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Light intensity effects on diffusion-influenced fluorescence quenching in a hard-sphere liquid: Molecular dynamics simulation and the many-body Smoluchowski equation approach

T. Bandyopadhyay

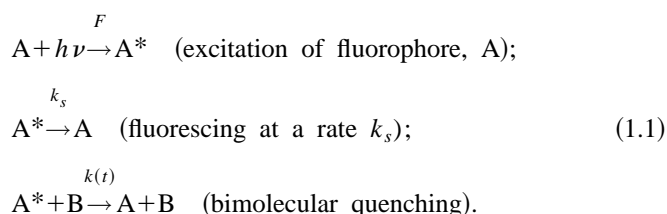
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Molecular dynamics simulation of a model fluorescence quenching reaction $A^* + B \rightarrow B$ (A^* is fluorophore and B is quencher molecule) in a hard-sphere liquid where the fluorophore is excited for the first time or reexcited shortly after a bimolecular quenching process is carried out. The effects of light intensity on the temporal behavior of the fluorescence quenching kinetics is obtained by a summed form of an appropriate convolution integral using the simulation data. The convoluted results are compared with the recently developed general theoretical framework for the quenching kinetics where the exciting light pulse has a short but finite duration. The theory is based on hierarchy of phenomenological kinetic equations involving reactant molecule distribution functions. The alone effect of potential of mean force is examined and the radiation boundary condition is considered. Improvements over the simplest version of the Smoluchowski theory has been found. Considering the error introduced due to truncation of repeated excitation of A at the level of first repeated excitation (after a bimolecular process) the agreement between theory and simulation is excellent under certain limiting time profile of the exciting light pulse. © 1995 American Institute of Physics.

I. INTRODUCTION

Diffusion plays an important role in a bimolecular reaction process in an ensemble of randomly distributed encounter partners. When mass transport becomes relatively slower compared to the intrinsic bimolecular reaction rate, the former becomes a rate limiting step for the reaction in a dense liquid and the reaction is said to be diffusion modulated.¹ From both an experimental and theoretical point of view fluorescence quenching is one of the simplest chemical processes in solution that could be used to study such processes. A typical fluorescence quenching scheme is



The above quenching mechanism is valid only when the concentration of A^* molecules is sufficiently low and B 's are in excess so that a B molecule can dispose of the energy it received from A^* before it gets a chance to quench again. One is interested in the time dependence of the concentration of A^* following excitation by a light pulse and in the ratio of steady-state intensity of fluorescence in the presence of quencher (I) to that in the absence of quencher (I_0) when excited states are being produced by an illumination at constant intensity. The time dependence of the concentration of A^* , $[A^*]_t$ can be expressed by a phenomenological rate law involving the rate constants as they appeared in Eq. (1.1), namely, rate of production (F), rate of natural fluorescence (k_s) (both radiative and nonradiative) and the rate of bimolecular quenching reaction $[k(t)]$.

$[A^*]_t$ may also be deduced from the convolution concept (when the excitation function, $F(t)$ is not a δ function) and can be represented by a time integral of concentration of A^* excited at time τ and its survival probability at a later time t . In conventional theories,^{1(a)} it is assumed that the survival probability of A^* depends only on the time elapsed between moment of excitation and time of measurement regardless of when the excitation has occurred. This can be so if the A^* molecule that has been just excited is surrounded by an equilibrium distribution of B 's. The progress of our understanding of the dynamics of fluorescence quenching in dense liquid witnessed the success and the utility of this approach both from theoretical^{1,2} and experimental³ perspectives. On the other hand, one naively expects that if the A molecule is excited repeatedly shortly after a bimolecular quenching process, it will experience a nonequilibrium distribution of quencher molecules surrounding it and the decay law (survival probability) of such A^* molecule will be different⁴⁻⁶ from that where an equilibrium distribution of B 's were assumed.

Wilemski and Fixman⁴ had shown how to tackle this reexcitation problem. However, they have adopted several coarse approximations leading to a linear variation of Stern-Volmer curve (I_0/I vs concentration of quencher, C_B) for all values of C_B in spite of the theoretical expectation of non-exponential decay of the survival probability.^{1(d)}

Recently Lee *et al.*^{5,6} have considered the reexcitation problem based on a hierarchical system of phenomenological kinetic equation of the distribution functions of reactant molecules.⁷ The general formalism adopted by these authors essentially advocates the many-particle nature of the problem. The reexcitation problem has been considered through a time dependent source term in the phenomenological rate law of A^* concentration. The importance of reexcitation of

fluorophore has been recognized, as stated by Lee *et al.*⁶ “the opportunity of repeated excitation grows with increase in the intensity and the time width of the light pulse, and the fraction of A* molecules reexcited after bimolecular quenching rather than after unimolecular decay increases as the quencher concentration increases.” It is clearly shown^{5,6} how the conventional theories break down under such situations.

Dong, Baros, and Andre⁸ (DBA) have elaborated a molecular dynamics (MD) simulation method based on first principles for a model diffusion-controlled fluorescence quenching kinetics in a dense hard sphere liquid where the fluorophore is excited by a light flash of δ -pulse response. The influence of molecular nature of the reactants and the solvent has been studied by them. The authors have used the simplest version of the Smoluchowski theory using an absorbing boundary condition and the solvent influence on the potential of mean force between two molecules has been neglected. Large discrepancies especially at short times have been found and have been attributed to memory effects.⁹

Recently Zhou and Szabo¹⁰ (ZS) have compared the simulation data with the alone effect of the potential of mean force incorporated in the Smoluchowski theory and have solved the resulting equation with a more appropriate radiation boundary condition of Collins–Kimball.¹¹ Excellent agreement between theory and simulation data has been obtained in the short time limit. More recently Dong and Andre¹² have proposed a general diffusion equation considering the non-Markovian effect through a time dependent diffusion coefficient. When the Collins–Kimball boundary condition is considered an approximate analytical solution is obtained only in short and long time regions. However, the predicted effects are yet to be confirmed either by experiments or by simulation.

In the present work, the problem of repeated excitation of fluorophore by a short but finite duration exciting light pulse is considered. As stated above the decay law for such excited fluorophores will be different from those which has been excited for the first time or repeatedly excited after unimolecular decay processes.^{5,6} MD simulations are carried out for such excited fluorophores and results are compared with the theory^{5,6} for the dependency of fluorescence quenching kinetics on the intensity and pulse width of exciting light. We reexamine the alone effect of potential of mean force determined by pair distribution function of the liquid and use the Collins–Kimball boundary condition at contact with an intrinsic reaction rate constant equated to the gas-density collisional rate.¹⁰

The remainder of the paper is organized as follows: Section II summarizes the current general theoretical framework^{5,6} and the relevant kinetic equations to describe the quenching kinetics. The resulting equations are solved numerically. We then describe the MD simulation of the survival probability following the method elaborated by DBA. Survival probability of A* for an equilibrium distribution of B's and that for a nonequilibrium distribution of B's (after a bimolecular collisional process between A* and B) are obtained in this section. The comparison between the theoretical predictions and the MD simulation results are discussed and our conclusions are summarized in Sec. III.

II. KINETIC EQUATIONS AND MD SIMULATION

Lee *et al.*^{5,6} starting from a hierarchy of a many-body Smoluchowski equation for the reduced distribution functions of reactant molecules⁷ have derived the following rate law for the reaction scheme given by Eq. (1.1):

$$\frac{d}{dt} [A^*] = -k_s[A^*]_t + F(t)[A]_t - k(t)[A^*]_t[B], \quad (2.1)$$

where $[A^*]_t$ and $[A]_t$ denote the time dependent number densities of A* and A, respectively, and $[B]$ is the number density of quencher molecules present in large excess in the liquid medium and therefore assumed constant in time. The time dependent quenching rate constant, $k(t)$, depends on the details of the time evolution of distribution functions of reactant molecules.

From the first principles the temporal evolution of A* at time t can also be expressed by a convolution integral of the rate of production of $[A^*]$ at time τ dictated by the excitation function, $F(\tau)$ and the subsequent survival probability of A* at time t , $G(\tau, t)$, i.e.,

$$[A^*]_t = \int_0^t d\tau F(\tau)[A]_\tau G(\tau, t). \quad (2.2)$$

In conventional theories, where light intensity effects on the quenching kinetics are not considered, it is simply assumed that the life history of each A* molecule after the photostimulation event is same irrespective of the temporal event when the photostimulation has occurred. $G(\tau, t)$ in expression (2.2) embodies the essential difference from the conventional theory indicating that the survival probability at time t depends on the instant of time, τ when the excitation occurred. $G(\tau, t)$ essentially contains, as mentioned in Sec. I, the different decay laws that could arise due to a exciting pulse of short but finite duration. We will be using Eq. (2.2) after we obtain the simulation data that is to be discussed shortly after.

When no long range interactions are present, the time dependent rate coefficient $k(t)$ appeared in Eq. (2.1) is obtained from time dependent pair distribution function $p_{A^*B}(r, t)$ of A* and B, given by

$$k(t) = 4\pi D \sigma^2 [p'_{A^*B} + \beta p_{A^*B} U']_{r=\sigma}. \quad (2.3)$$

In Eq. (2.3) the prime denotes first-order differentiation with respect to spatial separation, r and σ is the contact distance, i.e., the hard-sphere diameter. Here, $\beta = 1/k_B T$ (k_B is the Boltzmann constant and T is the absolute temperature) and D is the relative diffusion coefficient between A* and B.

To evaluate the time dependent rate coefficient, $k(t)$ from the time dependent pair distribution function $p_{A^*B}(r, t)$ between A* and B we need an expression for the latter. Starting from the definition of one-particle, two-particle, and three-particle reactant distribution function and using a superposition approximation Lee *et al.*^{5(a)} have derived the kinetic equation for the temporal evolution of the pair distribution function between A* and B. This in the limit that long-range interactions are absent is given by

$$\begin{aligned} \frac{\partial}{\partial t} p_{A^*B}(r, t) = & \frac{D}{r^2} \frac{\partial}{\partial r} r^2 e^{-\beta U(r)} \frac{\partial}{\partial r} e^{\beta U(r)} p_{A^*B}(r, t) \\ & + F(t) \frac{[A]_t}{[A^*]_t} [p_{AB}(r, t) - p_{A^*B}(r, t)]. \end{aligned} \quad (2.4)$$

We assume that dynamical correlations which result into short-range reduction of relative diffusion coefficient D between A^* and B are absent. D is equated to twice the self-diffusion coefficient of a dense hard-sphere liquid. The solvent influence on the potential of mean force, $U(r)$ between two molecules perturbs the relative motion and is related to the radial distribution function $g(r)$ of the solvent following:

$$\exp[-\beta U(r)] = g(r). \quad (2.5)$$

We obtain $g(r)$ through MD simulation of the liquid. Equation (2.4) is to be solved for $p_{A^*B}(r, t)$ with the appropriate initial and boundary conditions

$$p_{A^*B}(r, t=0) = g(r), \quad (2.6)$$

$$\lim_{r \rightarrow \infty} p_{A^*B}(r, t) = 1, \quad (2.7)$$

and the inner boundary condition is given by radiative boundary at contact distance σ ,

$$4\pi D \sigma^2 [p'_{A^*B} + \beta p_{A^*B} U']_{r=\sigma} = k_0 p_{A^*B}|_{r=\sigma}. \quad (2.8)$$

Here, k_0 represents the finite reaction rate constant at contact distance. Following ZS we equate k_0 to the collision rate constant between hard sphere in a dilute gas,

$$k_0 = 4\sigma^2 (\pi/m\beta)^{1/2}, \quad (2.9)$$

where m is the mass of hard sphere.

To solve Eq. (2.4) for $p_{A^*B}(r, t)$ we need another expression for the time dependent pair distribution function, $p_{AB}(r, t)$ between ground state A and B molecules. The Smoluchowski equation for $p_{AB}(r, t)$ under the condition that long-range interactions are absent is given by^{5(a)}

$$\begin{aligned} \frac{\partial}{\partial t} p_{AB}(r, t) = & \frac{D}{r^2} \frac{\partial}{\partial r} r^2 e^{-\beta U(r)} \frac{\partial}{\partial r} e^{\beta U(r)} p_{AB}(r, t) \\ & + \frac{[A^*]_t}{[A]_t} [k_s + k(t)p_B] \\ & \times [p_{A^*B}(r, t) - p_{AB}(r, t)], \end{aligned} \quad (2.10)$$

where p_B is the density of quencher molecules.

In Eqs. (2.4) and (2.10) we have assumed that the potential of mean force between the quencher and fluorophore in ground and excited states are the same. With this assumption Eq. (2.4) becomes free from $p_{AB}(r, t)$ to yield^{5(a)}

$$\begin{aligned} \frac{\partial}{\partial t} p_{A^*B}(r, t) = & \frac{D}{r^2} \frac{\partial}{\partial r} r^2 e^{-\beta U(r)} \frac{\partial}{\partial r} e^{\beta U(r)} p_{A^*B}(r, t) \\ & + \{F(t)C_A^0/[A^*]_t\} [g(r) - p_{A^*B}(r, t)], \end{aligned} \quad (2.11)$$

where C_A^0 is the total number density of fluorophore molecules in ground and excited states. We thus need to solve

Eqs. (2.1) and (2.3) along with Eq. (2.11) subject to the initial and boundary conditions given by Eqs. (2.6)–(2.8).

Equation (2.11) with the corresponding boundary conditions can only be solved numerically. We employ the Crank–Nicholson finite difference technique¹³ for this purpose. However Eqs. (2.1), (2.3), and (2.11) are a coupled set of equations and are solved following the iterative scheme of Lee *et al.*^{6(a)} The zeroth order initial ($t=0$) value of $k(t)$ is taken to be equal¹⁴ to $k_0 g(\sigma)$ and the pair distribution function at contact $[g(\sigma)]$ is obtained from collisional virial.¹⁵ Extreme care was taken for the accuracy of the numerical technique.

To compare with the primitive Smoluchowski framework of diffusion–reaction we have also solved the same set of equations namely, Eqs. (2.1), (2.3), and (2.11) under the condition that $U(r)=0$ and reaction occurs with unit probability when a B molecule comes in contact with A^* (i.e., $k_0 \rightarrow \infty$). DBA had employed this primitive version of the theory while comparing with the MD simulation results of the survival probability of $A^*(t)$.

Up to now, we were considering the kinetic equations governing time evolution of the excited fluorophores. We now turn to discuss the MD simulation method.

Our simulation system consists of one A molecule and N_B other particles are labeled as B molecules dissolved in a dense hard-sphere solvent. The above system is chosen since theories based on the Smoluchowski model of irreversible diffusion-modulated reactions have recently been compared^{8,10} with such simulation framework. In addition such comparisons were made for an equilibrium distribution of B's around an excited A molecule. Our aim is to test this theory under a situation when an excited A molecule may also be surrounded by a somewhat nonequilibrium distribution of B's.

The simulations were carried out in a face-centered-cubic (fcc) box, which contains 256 hard spheres. The initial velocities were chosen from the Maxwell–Boltzmann distribution. The liquid density is taken to be $\rho\sigma^3=0.786$ (with $\sigma=6$ Å). A good description on the generation of trajectories of hard-sphere system is found in Ref. 16. Periodic boundary conditions along with the minimum image convention were implemented in the calculations. Conceptually the simulation involves three steps.⁸ They are (i) initiation and equilibration: the fcc lattice positions along with Maxwell–Boltzmann distribution of velocities are allowed to equilibrate. Then a molecule of type A^* and N_B other molecules of type B are chosen randomly, the rest of the $(255-N_B)$ molecules make up the solvent, (ii) propagation: trajectories are generated¹⁶ and the spheres are allowed to undergo inertial motion, (iii) modeling of reaction: A^* reacts when it elastically collides with any of the randomly chosen B molecules. Time intervals between “creation” and elastic collision of A^* with B are recorded.

The quantity of interest, the survival probability of A^* [$S_{A^*}(t)$] for an equilibrium distribution of B's around A^* is then calculated after averaging over a sufficient number of collisions.⁸ However, this sequential counting of collisional events is only prohibitively time consuming. Instead, aided by the two prescriptions⁸ that each collisional event is inde-

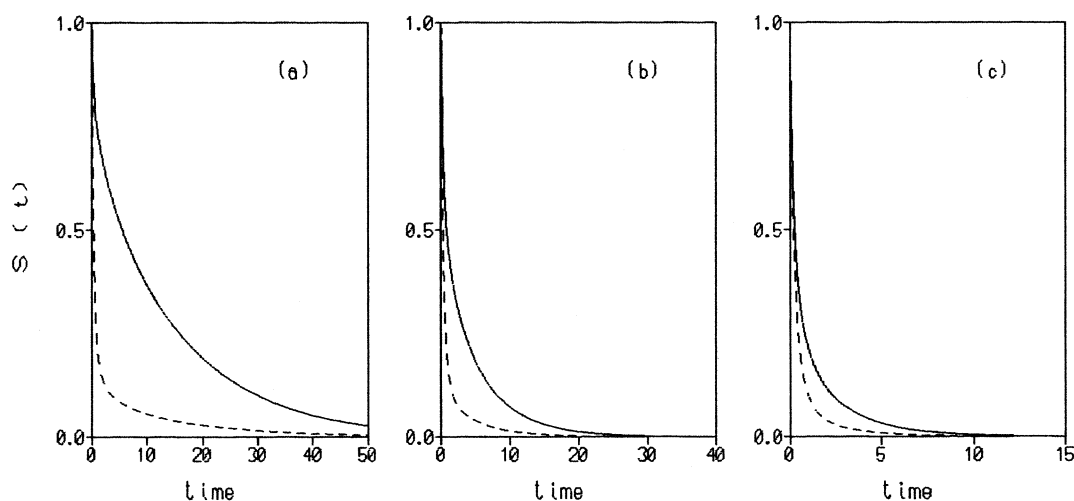


FIG. 1. MD results of survival probabilities, $S(t)$ obtained from two simulations, $S_{A^*}(t)$ (—) and $S'_{A^*}(t)$ (---) (see the text); (a) $N_B=8$ (0.2 M), (b) $N_B=21$ (0.5 M), and (c) $N_B=42$ (1.0 M).

pendent of each other and that other than they are being labeled (to help count the reactive events), all hard spheres are equivalent—each sphere can be thought of as A^* molecules with its associated equilibrium distribution of B molecules.

In the present work we carried out two simulations with $N_B=8, 21, 42$, and 255. For $N_B=255$, each of the hard spheres is associated with all other 255 hard spheres with solvent molecules missing. In the first simulation when an A^* molecule collides with its randomly chosen sets of N_B B molecules, the time taken for such events (survival time) is recorded. Thereafter, again a random distribution of B's are chosen and counting of another collisional event is restarted and the process is repeated. The survival time thus collected for about 10^5 collisions is used to calculate the survival probability of A^* at time t [$S_{A^*}(t)$], defined by the fraction of collisional events (between A^* and B) those have survival time longer than t .

The second simulation was performed using the same algorithm with only one difference. That is, any of the randomly chosen B molecules are first allowed to collide with A^* and then the time is recorded between this first collision and a second collision of A^* for the same choice of B's. Using the same prescription as above, after a large number of survival times being collected, this provides another survival probability, $S'_{A^*}(t)$. This mimics the phenomena of repeated excitation and the consequent decay of a fluorophore after a bimolecular quenching process.

The equilibrium pair distribution function $g(r)$ of the liquid is calculated using the standard simulation technique¹⁶ and the value of $g(r)$ at $r=\sigma$ is found to be 3.91 obtained from the collisional virial.

Using the data from simulation for $S_{A^*}(t)$ and $S'_{A^*}(t)$, the effects of light intensity on the temporal behavior of fluorescence kinetics is obtained. To obtain this we have used the summation form of the convolution integral Eq. (2.2) with the associated time dependent source term and survival probabilities. After the excitation source is turned on, the time

evolution of $[A^*]$ involves contributions from three terms. The first term includes excitation of ground state A molecule for the first time. The second term is a summation of number densities of A^* molecules those were excited in the previous time steps. The third term includes summation of excited state number densities of A^* molecules those are obtained after reexcitation of any previously deactivated molecules. As mentioned earlier the survival probabilities of the A^* molecules included in the third term are characterized by $S'_{A^*}(t)$. It is to be noted that we have not considered any reexcitation of A molecules those are obtained from the decay of reexcited A^* molecules included in the third term. In other words, we have truncated the repeated excitation of the ground state A molecule at the level of first reexcitation after a bimolecular quenching process.

In all our calculations we assume that the time-dependent intensity of the exciting light pulse is given by⁶

$$F(t) = (F_0 t / t_1) \exp[-(t^4/t_1^4 - 1)/4], \quad (2.12)$$

where F_0 is the maximum excitation probability of A molecules per unit time at $t=t_1$. Following DBA the natural lifetime of the fluorophore, $\tau_0 (=k_s^{-1})$ was taken to be 41.28. We use the reduced form of time in the units of $(\sigma^2 m / k_B T)^{1/2}$.

III. RESULTS AND DISCUSSIONS

Using the data for survival times from simulation, we first consider the survival probability at three concentrations of B [0.2 M ($N_B=8$), 0.5 M ($N_B=21$), 1.0 M ($N_B=42$)]. The survival probability, $S_{A^*}(t)$, for an equilibrium distribution of B's around A^* and $S'_{A^*}(t)$ for the situation that mimic the repeated excitation are shown in Fig. 1. The curves on the figure demonstrate the difference between survival probabilities of our two considerations. The fact that an A^* molecule will on the average experience a higher number of B molecules around it (in comparison to an equilibrium distribution) immediately after a bimolecular collision process leads

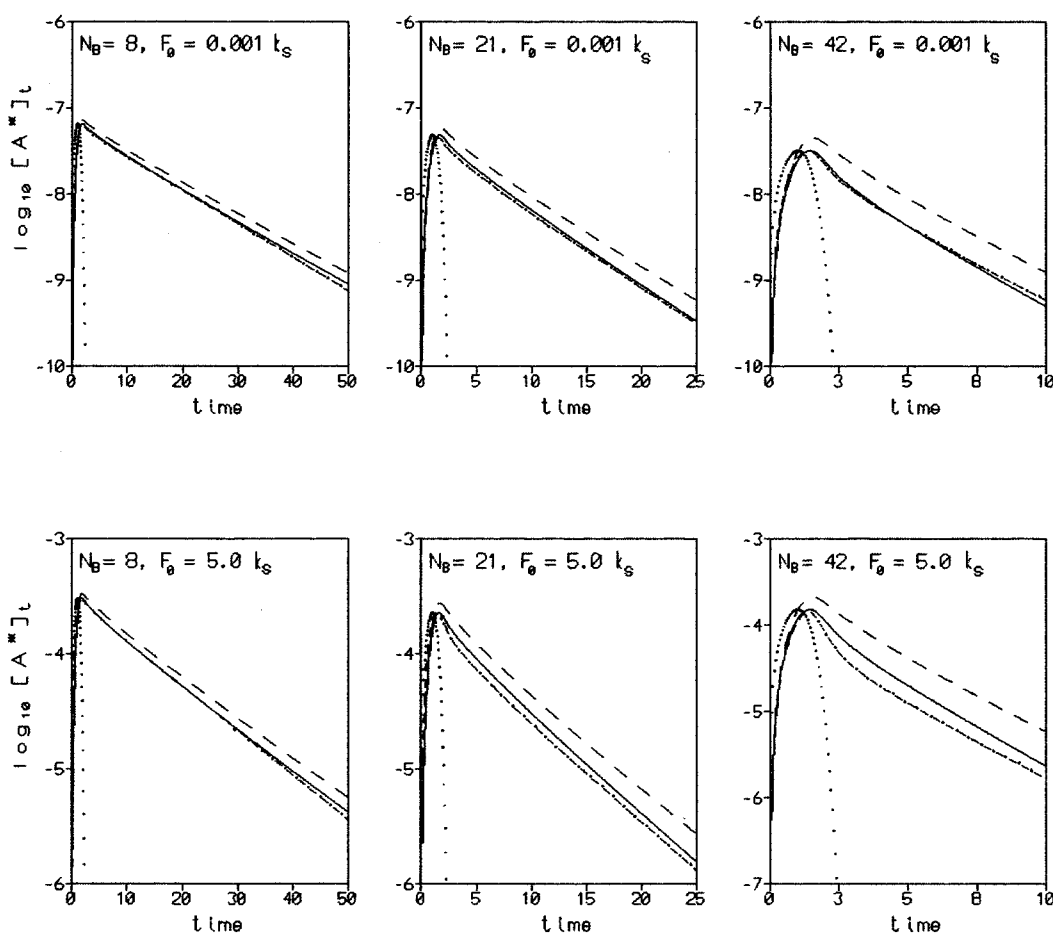


FIG. 2. The fluorescence decay curves obtained from Smoluchowski theory using a radiation boundary condition at contact and potential of mean force (—), the simplest version of the theory using absorbing boundary condition and $U(r)=0$ (---) and convoluted results of simulated survival probabilities (.....) [upper panel: absolute values, lower panel: scaled values (see the text)]. The shifted lamp profile (with $t_1=1.0$) is represented by dots.

to such differences. This fact becomes more evident from the figure that as the concentration of B is increased the relative difference between the curves for $S_{A*}(t)$ and $S'_{A*}(t)$ decreases. In the case of $N_B=255$ (i.e., in the absence of solvent molecules) this difference completely vanishes.

Using a refined version of the Smoluchowski theory ZS have shown¹⁰ on the basis of exact statistical mechanical ground that in spite of the many-particle diffusive dynamics the theory is exact especially at short times and works extremely well for a wide range of concentrations. It is to be mentioned that our results of $S_{A*}(t)$ corresponds to survival probabilities considered by DBA and ZS. The faster decay of $S'_{A*}(t)$ suggests that the memory effects^{9,12} might be of importance to explain such behavior.

The relative difference between $S_{A*}(t)$ and $S'_{A*}(t)$ at low concentrations of B clearly suggests the importance of considering the effects due to exciting light pulse of short but finite duration on the fluorescence quenching kinetics. At higher concentrations of quenchers the chances of repeated excitation increases because of the reduction in mean fluorescent lifetime of A^* .

In Figs. 2 and 3 we display the results of dependence of the fluorescence decay curve on the exciting light pulse in-

tensity obtained from convolution integral, Eq. (2.2) (using the simulation data) along with the results obtained from the simplest version of the theory [$U(r)=0$ and $k_0 \rightarrow \infty$] and the modified version of it [$U(r)=-k_B T \ln g(r)$ and k_0 is finite]. Figures 2 and 3 represent the effects of a light pulse of relatively short and longer duration, respectively. In this figures the time profile of the light pulse is also shown in the form of $\log_{10} [F(t)/F_0]$ and it is to be noted that this has been shifted so that the maximum value of this becomes equal to $[A^*]_{\text{maximum}}$ obtained from a modified version of the theory.

Like Lee *et al.*,^{6(a)} we have also found that the peak value of $[A^*]_t/[A^*]_{\text{max}}$ results obtained from convoluting the simulated survival probabilities shifts to a shorter time as F_0 increases (not shown in the figure). This suggests that the reexcitation effect due to a finite pulse width becomes more prominent as F_0 increases and consequently the peak value of $[A^*]_t$ shifts to a shorter time.

The upper panel of Figs. 2 and 3 is for a light pulse of weak intensity ($F_0=0.001k_s$) and the lower panel is for a high intensity exciting lamp for the three concentrations of quenchers ($N_B=8, 21$, and 42). As we observe in the upper panel of Fig. 2, the fluorescence decay curve corresponding

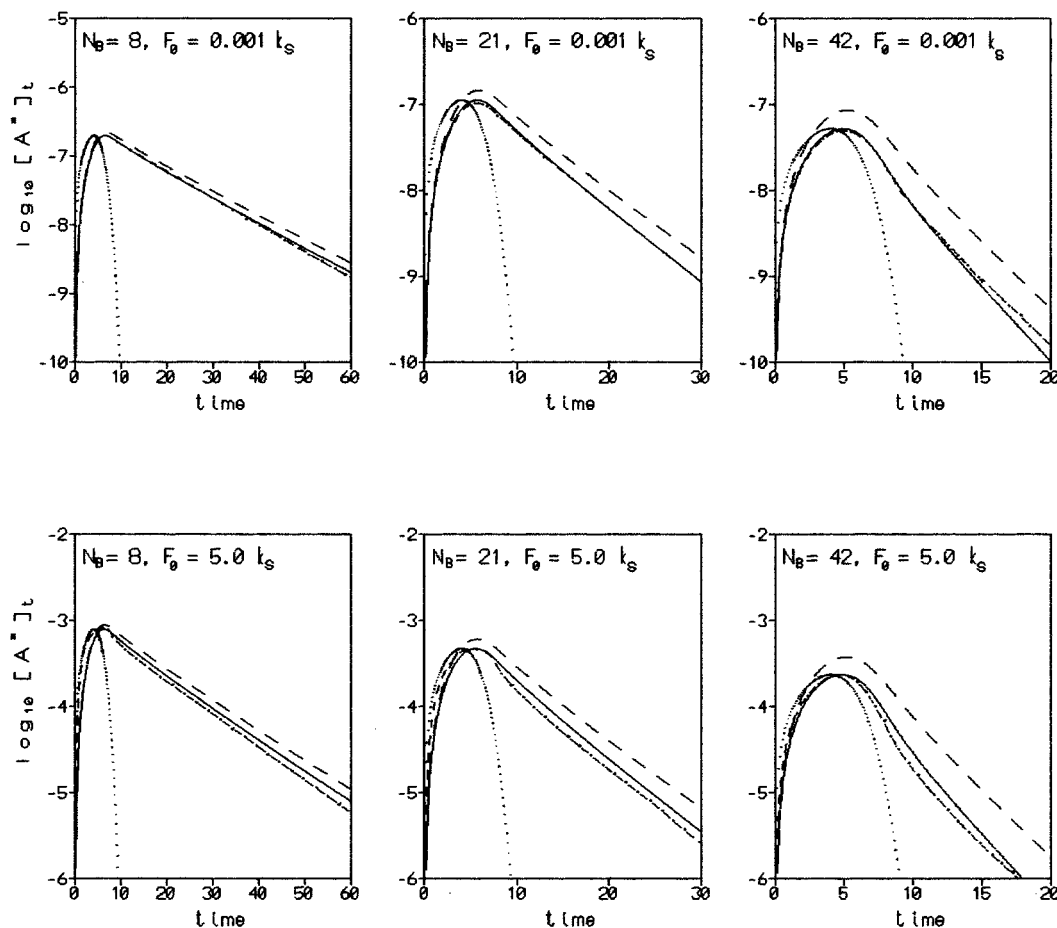


FIG. 3. Same as Fig. 2 with exciting lamp width parameter, $t_1=4.0$.

to convoluted results of simulated data agrees reasonably well with the theory modified by inclusion of potential of mean force and a finite reaction rate at contact in the low F_0 condition. This is more so in the case of low concentration of quencher molecules. At a higher concentration there is some degree of disagreement between simulation and theoretical results. This is due to the assumption made in the Smoluchowski theory that B's are noninteracting with each other even at high concentration. The upper panel of Fig. 3 displays the same behavior of fluorescence decay curve with an exciting pulse of longer duration ($t_1=4.0$). Under such situations the reexcitation event becomes more probable, and therefore the effect due to this on the temporal evolution of $[A^*(t)]$ will be more pronounced with intense pulse (high F_0) than with a pulse with low F_0 . The agreement between the modified version of theory and MD results are quite satisfactory at low F_0 (upper panel of Fig. 3) but becomes poor at high F_0 (the simulated curve drawn in the lower panel of Figs. 2 and 3 are scaled results to be discussed shortly).

The poor agreement at high F_0 is primarily due to the fact that during convolution of survival probabilities we have neglected the chances of second and successive repeated excitation of the fluorophore each after a bimolecular quenching process.

To take into account the error introduced in truncating

the repeated excitation of A at the level of first reexcitation after a bimolecular quenching process, we have scaled the convoluted results of simulated survival probabilities such that the maximum of $[A^*]_t$ obtained by this way matches with that obtained from a modified version of the theory. These scaled data are given by

$$[A^*]_{t,\text{scaled}} = [A^*]_{t,\text{max}}^{\text{modified theory}} \{ [A^*]_t^{\text{convoluted}} / [A^*]_{t,\text{max}}^{\text{convoluted}} \}.$$

This is also not unphysical, since in experiments usually one is interested in the relative intensity of fluorescence rather than its absolute magnitude. The convoluted results are thus scaled and displayed in the lower panel of Figs. 2 and 3 for intense exciting source ($F_0=5.0k_s$). Once again the agreement between theory and the scaled convoluted result is quite well. This suggests that the modified version of the theory¹⁰ works extremely well even under this situation.

Both in Figs. 2 and 3 the poor performance of the primitive and simplest version of the theory [i.e., $U(r)=0$ and $k_0 \rightarrow \infty$] is also observed. At this point we would like to mention the connection between the use of a radiation boundary condition in the diffusive dynamics formalism of Smoluchowski and the trajectory computations of bimolecular reactions in solution.¹⁰ The reactions in the simulation is modeled in a way such that when the A^* molecule collides with B, they react. This represents an absorbing boundary condi-

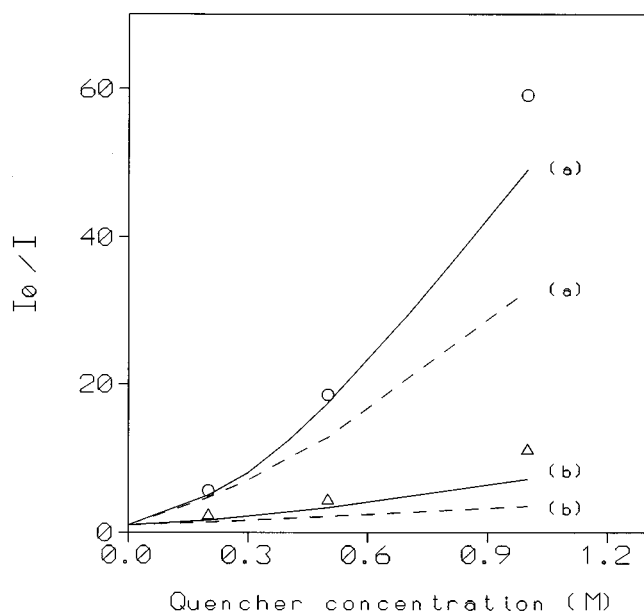


FIG. 4. Stern-Volmer plots obtained for (a) weak ($F=0.001k_s$) and (b) intense ($F=10.0k_s$) illumination. The solid and dashed curves are from the two versions of the theory as stated in Fig. 2. Circles and triangles represent the MD simulation results for the same weak and intense illumination, respectively.

tion in phase space. However, the MD approach is like a very detailed mechanical description that the very complexity of such a process makes it necessary to model the role of solvent through a frictionlike term in the Langevin equation to characterize the motion. And as mentioned by ZS the Langevin dynamics with an absorbing boundary condition in the high friction limit (in dense liquid) reduces to solving the Smoluchowski equation with the radiation boundary condition at contact.

Let us now study how the inclusion of potential of mean force and finite intrinsic reaction rate at contact improves the theory when we consider the light intensity effects on steady-state fluorescence quenching kinetics. In this kind of experiment the excitation rate of fluorophore may be considered independent of time, i.e., $F(t)=F$. The ratio of I_0/I is given by

$$I_0/I = [A^*]_s(p_B=0)/[A^*]_s(p_B \neq 0), \quad (3.1)$$

where $[A^*]_s$ denotes the long-time results of steady-state concentration of A^* under an exciting source with constant intensity. Following the formal solution^{5(a)} of Eq. (2.1) the value of $[A^*]_s(p_B=0)$ is given by

$$[A^*]_s(p_B=0) = C_A^0 F / (k_s + F). \quad (3.2)$$

The value of $[A^*]_s(p_B \neq 0)$ is obtained from the long-time steady-state results of concentration of A^* for the situation $F(t)=F$ (for both the simulated and convoluted data and the two versions of the theory).

In Fig. 4 we compare the results of the Stern-Volmer plot obtained from convoluting the simulated data with that of the two versions of the theory at low ($F=0.001k_s$) and high ($F=10k_s$) intensity of constant illumination. As mentioned in the introductory section, with such a low intensity

[denoted in Fig. 4 by (a)] the phenomena of repeated excitation is not appreciable and the present framework of such effects reduces to conventional theories where light intensity effects are not considered. All the theoretical curves denoted by (a) in Fig. 4 and the circles for simulated results under weak intense illumination show a positive deviation from the linear behavior. The simulated results agree reasonably well with the modified form of the theory up to 0.5 M concentration of quencher with finite reaction rate at contact and potential of mean force incorporated. However, the theory with infinite reaction rate at contact and no consideration of potential of mean force leads to a more drastic positive deviation. The same kind of behavior of the Stern-Volmer plots have also been observed by ZS and as expected our results with low F values can be compared with the results of ZS.

The Stern-Volmer plot with an intense illumination of constant intensity ($F=10k_s$) obtained from theories are denoted by (b) and displayed in Fig. 4 along with the simulated results denoted by triangles. With an increase in F the curvature of Stern-Volmer plots decreases. As mentioned by Lee *et al.*,^{5(a)} an increase in F results in an increase of steady-state quenching rate coefficient but relatively at a slower rate. This leads to a decrease in the slope of the Stern-Volmer plot [cf. Eqs. (3.5) and (3.20) of Ref. 5(a)]. The improvement of the modified form of theory over its simplest form is clearly manifested.

In conclusion, we have studied the light intensity effects on the fluorescence quenching kinetics in a simple hard-sphere fluid using the MD simulation technique and the results are compared with the recently proposed theory.^{5,6} The attitude in this work is that the reexcitation problem and subsequent quenching effects on the total fluorescence quenching kinetics is like a phenomena that calls for a separate interpretation through non-Markovian effects.^{8,9,12} However, the modified form of the theory that we have employed and our modeling of such reactions in hard-sphere liquid compares well without any drastic need of considering the non-Markovian effects.

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