important. Assigning starting positions farther apart for the 3 mM case, i.e. the deepest potential in fig. 1, leads to almost no change in the first passage time distribution unless the particle pair is started off about half-way up the well. For such relatively wide

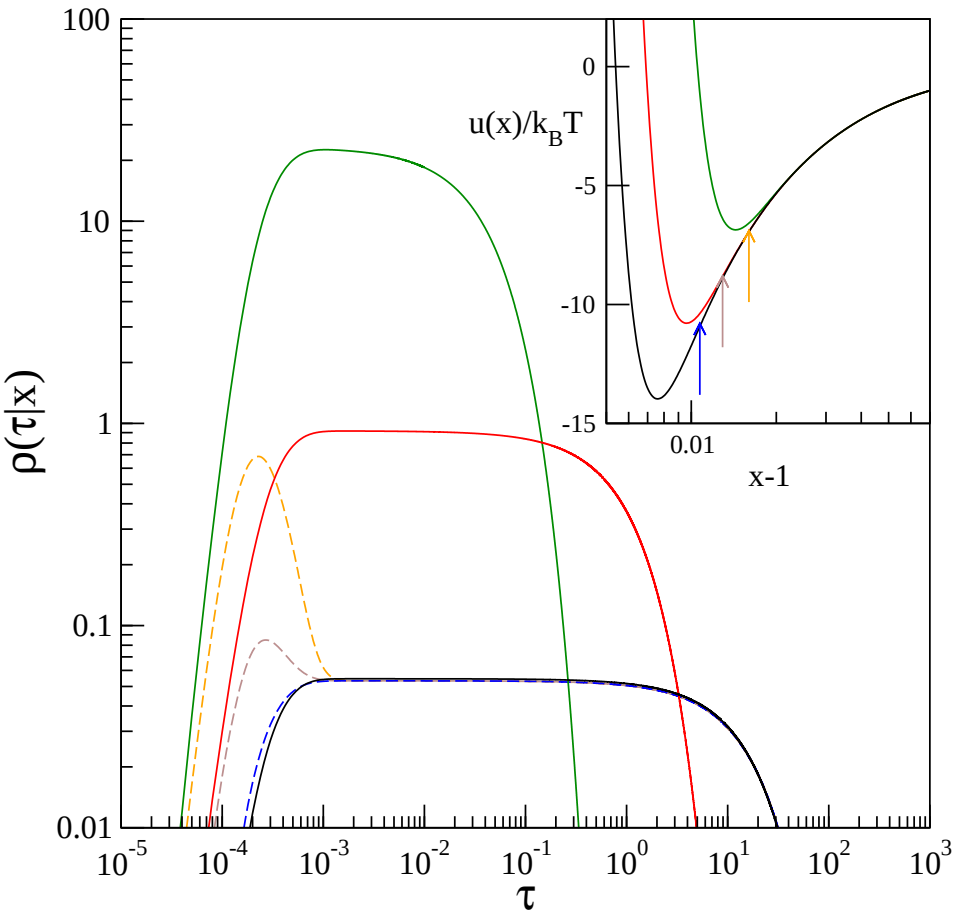

Fig. 1: First passage time distribution as a function of time τ for varying ionic strengths, 1, 2, and 3 mM, corresponding to the interaction potentials shown in the inset. The first passage time distributions shown as solid lines employed an initial separation distance corresponding to the secondary minimum of the DLVO potential, whereas the ones shown as dashed curves were started from $x = 1.0107$, 1.0129, and 1.0160 (shown by arrows in the inset) all at 3 mM salt concentration.

separations the short-time dynamics changes; the distribution acquires a peak, which corresponds to a finite probability of the doublet separating without first having explored the minimum of the potential. The long-time dynamics, however, remain the same regardless of the starting separation.

Mapping onto surface-adhesive model. – For some simple potentials analytical or semi-analytical solutions of eq. 1 can be obtained. A square-well interaction, with well depth ϵ and dimensionless range λ, is such a case. Separation of variables applied to eq. 1 leads to an equation that conforms to Sturm-Liouville form and the following orthogonality condition for two different eigenvalues is found

$$e^{\beta\epsilon}\int_1^{\lambda} x^2 v_m(x)v_n(x)dx + \int_{\lambda}^{x_b} x^2 v_m(x)v_n(x)dx = 0 \tag{3}$$

The eigenvectors $v_m(x)$ are given by zeroth-order spherical Bessel functions of the first and second kind and form part of the solution

$$\Sigma(\tau|x) = \sum_{m=1}^{\infty} \gamma_m e^{-\alpha_m^2 \tau} v_m(x) \tag{4}$$

involving the eigenvalues α_m. The constants γ_m are determined by imposing the initial condition $\Sigma(0|x) = 1$, corresponding to the particle pair initially being separated by distance x. The square-well interaction can be further simplified by applying the limiting procedure of Baxter [17], in which simultaneously $\lambda \to 1$ and $\epsilon \to \infty$ while maintaining a finite second virial coefficient. For this surface-adhesive interaction the structure of the solution is the same as for the square-well model in eq. 4, but the characteristic equation governing the eigenvalues simplifies to

$$\tan\left[\alpha_m(x_b - 1)\right] = \frac{12\tau_s\alpha_m}{12\tau_s - \alpha_m^2} \tag{5}$$

where $\tau_s = \lim_{\epsilon\to\infty,\lambda\to 1} e^{-\beta\epsilon}/(12(\lambda - 1))$ is the stickiness parameter. The eigenvalues in the above were analytically bracketed and identified numerically by bisection.

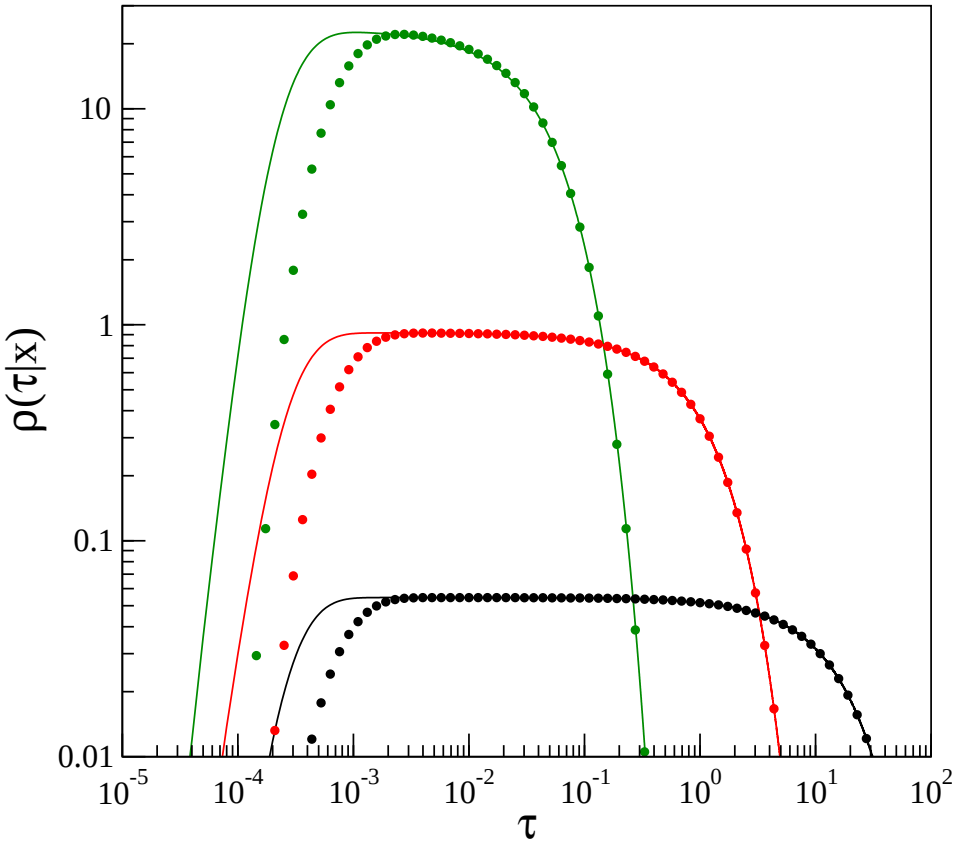

Fig. 2: First passage time distribution as a function of time τ for varying ionic strengths, as also shown in fig. 1 (lines). Shown also (symbols) are first passage time distributions for the semi-analytical solution of the Baxter model with τ_s determined so as to match the mean first passage time, which results in, form top to bottom, $\tau_s = 0.133$, 0.00505, and 0.000300. The absorbing boundary condition has been applied at $x = 1.0705$ in both models.

Small values of τ_s imply strong adhesive interactions between spheres and for such situations the first passage time distribution from the semi-analytical solution in eqs. 4 and 5 take on the same qualitative features as seen for the DLVO potential in fig. 1. This behavior suggests that use can be made of the simpler Baxter solution through a mapping procedure. For the Baxter potential the mean first passage time is given by $\bar{\tau} = \frac{1}{6}\left(x_b^2 - 1\right) + \frac{1-x_b}{3x_b}\left(1 - \frac{1}{4\tau_s}\right)$, where the starting separation has been set to $x = 1$ and the last term in parenthesis is recognized as the reduced second virial coefficient for the Baxter potential. Given the parameters

of the DLVO potential, the mean first passage time is determined from eq. 2. The DLVO case is now mapped onto the Baxter model by determining τ_s so that the mean first passage time for the DLVO potential is matched by the Baxter result. This mapping leads to the results shown in fig. 2. Aside from the shortest-time dynamics the distribution for the DLVO doublet can be described quantitatively through this simple mapping. This holds even though the mean first passage time, being a single parameter, cannot be considered anything but a poor measure of the escape dynamics at the higher salt concentrations. For these strongly attractive Baxter doublets the first passage time dynamics is fully dominated by the smallest non-zero root of eq. 5, which decreases towards zero as the adhesion is increased. The second smallest eigenvalue, on the other hand, is bounded from below by $\pi(x_b-1)^{-1}$. In addition, for strong adhesion, i.e. for small τ_s, the left-hand side of eq. 5 can be linearized so that the following asymptotic expression for the smallest eigenvalue follows

$$\alpha_1^2 \quad = \quad \frac{12\tau_s x_b}{x_b - 1} \tag{6}$$

Furthermore, in this limit the survival probability tends to $\Sigma(\tau|1) \approx e^{-\alpha_1^2\tau}$ and the first passage time distribution behaves as $\varrho(\tau|1) \approx \alpha_1^2 e^{-\alpha_1^2\tau}$. This result furnishes a near analytical prediction, free of adjustable parameters, of the dissociation process, which becomes more accurate the deeper the potential well.

A Simple Algorithm for Peptization (ASAP). – Physically, exponential distributions such as these are waiting time distributions of Poisson processes in which the dynamics is characterized by a constant probability. A stochastic realization of the long-time asymptotic dynamics for the strongly attractive particles can be constructed by taking particle pairs as being in one of two states, either associated or dissociated. In this simple algorithm n_{tot} initial doublets are subjected to a sequence of detachment attempts. Each attempt will be governed by a probability p for detachment. After the first attempt, which is taken as a random number between 0 and 1 being smaller than p, $n_{\mathrm{tot}}p$ clusters will have dissociated. The $n_{\mathrm{tot}}(1-p)$ intact clusters will yield $n_{\mathrm{tot}}p(1-p)$ dissociated clusters by the second attempt. After the ith attempt, $n_{\mathrm{tot}}(1-p)^{i-1}p$ clusters will dissociate for the first time. Next, the following identifications are made

$$p = \alpha_1^2\Delta\tau \qquad\qquad \tau = i\Delta\tau \tag{7}$$

where α_1 is the smallest eigenvalue of the characteristic equation in eq. 5 and a time step $\Delta\tau$ has been associated with the sequence of attempts. For small $\Delta\tau$ the distribution $n_{\mathrm{tot}}(1-p)^{i-1}p$ asymptotes to $n_{\mathrm{tot}}\alpha_1^2\Delta\tau e^{-\alpha_1^2\tau}$. It follows that the exponential distribution can be quantitatively reproduced by this simple two-state model if a sequence of random numbers are generated and the instance i is recorded when the first random number below p occurs. This is repeated n_{tot} times to generate a histogram comprising the number of detachments at a particular time $i\Delta\tau$, which is brought in quantitative agreement with theory by dividing the number of detachments $n(\tau)$ by n_{tot} and $\Delta\tau$.

The result of applying this algorithm is shown in fig. 3, where it is compared to the first passage time distribution from the numerical solution of eq. 1 for a 10 k_BT-deep DLVO potential. As seen, the two-state model, which incorporates the mapping of the DLVO potential onto the Baxter model based on matching of the mean, in this case $\bar{\tau} = 0.522$, captures the solution quantitatively except for the short lag period at the earliest times. When sampling such slowly decaying dynamics it is more natural to use logarithmic binning in time. Figure 4 shows an example where the first passage time distribution has been determined by Brownian dynamics simulation [4]. The mean first passage time has been determined from which a stickiness parameter follows and the lowest eigenvalue is determined either numerically (eq. 5) or analytically (eq. 6). A time step $\Delta\tau$ is selected, in this case four orders of magnitude larger than in the simulation, and the detachment probability in

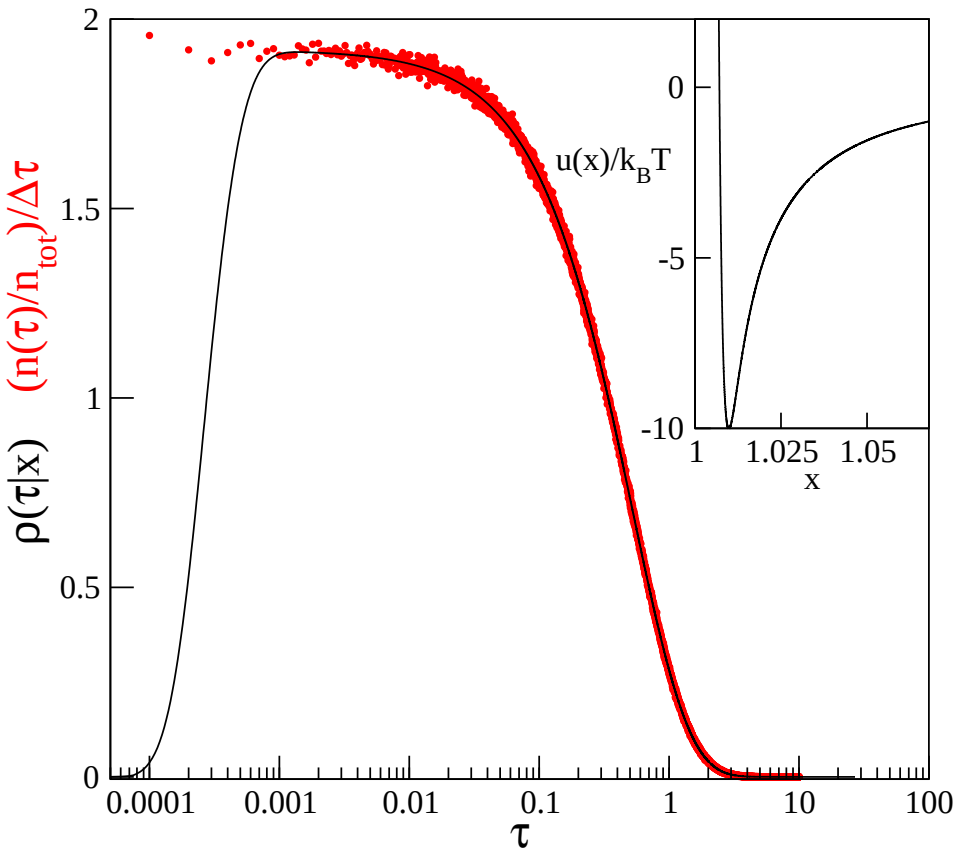

Fig. 3: First passage time distribution for the DLVO potential shown in the inset as obtained numerically by solving eq. 1 (line) and from the two-state stochastic model (symbols) with $\tau_s = 0.01022$, which results in $\alpha_1^2 = 1.919$, and $\Delta\tau = 1 \cdot 10^{-4}$.

eq. 7 is determined. The distribution in fig. 4 has been sampled logarithmically along the time axis and because of this it becomes the linearly sampled distribution scaled by τ [18], which is the reason the distributions in figs. 3 and 4 appear different. For the same reason the discrepancy at very short times, seen in fig. 3, cannot be observed in fig. 4.

Conclusions. – In summary, for strongly associated particle pairs distributions of first passage times become broad and simply considering the mean does not do the dissociation dynamics justice. The dynamics for all but the shortest times is insensitive to the details of the potential, but it remains sensitive to an overall measure of the attraction. This property can be exploited to capture the dynamics quantitatively by a surface-adhesive model by requiring that the mean first passage time be matched. For strong attractions the first passage time distribution tends to an exponential distribution, which allows for formulating a simple coin-flip model for the dissociation dynamics. This is expected to be valuable as a starting point for developing simplified algorithms for dissociation of more complex clusters. However, experiments [19] and computer simulations [4, 20] show that in such cases cluster reorganizational moves need to be incorporated.

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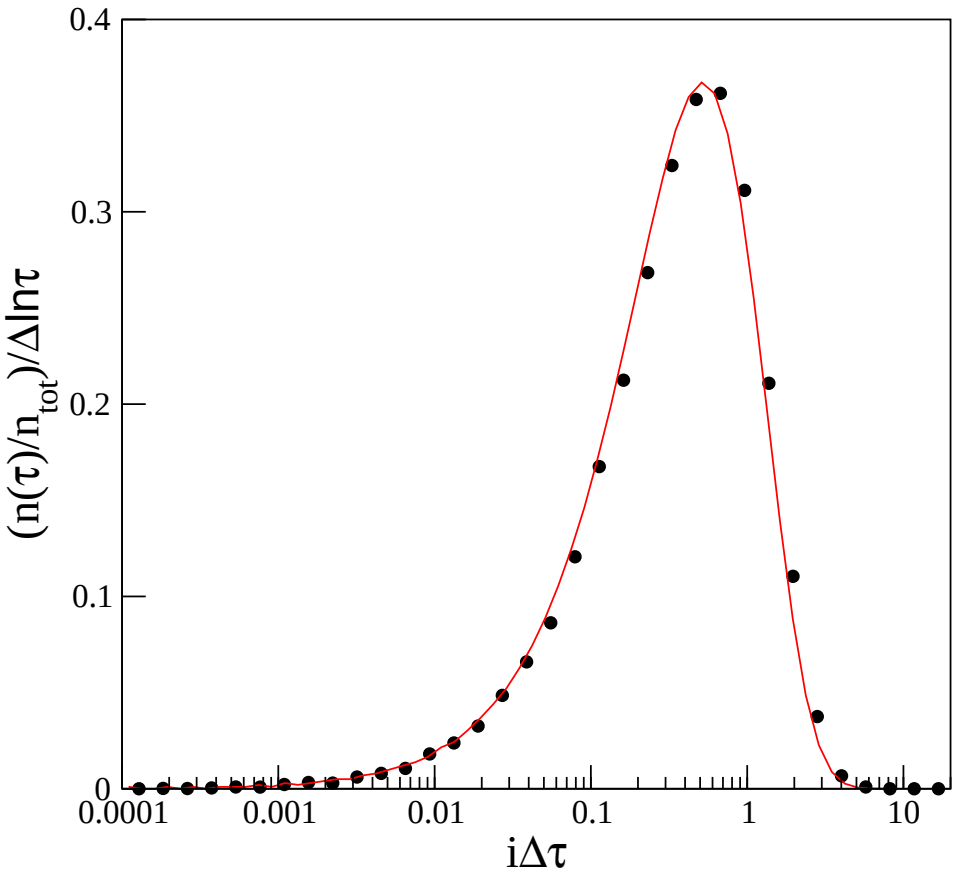

Fig. 4: Comparison between the first passage time distribution for the same DLVO potential as in fig. 3, this time determined by Brownian dynamics simulation (symbols) and the two-state model described in the text (line).

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