

Kinetics of Two-Dimensional Diffusion-Controlled Reactions: A Monte Carlo Simulation of Hard-Disk Reactants Undergoing a Pearson-Type Random Walk

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The Monte Carlo method has been used for simulating two-dimensional diffusive motion of hard disks as a Pearsonian random walk (in which each displacement is of equal length but in a random direction) and for analyzing the kinetics of a diffusion-controlled irreversible bimolecular reaction between the diffusing entities. The results are compared with predictions based on hydrodynamic theory (the diffusion equation), which was recently shown to be consistent with the experimental data on the self-quenching of 1-palmitoyl-2-(1-pyrenedecanoyl)-*sn*-glycero-3-phosphocholine (py₁₀-PC) in 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC) fluid bilayers (Martins et al. *J. Phys. Chem.* **1996**, *100*, 1889). Regardless of the time range analyzed and of the physical characteristics (diffusion constants and radii) of the reactants, the agreement between the random walk picture and the hydrodynamic treatment improves as the magnitude of the step of the diffusive displacement becomes smaller and one approaches the continuum limit. The study confirms earlier deductions about the limits of validity of the hydrodynamic theory (for reactions in 2D space) and reveals the need for more comprehensive experimental data.

Introduction

Reactions between components of biological membranes—which may be regarded as two-dimensional (2D) structures—are widely recognized to play paramount roles in cell physiology and metabolism.¹ Numerous theoretical and experimental works have therefore attempted to unravel how a reduction, from three to two, in the spatial dimensionality of the reaction medium affects biochemical or biological systems,^{2,3} and to investigate the kinetics of 2D bimolecular reactions.^{4–6} Whether or not there are biochemical reactions in biomembranes which are diffusion-controlled cannot be ascertained until their kinetics are analyzed with the appropriate formalism; however, experimental data for some sequential reactions involving a series of molecules concentrated in the plane of the membrane indicate rates approaching the diffusion-control limit.⁷

Traditionally, diffusion-controlled bimolecular processes have been examined from a hydrodynamic viewpoint, rooted in Smoluchowski's pioneering work,⁸ which has proved to be exceedingly fruitful for interpreting the kinetics of fast reactions with no activation energy and is applicable to reactions or processes in the liquid (or solid) phase—three-dimensional (3D) media—for which the mobility of the reactants is the rate-determining step. His treatment, which takes the diffusion equation (DE) as its starting point, was adapted for 2D media by one of us,⁹ and the prediction of this 2D model was experimentally validated by an investigation, conducted by Martins et al.,¹⁰ of the kinetics of pyrene excimer formation in fluid phospholipid bilayers. Their work established that diffusion-limited reactions in 2D follow a distinctive course, which cannot be analyzed within the framework of 3D kinetics without

incurring large errors in, and an attendant ambiguity concerning the physical meaning of, the ensuing molecular parameters. In fact, when 3D models or approximate expressions for the 2D rate coefficients are used for the interpretation of experimental data, the molecular diffusion coefficients found often turn out to be 1 or 2 orders of magnitude larger than those obtained by reliable independent means (such as fluorescence recovery after photobleaching or pulsed-field-gradient NMR).

Monte Carlo (MC) techniques have been used in the past for studying lateral diffusion as well as diffusion–reaction processes in simulated biological membranes. All these studies make use of mathematical planes, with triangular^{11–13} or square^{4,5,14} lattices, and the particles or tracers are placed in regular positions either as lattice points or as regular geometric figures such as hexagons. When the reactants are represented as point particles occupying lattice sites, a comparison of the simulated results with those predicted by the DE is not straightforward, for the two treatments are couched in terms of physically different parameters. If a comparison is desired, a relation of the form $l = \alpha R$ must be imposed, where l is the lattice spacing, R is the encounter distance (the sum of the radii of the two reactants), and α is a constant whose value can be determined only by appealing to extraneous arguments. The kinetics of annihilation of point particles performing a diagonal random walk on a square lattice have been found to share some features with the picture portrayed by the DE,^{4,5} but the decay predicted by the simulations was found, with the particular choice of α , to be significantly slower, even for a pseudo-first-order reaction, than that predicted by the DE;⁵ what is more, the simulated decay for the situation in which one majority species is mobile and the other immobile was found to differ from that for the converse situation (other things being equal), whereas the two situations should lead, according to the DE description, to the same form of decay.⁵

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In the present study, we adopt Pearson's model for a random walk (in which the length of each step remains constant but the direction changes randomly at each jump) and investigate, with the aid of MC techniques, the dynamics (random walk and binary collisions) of diffusion-controlled interaction between circular rigid particles. With this model, there is no compulsion to change the radii of both reactants at the same time, and the jump length can be varied independently of the two radii; it is this flexibility that permits us to probe more deeply the limits of validity of the DE approach than has heretofore been possible in simulation studies. We confine attention throughout to a pseudo-first-order reaction; otherwise, it would not be legitimate to confront our results with the Smoluchowski approach, which neglects competition between different sinks, or with the vast majority of quenching experiments, where the quencher concentration far exceeds that of the species that is quenched.

A procedure for the simulation of diffusion-controlled reactions in phospholipid fluid bilayers within the context of the hydrodynamic theory is presented here and illustrated by some results. In these simulations, systematic changes have been made in the following parameters: the particle mobility, the encounter radius, and the time span over which the reaction can be followed, which is determined by τ_0 , the lifetime of the excited state; the influence of these parameters is analyzed, and the results are compared with those predicted by the existing formalism for 2D diffusion-controlled reactions. For a particular set of parameters, those modeling the pyrene fluorescence self-quenching yielding an emissive excimer, our simulations are shown to be consistent with experiment.¹⁰ In future work, using long-lived luminescent probes, we will extend experiments to the millisecond range, more appropriate for mimicking biological processes.

Methods

The lipid bilayer is represented by a square plane of side L ; considerations that dictate the area of the plane are discussed below. Assuming that the bilayer is in the fluid phase, the number of phospholipid molecules for a given area of the simulation plane follows from the cross-sectional area (assumed to be known) of phospholipid molecules, which is typically 60 Å² in the L_α phase. The diffusion-controlled quenching of the luminescence of excited molecules (species E) by quenchers (species Q) is studied by placing a certain number of particles of each species in the simulation plane. The radius of an E particle will be denoted by R_E and that of a Q particle by R_Q ; the corresponding diffusion coefficients, by D_E and D_Q , respectively.

The modeling is performed in two stages: (i) generation of the initial random distribution of E and Q and (ii) simulation of the decline in the luminescence intensity (decay of the E population) on account of spontaneous emission and of the overlap of E and Q due to the motion of either particle leading to the annihilation of E, which is assumed to occur instantaneously.

The random number generator, the heart of the MC approach, used by us is a routine from the MS-FORTRAN 90 package, whose algorithm is based in the linear congruential generator method.¹⁵ To verify that the randomness in the range [0,1] is acceptable for our purposes, the sequences generated by the routine were subjected to several tests^{16–18} whose outcomes were satisfactory; furthermore, tests for correlation in the k -space¹⁸ and for autocorrelation¹⁹ did not reveal any noticeable sequential correlations. For the task at hand, the period of the generator can therefore be regarded as infinite. All calculations were performed with Intel-PENTIUM based personal computers.

Simulation Algorithm. In the first step of the algorithm N_E particles of species E and N_Q particles of species Q are placed sequentially at random positions (coordinates of the circle center) in the chosen plane. Any draw in which a new particle overlaps an existing one is eliminated. N_Q reflects the desired quencher-to-lipid ratio and yields the 2D concentration (in mol cm⁻² units), calculated on the basis of the phospholipid molecular area and the probe-to-lipid ratio, as previously described.¹⁰ The total number of particles, $N_E + N_Q$, is such that the initial fractional area of the simulation plane occupied by the particles is small (less than 1.5×10^{-3}).

The interval between successive MC steps, t_c , will be used to establish the time scale; to this end, we use the identity between the mean square displacement, $\langle r^2 \rangle$, traveled after a sufficiently large number (say M) of MC steps, each of length l , and the prediction of hydrodynamics for the same event for a given molecular diffusion coefficient, D :^{20–22}

$$\langle r^2 \rangle = 4Dt = Ml^2 \quad (1)$$

Using the fact that $t = Mt_c$, one arrives at the desired relation, namely

$$t_c = \frac{l^2}{4D} \quad (2)$$

Spontaneous decay and random walk algorithms were submitted to preliminary verifications. Whenever the values of the parameters were varied, quenching was switched off and luminescence decay in the absence of quenching was simulated to ascertain that it adhered to monoexponential decay with intrinsic lifetime τ_0 . Experience showed that setting L at least equal to 0.3 μm guaranteed reliable results for all simulation conditions. In fact, for each family of simulations the results obtained with a $L \times L$ plane were compared with those from a $5L \times 5L$ plane and the minimum value of L for which no differences were detected was used in subsequent runs. To account for particles that jump outside the plane boundary periodic boundary conditions were used, thereby avoiding concentration depletion. The total number of particles E and Q, respectively, N_E and N_Q , and l , the jump length used, are discussed in further detail in the Results and Discussion.

Each random step is taken by choosing a random angle θ in the range $[0, 2\pi)$ and setting

$$\begin{aligned} \Delta x &= l \cos \theta \\ \Delta y &= l \sin \theta \end{aligned} \quad (3)$$

In each step, the relative number (N_E/N_Q) and the relative diffusion coefficients (D_Q/D_E or D_E/D_Q) determine the probability that a given particle is moved; afterward, the MC step counter is incremented by one. The E and Q particles are treated as totally impenetrable disks, which cannot overlap;²³ therefore movements resulting in the overlap of the same type of particles are discarded and another particle of the same type is randomly selected and moved instead. If during a step an E–Q encounter occurs, instantaneous reaction takes place, and the reactant E (excited chromophore) is annihilated. If both reactants have the same mobility, this ensures that on average every particle is moved once during a step; on the other hand, if, for instance $D_E > D_Q$, only a fraction, proportional to the ratio D_Q/D_E , of randomly selected Q particles are moved. In any case, t_c is set for the higher mobility.

The probability that a particle of species E will survive unimolecular first-order decay at the end of a single step is

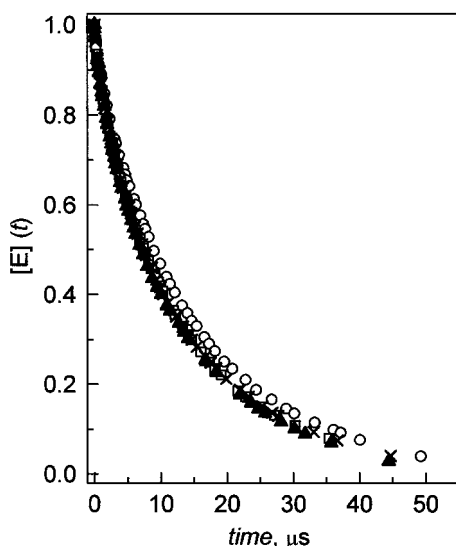


Figure 1. Dependence of the simulated decay of a long-lived luminescence probe ($\tau_0 = 1$ ms), on the magnitude of the step length. Step = 10 Å (○); step = 5 Å (□); step = 2 Å (×); step = 0.5 Å (▲). In all the decays the same physical characteristics of the particles are used: $D_E = D_Q = 5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ and $R_E = R_Q = 5$ Å; and a Q to phospholipid ratio of 1:500.

$1 - \exp(-t_c/\tau_0)$, which can be approximated, for the situation considered here, by t_c/τ_0 . This means that a randomly chosen E molecule must be eliminated if a random number turns out to be lower than t_c/τ_0 .

It should be noted that the above algorithm contrives to maintain the number of quencher molecules at a fixed value, and to treat all excited molecules as independent of each other; the resulting decay curves can therefore be compared both with experimental data pertaining to pseudo-first-order reactions and with predictions based on the DE.

To avoid large statistical fluctuations in the outcome of the simulation, a run is stopped when N_E falls to 5–10% of its initial value. Each run has typically 5×10^3 MC steps and the decay curves are averaged over N runs ($N \geq 20$), and it is t_c that determines the time resolution in a simulation. The total number of MC steps ($M \times N$) is maintained, when one follows the above procedure, at a value large enough to ensure statistically significant outcomes.

Results and Discussion

Besides the usual syntax-checking and debugging, and other preliminary tests described in the Methods, the response of the simulation algorithm to the change of the parameters—namely step length, diffusion coefficient, and reactant radius—was also examined. Rayleigh histograms were produced to certify the correctness of our algorithm in simulating a Pearson type random walk, and the linearity of span plots ($\langle r^2 \rangle$ versus M plots) to diagnose biased particle mobility.

Test of the Algorithm. *Influence of the Size of the Step Length.* Figure 1 shows the influence of the magnitude of the step length on the decay pattern, for a simulation of the quenching of a probe with an intrinsic luminescence lifetime of 1 ms. For steps of the order of half the particle radii or lower, the decays obtained do not differ from one another, but when the step length equals the encounter radius, the rate of quenching becomes noticeably smaller. In principle, the hydrodynamic (or continuum) limit envisaged by the DE and the Smoluchowski boundary condition can be attained only by letting $l \rightarrow 0$ and $t_c \rightarrow 0$,^{24,25,28–31} and one should endeavor to go to these limits;

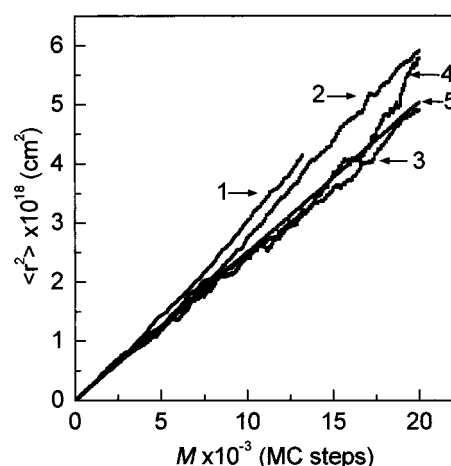


Figure 2. Span plots showing the dependence of the mean-squared distance, $\langle r^2 \rangle$, traveled by the particles on the number of jumps, M . The simulations were done with only one kind of particles with a radius of 5 Å, and a step = 2 Å was used: $P = 1000$ (line 1), $P = 500$ (line 2), $P = 300$ (line 3), $P = 100$ (line 4) compared with the straight line $\langle r^2 \rangle = 4Dt = Ml^2$ (line 5).

however, our findings show that values of the order of $R/5$ are already small enough to simulate the hydrodynamic description with adequate precision.

Stochastic Aspect, Number of Particles, and Number of Runs vs Time Scale and Time Resolution. As already stated, for a given time range under analysis, both N_E and N must be large enough to subdue statistical fluctuations. We observed that at least 20 runs have to be performed to reach this limit. However, the number of surviving E particles cannot fall below a certain number depending on the time range under analysis, 100 for submicrosecond decays or 25 for millisecond decays; the difference originates in the fact that the time resolution, defined on the basis t_c (which depends on l and D), remains the same whatever the time range under analysis. Under these restrictions one needs, if the decay is to be fitted to the expected exponential law ($[E](t) = [E]_0 \exp(-t/\tau_0)$) with absolute errors in $[E]_0$ (proportional to N_E at $t = 0$) and τ_0 smaller than 0.5%, at least 250 initial particles for the simulation of a millisecond decay and about 1000 particles for a submicrosecond decay. With this number of particles and step length, simulation of a 2D luminescence decay with diffusion-controlled quenching in a personal computer takes a few hours.

Particle Mobility. Span plots showing the dependence of $\langle r^2 \rangle$ on M are used to test for biased particle mobility. The (cumulative) mean square displacement of each particle, j , after each step, i , is calculated as the square of the Euclidean distance to the point of departure:

$$r_{ij}^2 = [(x_j, y_j)_0 - (x_j, y_j)_i]^2 \quad (4)$$

The result is averaged for the total number of particles of one particular kind, P , at each of the M steps:

$$\langle r^2 \rangle_i = \frac{1}{P} \sum_{j=1}^P r_{ij}^2 \quad (5)$$

The span plot so obtained does not show systematic deviations from the linear behavior predicted by eq 1 until $\approx 4 \times 10^6$ consecutive single steps, Figure 2. This is the result of the procedure used for avoiding particle overlap. As explained in the Methods section, each time a movement gives rise to the overlap of two identical particles, another randomly chosen

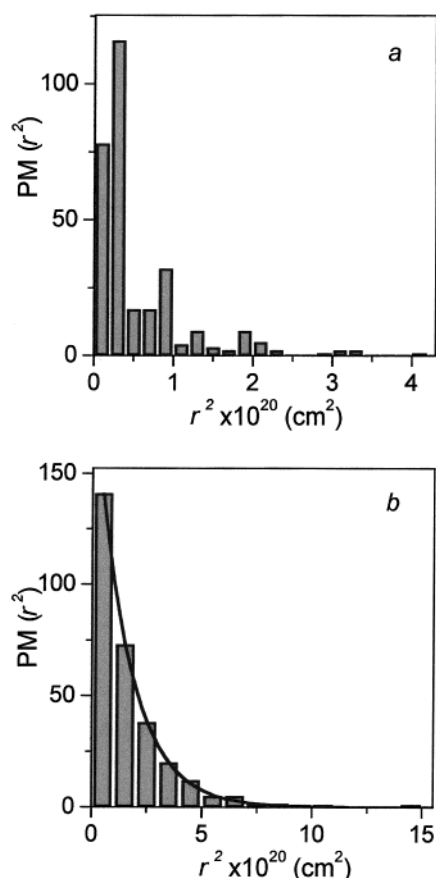


Figure 3. Histograms showing the probability distribution $PM(r^2)$ as a function of r^2 for (a) $M = 2$ (BIN size = $2 \times 10^{-21} \text{ cm}^2$) and (b) $M = 6$ (BIN size = 10^{-20} cm^2). $PM(r^2) dr^2$ is the probability that after M steps r^2 will have a value in the interval r^2 and $r^2 + dr^2$. For the simulations, 300 particles with radius of 5 Å were used and the step was of 2 Å. In (b), the theoretical exponential curve is included for comparison purposes.

particle of the same kind is moved instead.²⁶ In this way, even if the mean displacement of the average particle is the same, the mean square displacement is larger. Since these distortions are proportional to the number of random steps performed, the moment after which they become apparent depends on $M \times P$. In the present work, the simulations were always performed with less than 4×10^6 consecutive steps for one particular kind of particles.

Test for Pearson Random Walk. Additionally, we show that our algorithm, based on a Pearson random walk, leads to the correct histograms for the distribution of r^2 values in the population of particles.²⁷ In Figure 3 we display the histograms calculated for 300 particles. In the first steps (e.g., step 2) the distribution for r^2 values is not exponential, but after ca. 6 steps it becomes exponential, as found by Merzbacher et al.²⁷

Simulation Results and Comparison with Models for 2D Diffusion-Controlled Luminescence Quenching. *Effect of $[E]_0$.* Simulation of luminescence decay of species subjected to diffusion-controlled quenching is described by eq 6 where the time-dependent rate coefficient $k(\zeta)$ is independent of $[E]_0$.

$$[E](t) = [E]_0 \exp \left\{ - \left(\frac{t}{\tau_0} + \int_0^t k(\zeta) [Q] d\zeta \right) \right\} \quad (6)$$

In this equation τ_0 is the intrinsic luminescence lifetime, and for a reaction taking place in a 2D geometry, $k(\zeta)$ is the rate coefficient for the 2D diffusion-controlled reaction;⁹ $[E]_0$ is

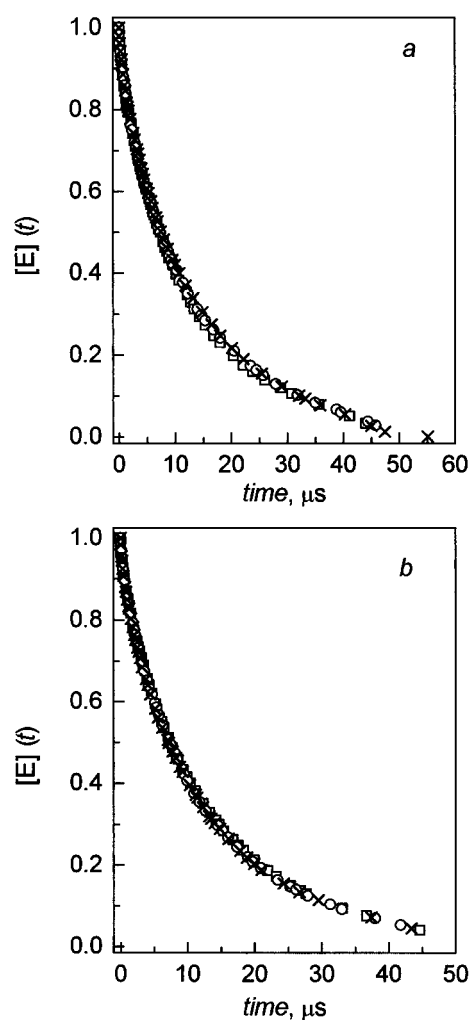


Figure 4. Results of tests for investigating the dependence of the simulated decay on the parameters of individual reactants, with $\tau_0 = 1 \text{ ms}$ and a Q-to-phospholipid ratio of 1:500. In all the plots of (a) $D_{\text{eff}} = 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ is the same, and $R_E = R_Q = 5 \text{ Å}$ and step = 2 Å, but the individual diffusion coefficients of the particles are $D_E = D_Q = 5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ (\square), $D_E = 9.9 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ and $D_Q = 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ (\circ), $D_E = 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and $D_Q = 9.9 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ (\times). In (b) all the points are from simulations using the same $R = 10 \text{ Å}$, and fixed $D_E = D_Q = 5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ and step = 1 Å, but the dimension of each particle is different for each set of points: $R_E = R_Q = 5 \text{ Å}$ (\square); $R_E = 2 \text{ Å}$ and $R_Q = 8 \text{ Å}$ (\circ); $R_E = 8 \text{ Å}$ and $R_Q = 2 \text{ Å}$ (\times).

proportional to the initial density of E particles in the plane, and $[Q]$ is the 2D concentration of Q. Equation 6 is only valid in the absence of biphotonic processes, e.g. reactions between two excited-state molecules, which is our case since no reaction between two E particles is considered. For the same $[Q]$ the normalized decay must be independent of $[E]_0$, and it was verified that this condition is indeed satisfied by our simulations (data not shown).

Test with Constant $D_E + D_Q$ and Constant $R_E + R_Q$. It is crucial to test that the results of these simulations are consistent with the Smoluchowski hypothesis, according to which the probability of collision depends only on the mutual diffusion coefficient, $D_{\text{eff}} = D_E + D_Q$, and is insensitive to the values of the transport parameters of each particle.²¹ Figure 4a shows that three separate simulations, for a probe with $\tau_0 = 1 \text{ ms}$, with different values of D_E and D_Q but the same $D_{\text{eff}} = 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, do indeed yield coincident decays irrespective of which reactant has the higher mobility. It should be noted that if one uses an algorithm (which is less time-consuming) where all

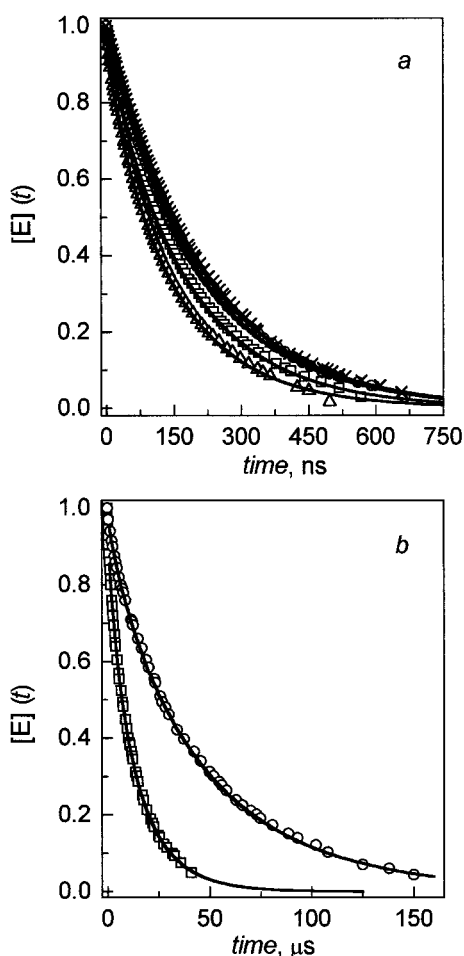


Figure 5. Comparison of the simulated and theoretical decay of luminescence at different values of the 2D concentration of Q particles. (a) Concentration dependence in the case of submicrosecond luminophores, with $\tau_0 = 210$ ns, $D_E = D_Q = 5 \times 10^{-8}$ cm² s⁻¹, $R_E = R_Q = 5$ Å, and step = 2 Å, for several values of [Q]. The cases presented are for a Q-to-phospholipid ratio of 0 (x), 1:500 (○), 1:100 (□), and 1:50 (Δ). Superimposed on each simulated decay is the respective theoretical decay obtained with $\tau_0 = 210$ ns, $D_{\text{eff}} = 10^{-7}$ cm² s⁻¹, and $R = 10$ Å: 0 (line with crosses), 1:500 (line with circles), 1:100 (line with squares), and 1:50 (line with up-triangles). (b) Case of millisecond luminophores. With the same physical characteristics used before for both kinds of particles and identical step but for $\tau_0 = 1$ ms and Q-to-phospholipid ratios of 1:500 (□) and 1:1500 (○). The theoretical law coinciding with the simulated data was obtained with $\tau_0 = 1$ ms, $D_{\text{eff}} = 10^{-7}$ cm² s⁻¹ and $R = 10$ Å: 1:500 (line with squares) and 1:1500 (line with circles).

particles of one kind are moved simultaneously, the final outcome depends on the individual diffusion coefficients. Results showing the insensitivity of the decays to the radii of the individual reactants (so long as their sum remains constant) appear in Figure 4b.

Comparison with Theory and Experiment for Submicrosecond Luminophores. Comparison of the results of MC simulations with the analytical equations for 2D diffusion-controlled luminescence quenching are presented in Figure 5. For the case of fluorophores with an unquenched lifetime in the submicrosecond time range comparison with the experimental results for pyrene self-quenching in fluid bilayers¹⁰ is also a possibility. With the system py₁₀-PC in POPC bilayers an excellent fit of theory with experiment was obtained under all experimental conditions. For example at 30 °C the molecular parameters that allow an excellent description of the decay are $D_{\text{eff}} = 7.8 \times 10^{-8}$ cm² s⁻¹, $R = 7.1$ Å (R being the sum of van der Waals

radii, i.e., $2R_{\text{py}}$), and $\tau_0 = 202$ ns. Figure 5a depicts the simulated decays and those calculated with eq 6 for $D_{\text{eff}} = 10^{-7}$ cm² s⁻¹, $R = 10$ Å, and $\tau_0 = 210$ ns, very similar to those for pyrene, for quencher-to-lipid ratios of 1:500, 1:100, and 1:50. For the calculated decays the 2D rate coefficient $k(\zeta)$ is calculated using equation

$$k(\zeta) = \frac{8D_{\text{eff}}N_A}{\pi} \int_0^\infty \frac{\exp(-\alpha\beta^2)}{\beta[J_0^2(\beta) + Y_0^2(\beta)]} d\beta \quad (7)$$

where $\alpha = D_{\text{eff}}\zeta/R^2$, $J_0(\beta)$, and $Y_0(\beta)$ are the zero-order Bessel functions of the first and second kind, respectively, N_A is the Avogadro constant, and β is a dummy integration variable.⁹ For the more diluted sample, for which the quenching is negligible, we observe the expected single-exponential decay with $\tau_0 = 210$ ns. For 1:100 and 1:50 the theoretical law is in perfect agreement with the simulations, as it already was with the experimental data.¹⁰

Comparison with Theory for Millisecond Luminophores. Simulations for long-lived luminescent species were also compared with hydrodynamic theory predictions. For $\tau_0 = 1$ ms and collisional distance and mutual diffusion coefficient identical to those used in the previous case, we simulated the luminescence decay for two different Q concentrations, 1:1500 and 1:500, Figure 5b. As observed in the case of the submicrosecond time range, prediction and simulation are in perfect accord. In the case of the “short” lifetime simulations, high quenching rates, if easy to simulate, are never attainable in practice because the high concentrations required would promote phase separation of the bilayer components. The advantage of long-lived luminophores is that a very small amount of quencher, forming an ideal solution with the phospholipid matrix, can compete efficiently with the natural decay of the excited species. Consequently, the observed decay has a major influence from the reactive deactivation channel.

Influence of D_{eff} and R on the Decay. We have tested the agreement between simulations and theoretical predictions for a large range of D_{eff} and R (chosen such that they are realistic for real biochemical systems) always obtaining the same good results. In Figure 6a we show the decays obtained with $R_E = R_Q = 10$ Å and $R_E = R_Q = 2.5$ Å, fixing both $D_{\text{eff}} = 10^{-7}$ cm² s⁻¹ and the Q to phospholipid ratio of 1:500; and in Figure 6b those for constant $R_E = R_Q = 5$ Å and making $D_{\text{eff}} = 10^{-8}$ cm² s⁻¹ with 1:500, and $D_{\text{eff}} = 10^{-6}$ cm² s⁻¹ with 1:4500, respectively. The good description of reactions obtained with parameters covering a broad range of possible experimental conditions described in Figure 6 makes the algorithm used a simple tool for the design of experiments of quenching of luminescence in 2D geometry, and enable the simulation of other types of reaction.

Conclusions

The Monte Carlo simulation of a diffusion-controlled reaction between hard disks performing Pearsonian random walk reproduces with remarkable accuracy the expression derived by one of us by adapting Smoluchowski's treatment to 2D media. It cannot be overemphasized that this agreement between a random-walk analysis and a theoretical, hydrodynamic description obtains only when the choice of the parameters characterizing the diffusing species does not conflict with, or at least approaches, the basic assumptions underlying the hydrodynamic approach. Investigations based on transport equations and various random walk models have shown that, so far as isotropic 3D media are concerned, the DE provides a satisfactory

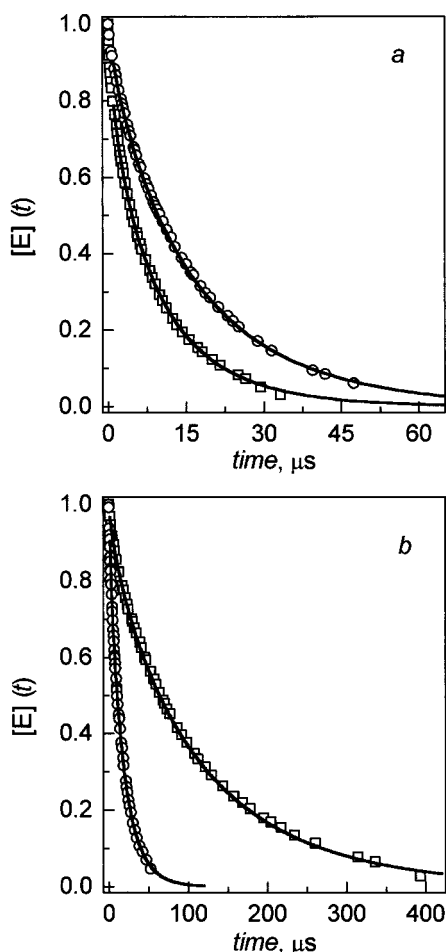


Figure 6. Dependence of the long-lived luminescence decay on D_{eff} and R . (a) With $\tau_0 = 1$ ms, Q-to-phospholipid ratio of 1:500, and $D_E = D_Q = 5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$: for $R_E = R_Q = 2.5 \text{ \AA}$ and step = 1 \AA (○), for $R_E = R_Q = 10 \text{ \AA}$ and step = 2 \AA (□). Superimposed on each simulated decay is the respective theoretical decay obtained with $\tau_0 = 1$ ms, $D_{\text{eff}} = 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, and 2D concentration: $R = 5 \text{ \AA}$ (line with circles) and $R = 20 \text{ \AA}$ (line with squares). (b) With the same τ_0 , $R_E = R_Q = 5 \text{ \AA}$, and step = 2 \AA : for $D_E = D_Q = 5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and a Q-to-phospholipid ratio of 1:500 (□) and for $D_E = D_Q = 5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and a Q-to-phospholipid ratio of 1:4500 (○). Superimposed on each simulated decay is the respective theoretical decay obtained with $\tau_0 = 1$ ms and $R = 10 \text{ \AA}$: $D_{\text{eff}} = 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ and 1:500 (line with squares), $D_{\text{eff}} = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and 1:4500 (line with circles).

description of diffusion-controlled reactions if $\Lambda/R \ll 1$, where Λ is the effective mean free path, and that if this ratio is smaller than 0.1, the rate constant predicted by the diffusion theory will not be in error by more than 2%.²⁸ Similar considerations lead one to expect that the DE description would coincide, for the case of an isotropic 2D medium, with a random walk such as that considered above if the jump length is sufficiently small, and the results of our simulation study are in complete accord with this expectation.

We return now to the work, mentioned in the Introduction, of Torney and coauthors,⁵ who investigated the kinetics of bimolecular diffusion reactions by placing point particles on a square lattice and letting them perform a diagonal random walk. Following Torney and McConnell,⁴ they set $\alpha = 3.56$ and found that even for a pseudo-first-order reaction ($N_E/N_Q = 1/64$), the simulated decay was noticeably slower than that predicted by the DE and that the discrepancy became more pronounced when N_E/N_Q was made larger. The difference between their approach

and that used by us is too great to warrant a close comparison; however, it may not be amiss to point out that the use of various lattice models in the context of chemical kinetics is fraught with many difficulties^{28–30} and that a random walk on a regular lattice becomes truly consistent with a continuum account of particle transport only when the lattice spacing l is made very much smaller than other physically important length scales under consideration.

Taking advantage of the flexibility of the MC simulations, we are designing an optimized system for the study of 2D reaction kinetics using long-lived excited-state species that will be the object of a future publication.

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