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ON THE APPLICABILITY OF THE SMOLUCHOWSKI APPROACH TO DIFFUSION CONTROLLED REACTIONS. MOLECULAR DYNAMICS SIMULATIONS AND THEORY*

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Dedicated to Professor Andrzej Fuliński on the occasion of his 70th birthday

The Smoluchowski approach to the kinetics of fluorescence quenching reaction in liquids is tested by comparing the results of molecular dynamics simulations for spherical molecules with the Smoluchowski–Collins–Kimball model and the Step Function Nonradiative Lifetime model. The reaction cross-sections used in the simulations are exactly the same as assumed in the models and the quencher concentration is very low. The discrepancies between the simulations and the models give a general indication on the scale of errors of the Smoluchowski approach. A large number of particles used (typically $N = 681472$) allow us to obtain quantitative results. The simulations show a decisive influence of the distribution function of the reagents, $g_{\mathrm{AB}}(r)$, on the accuracy of results. If the liquid structure is ignored ($g_{\mathrm{AB}}(r) \equiv 1$) the discrepancies between the model and the simulations are large especially for a very short times for which the models fail to match simulations even qualitatively. An inclusion of the distribution function significantly improves the description of the quenching process. For short time stages of the quenching the model excellently agrees with the simulations, if the characteristic reaction time is long. If it is very short (the SCK model), significant discrepancies appear due to ballistic motion of the reactants but the quantitative agreement is still good. For a long time the model that takes into account the liquid structure is typically burdened with a few times smaller errors than the model that assumes $g_{\mathrm{AB}}(r) \equiv 1$.

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1. Introduction

The fluorescence quenching [1] is an example of a very simple diffusion controlled chemical reaction. During this reaction an excited state of the A molecule (A*) de-excites by interacting with the B molecule called quencher. A standard approach to the kinetics of the diffusion controlled reaction was formulated by Smoluchowski [1, 2] over 80 years ago. The most popular model that bases on this approach is the Smoluchowski–Collins–Kimball (SCK) [1, 3] model. It assumes that the reactants are spherical and the reaction occurs instantaneously when the interparticle distance, r, is equal to the reaction radius, a. The model gives a simple analytical formula for the reaction rate [1, 4], which is widely used to interpret experimental data of fluorescence quenching [5–9]. Many experiments [10–13] show inconsistencies between the model and reality. The recent works of Krystkowiak and Maciejewski [12, 13] report significant differences between the parameters obtained by fitting the experimental results of fluorescence quenching with the SCK model and the values obtained by different methods. On the other hand, the report on consistency between the model and experimental results can be also found in the literature [14]. Another model which applies the Smoluchowski approach is the Step Function Nonradiative Lifetime model [1, 15, 16]. It assumes that the reaction occurs with a given constant probability if r is lower than a given R parameter (unfortunately, also called as the reaction radius), which is a more reasonable approximation than that for the SCK model. It is shown [10, 17] that the model better fits experimental results than the SCK one.

The purpose of our work is to test the applicability of the Smoluchowski approach by comparing the results obtained from the SCK and the SFNL model with computer simulation results. We simulate reaction between A* and B using molecular dynamics (MD) and our assumptions match as closely as possible that of the models. Since most of the assumptions of the theory are satisfied, the differences between the models and the simulations give us information on the scale and the origin of the inconsistencies coming from the application of the Smoluchowski approach. The simulations also allow us to estimate the errors caused by the neglect of spatial correlations between A* and B ($g_{\mathrm{A^*B}}(r) = 1$) typical in analysis of experimental data.

A large scale of our simulations (typically, the total number of molecules $N = 681472$) has allowed us to make the quantitative test. Simple, qualitative comparisons for both the Smoluchowski [1, 2] and the SCK model with simulation results for a hard sphere liquid were performed over 10 years ago [18, 19]. The main conclusion [19] was that the SCK model gave surprisingly good results, much better than the Smoluchowski one. Zhou and Szabo [19] showed also that the agreement between the model and the simulations improved significantly when the shape of the two-particle radial distribution function was taken into account. This conclusion was only qualitative one and no quantitative analysis of differences between the model and the simulations have been performed. The scale of simulations was not sufficient to obtain quantitative results. As a consequence, they wrongly concluded that incorporating the $g_{\mathrm{AB}}(r)$ function into the model one obtains an exact description of the kinetics at short times [19]. As shown by our simulations, this is not true if the reaction is very fast (*i.e.* exactly the case that they studied).

The paper bases on the results of our two works [16,20]. It is organized as follows. Section 2 presents the Smoluchowski approach and both models considered: the SCK model and the SFNL model. The information on simulation technique, the interparticle interactions and methods of describing simulation results are given at the beginning of Section 3. The computer simulation results are presented in two subsections. Sec. 3.1 gives the results for short time of quenching reaction by comparing the time dependent rate coefficients obtained from simulation with that from the models for a few selected cases. The differences between the values of diffusion obtained by fitting the theoretical curve with the experimental results and the real values "measured" directly during the simulations are discussed in Sec. 3.2. These differences give us a measure of errors coming from the application of the Smoluchowski approach to the description of diffusion controlled reactions. The summary and conclusions are presented in Section 4.

2. Models

Following the Smoluchowski approach, we consider spherical molecules in three dimensional bulk liquid and a fluorescence quenching reaction in the form:

$$\mathrm{A}^* + \mathrm{B} \rightarrow \mathrm{A} + \mathrm{B}\,, \tag{2.1}$$

where A* is an excited A molecule and B is a quencher. We assume that from the mechanical point of view the system is in the equilibrium state and the excited and ground states of A are identical. We treat reaction as a sum of independent processes, which, in practice, means that the number fractions of A* and B molecules fulfill: $x_{\mathrm{A}^*} \ll x_{\mathrm{B}} \ll 1$. We assume that the probability of finding the A* particle around the B particle at the interparticle distance r and at time t, $p(r,t)$, satisfies the Smoluchowski equation [1,2] for spherical molecules, here (the formula (2.2)) written in the general form with the reaction governed by the sink term [21], $\kappa(r)p(r,t)$.

$$\frac{\partial p(r,t)}{\partial t} = \frac{D_{\mathrm{S}}}{r^2}\frac{\partial}{\partial r}\left(r^2 g_{\mathrm{AB}}(r)\frac{\partial}{\partial r}\left(\frac{p(r,t)}{g_{\mathrm{AB}}(r)}\right)\right) + \kappa(r)p(r,t)\,. \tag{2.2}$$

The initial condition is: $p(r,0) = g_{\mathrm{AB}}(r)$, where $g_{\mathrm{AB}}(r)$ is the equilibrium pair distribution function which, according to our assumptions, is identical to $g_{\mathrm{A^*B}}(r)$. The D_{S} coefficient is independent of r and equal to the sum of the diffusion coefficients of A and B of bulk liquid. The first boundary condition reads: $\lim_{r\to\infty} p(r,t) = 1$. The second, the reflecting boundary condition, results from the presence of the distance of minimum approach, a. Therefore:

$$\left[\frac{\partial}{\partial r}\left(\frac{p(r,t)}{g_{\mathrm{AB}}(r)}\right)\right]_{r=a} \equiv 0\,. \tag{2.3}$$

The kinetics of the reaction (2.1) is described by the rate coefficient, $k(t)$, which, in the absence of spontaneous de-excitation ($\mathrm{A}^* \to \mathrm{A}$), can be defined as:

$$k(t) = -\frac{1}{\rho x_{\mathrm{B}}}\frac{\partial \ln(N_{\mathrm{A}^*})}{\partial t}\,, \tag{2.4}$$

where $N_{\mathrm{A}^*}(t)$ is the current number of A*, $\rho(= N/V)$ is the numerical density and, $x_{\mathrm{B}}(= N_{\mathrm{B}}/N)$ is the number fraction of quencher. Considering (2.2) and (2.3) the rate coefficient can be also written as:

$$k(t) = 4\pi \int_a^\infty \kappa(r)p(r,t)r^2 dr\,. \tag{2.5}$$

We consider two cases of the Smoluchowski approach. First, when the $g_{\mathrm{AB}}(r)$ function is known (here we take it from simulations) and equation (2.2) is applied in the present form. Further, this case is called the full model (or case). Second, which is standard for interpreting experimental results, when the distribution function is not known. For such a case one assumes that the liquid is structureless, which means:

$$g_{\mathrm{AB}}(r) = \Theta(r-a) \equiv \begin{cases} 1 & \text{for } r \geq a\,, \\ 0 & \text{for } r < a \end{cases} \tag{2.6}$$

and (2.2) reduces to the diffusion equation completed by the sink term. Further, this case is called the simplified model (or case).

We are going to consider two models:

(A) The Smoluchowski–Collins–Kimball (SCK) model for which:

$$\kappa(r) = \frac{k_0}{4\pi a^2}\,\delta(r-a)\,, \tag{2.7}$$

where k_0 is the intrinsic rate coefficient. We consider only the special case that the reaction always occurs if $r = a$, which exactly determines [19, 22] k_0:

$$k_0 = 4a^2\left(\frac{\pi k_{\mathrm{B}}T(m_{\mathrm{A}}+m_{\mathrm{B}})}{2m_{\mathrm{A}}m_{\mathrm{B}}}\right)^{1/2}.$$

The introduction of the SCK model by the reflecting boundary condition (2.3) and the sink term in the form of (2.7) is equivalent [23, 24] to the standard definition by assuming $\kappa(r) = 0$ and imposing the Collins–Kimball boundary condition [1, 3]. According to Pedersen and Sibani [2, 4], the rate coefficient for the model can be written at long times as:

$$k(t \gg 1) = \frac{4\pi D_{\mathrm{S}} a_e}{1 + D_{\mathrm{S}}/f} \left(1 + \frac{f}{D_{\mathrm{S}}} \exp\left(\gamma^2 D_{\mathrm{S}} t\right) \operatorname{erfc}\left(\gamma\sqrt{D_{\mathrm{S}} t}\right)\right) , \quad (2.8)$$

where

$$f = \frac{k_0 g_{\mathrm{AB}}(a)}{4\pi a_e} , \quad \gamma = \left(1 + \frac{f}{D_{\mathrm{S}}}\right) a_e^{-1} , \quad a_e^{-1} = \int\limits_a^{\infty} \frac{dr}{g_{\mathrm{AB}}(r) r^2} .$$

For the simplified case, the formula (2.8) is the exact solution of the model for a whole range of t. The exact solution of the full model for short times is obtained numerically.

(B) The Step Function Nonradiative Lifetime model with the sink term:

$$\kappa(r) = \frac{1}{\tau} \Theta(R - r) , \quad (2.9)$$

where τ is the nonradiative lifetime. The exact solution of (2.2) and (2.9) is not known even if one assumes (2.6). For the full case (2.2) is solved numerically. For the simplified case a reasonable approximation has been presented in [16]:

$$\begin{aligned} k(t) \; &\cong \; \frac{4\pi}{3\tau} \left(R^3 - a^3\right) \exp\left(-\frac{t}{\tau}\right) \\ &+ 4\pi\sqrt{D_{\mathrm{S}}^3 \tau} \sum_{n=0}^{4} \gamma_n \int\limits_0^{t/\tau} G_n(q, y) \exp\left(-\frac{t}{\tau}\right) dy , \end{aligned} \quad (2.10)$$

where the parameters q and γ_n are functions of $a/(D_{\mathrm{S}}\tau)^{1/2}$ and $R/(D_{\mathrm{S}}\tau)^{1/2}$ only. The $G_n(q, y)$ functions are expressed by simple analytical functions [16].

3. Computer simulations [16, 20]

The computer simulations were performed using standard molecular dynamics (MD) constant volume and energy (NVE) method [25]. The cubic box and the periodic boundary conditions were applied [25]. The total number of particles, N, was typically equal to 681472. During a single simulation run all particles interacted via the potential of the same kind. Three various kinds of spherical interparticle potentials were considered: Lennard–Jones (LJ), modified Lennard–Jones with $(\sigma/r)^{12}$ replaced by $\exp[18(1-r/\sigma)]$ (denoted by R6e), and soft spheres (SS). The cut-off distance was very short ($R_{\mathrm{C}}/\sigma = 1.65$–$2.15$) and the LJ and the R6e potentials were truncated using the switch function.

For all the investigated systems the reagents (A, A*, and B) were mechanically identical (identical ε, σ, and mass — m) and differed only by a chemical identity parameter. The reaction (2.1) was realized by simple re-labeling A* to A so the simulated system was always in the mechanical equilibrium state. At the beginning of each evolution (after equilibration) some of the reagents were randomly labeled as the B particles. We considered two kinds of microscopic models of the reaction (2.1): the SCK reaction and the SFNL reaction, exactly corresponding to the sink terms of discussed models. The SCK reaction occurred instantaneously (probability $= 1$) if $r = a$. If at $t = 0$, $r < a$ the reaction was assumed to occur earlier and it was not taken into account in the evaluation of $k(t)$. For the SFNL reaction, according to (2.9), the probability that the reaction occurs within the time interval $[t, t + \Delta t]$ is equal to $\Delta t/\tau$ if $r \leq R$ and 0 otherwise.

We considered two kinds of liquids. First, called the simple liquid, consisted only of A and B. Second, called the mixture, consisted of the heavy components (A and B) and the light solvent, S, (90% molar fraction). The parameters of the heavy particles were: $\sigma_{\mathrm{A}} = \sigma_{\mathrm{B}} = 1.35$ and $m_{\mathrm{A}} = m_{\mathrm{B}} = (\sigma_{\mathrm{A}}/\sigma_{\mathrm{S}})^3 m_{\mathrm{S}}$. The σ_{AS} parameter ($= \sigma_{\mathrm{BS}}$) of the A–S interaction satisfied the Lorentz–Berthelot rule [25]: $\sigma_{\mathrm{AS}} = (\sigma_{\mathrm{A}} + \sigma_{\mathrm{S}})/2$. The mixture modeled the system with strong solute–solvent correlations. The energy parameter ε was the same for all the A–A, B–B, A–B and S–S interactions. For the solute–solvent interaction, the energy parameter $\varepsilon_{\mathrm{AS}} = \eta\varepsilon$, where η was equal or sometimes even higher than 1. The numerical values presented further are expressed in reduced units (*i.e.* for: $\sigma = \epsilon = m = 1.0$) of A ($=$ B) for the simple liquids and the reduced units of S for the mixtures. Otherwise the units are explicitly written in the text.

According to the Smoluchowski approach $D_{\mathrm{S}} = D_{\mathrm{A}} + D_{\mathrm{B}}$, where D_{A} and D_{B} (here, the same) are the diffusion coefficients of the reactants of a bulk liquid. The value of the coefficient was "measured" during simulations by using the Einstein formula [25]. The remaining parameters of the models

(a for the SCK model and R, τ for the SFNL model) were the reaction parameters taken to the simulations. More information about the simulation details (interparticle potentials, optimization, *etc.*) is given in Ref. [20].

In order to analyze the simulation data we calculated the time dependent rate coefficient by omitting in (2.4) the higher order terms in δt:

$$k(t) = -\frac{1}{\rho x_{\mathrm{B}}} \frac{N_{\mathrm{A}^*}(t+\delta t) - N_{\mathrm{A}^*}(t-\delta t)}{2\delta t N_{\mathrm{A}^*}(t+\delta t)} \,. \tag{3.1}$$

Our idea was to treat the simulation results like experimental ones. The theoretical values of $k(t)$ obtained from (2.5) were fitted to the simulation results (from (3.1)) by the least square method. The minimizations were performed with respect to one parameter (X) or to two parameters. In further considerations, X^{fit} denotes the value of X corresponding to the best fit.

It is shown in Sec. 3.1 that in the case of the simplified model the discrepancy between the model and the simulations is significantly higher at short times than at $t \to \infty$. As a result, the values of X^{fit} strongly depend on the total time of simulation, t_{T}, if the short time data are not excluded. In order to eliminate this effect we determined the limit of X^{fit} attained for $t_{\mathrm{D}} \to \infty$, where t_{D} (discarded time) is defined as the upper limit of the time interval $\{0, t_{\mathrm{D}}\}$ that is not taken into account in the minimization. The limit obtained this way, $\mathrm{Lim}(X^{\mathrm{fit}})$, is well defined (here, independent of t_{T}) and may be used to test the accuracy of the model by comparing the obtained value with that from the simulation. More information on the problem and discussion about t_{D} is given in Ref. [20] ($\mathrm{Lim}(X^{\mathrm{fit}})$ are called there the “idealized” values).

3.1. The early phase of fluorescence quenching process

Figs. 1 and 2 show a typical time evolution of $k(t)$ for the early phase of fluorescence quenching for the SCK reaction at $a = \sigma_{\mathrm{AB}}$ for the simple liquid R6e (Fig. 1) and the mixture R6e (Fig. 2). The simulation parameters are given in the captions of the figures. $k(t)/k(0)$ obtained from the simulations (circles — calculated from (3.1)) is compared with the prediction by the full model (the solid line — the numerical solution of (2.2) and (2.6) with $g_{\mathrm{AB}}(r)$ from simulations) and by the simplified model (the dashed line — the formula (2.8) for $g_{\mathrm{AB}}(r) \equiv 1$). In this paper, the prediction always means that the theoretical model corresponds to the kind of reaction (SCK or SFNL) and all parameters are the same as that in the simulation. In Sec. 3.2 it is shown that $\mathrm{Lim}(D_{\mathrm{S}}^{\mathrm{fit}})$ may significantly differ from D_{S}. In order to minimize the influence of the long time effect on the comparison for the early phase of quenching the results presented in Figs. 1 and 2 are taken from the simulations that, for the full model, $\mathrm{Lim}(D_{\mathrm{S}}^{\mathrm{fit}}) \approx D_{\mathrm{S}}$.

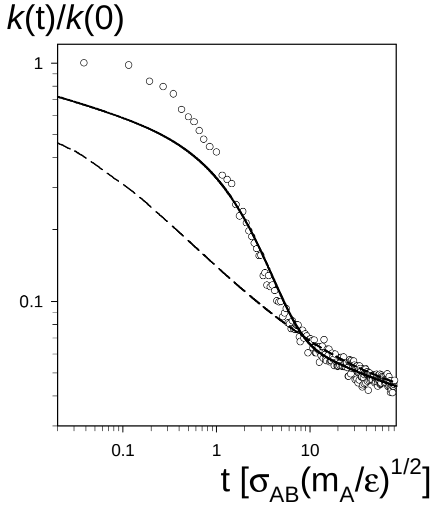

Fig. 1. $k(t)/k(0)$ as a function of time for the early phase of fluorescence quenching from simulation of the SCK reaction at $a = \sigma_{\mathrm{AB}}$ (circles) and the prediction by the SCK model: solid line — the full model, dashed line — the simplified model. Simulation: the simple liquid R6e, $\rho = 0.9358$, $k_{\mathrm{B}}T = 1.0$, $x_{\mathrm{B}} = 0.001$ and, $D_{\mathrm{S}} = 0.0266$ (all in the reduced units of A).

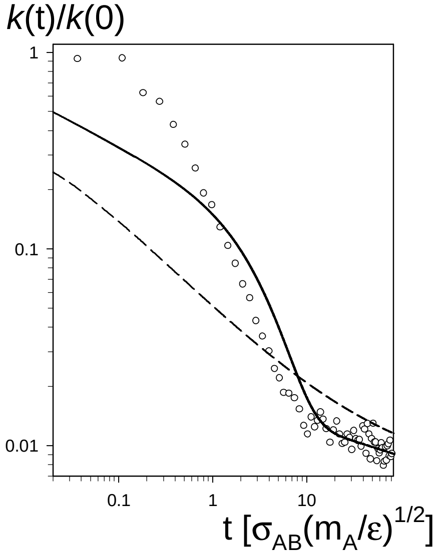

Fig. 2. The same as in Fig. 1. Simulation: the mixture R6e, $\rho = 0.8594$, $k_{\mathrm{B}}T = 1.0$, $x_{\mathrm{B}} = 0.0005$ and, $D_{\mathrm{S}} = 0.0057$ (all in the reduced units of S).

The figures clearly show that it is impossible to describe, even qualitatively, the initial stage of the process, if the simplification (2.6) is applied (dashed line). The curve resulted from the simplified model completely does not fit the simulation results at short times. It is evident that a successful minimization is possible only if one discards the initial stage data. This conclusion is important since, in experimental practice the data are treated as a whole without discarding the initial stage. In such a case, the errors in the parameters extracted by fitting experimental results with the model may be extremely large [20]. The description by the full model (solid line) is qualitatively correct but quantitative differences at short times are significant. The discrepancy for very short times ($t \leq \sigma_{\mathrm{AA}}(m_{\mathrm{A}}/\varepsilon)^{1/2}$) is due to ballistic motion of reactants, which is ignored by the Smoluchowski approach. At very short times the reaction rate is increased by ballistic inflow of the reactants. The effect is quite strong, since here the reaction occurs instantaneously with probability equal to one. As a consequence, the inflow is not balanced by the outflow, which, in this special case, is equal to zero. This discrepancy was not noticed by Zhou and Szabo [19] probably because of a very low number of particles used in their simulations. As a result, they concluded wrongly that the full model provides an exact description of the kinetics at short times. Figs. 1 and 2 clearly show that for very fast reactions this is not true (however, this is still true for $t = 0$). The discrepancy in Fig. 2 spreads for a time of an order of magnitude larger than in Fig. 1. This effect is probably due to the strong solute–solvent correlations, which are also not taken into account by the Smoluchowski theory.

Fig. 3 shows k(t)/k(0) as a function of time for the SFNL reaction for $\tau = 5.787\sigma_{\mathrm{SS}}(m_{\mathrm{S}}/\varepsilon)^{1/2}$ and $R = 1.0667\sigma_{\mathrm{AB}}$ for the mixture R6e. The simulation parameters are given in the figure caption. The circles show the simulation results. The solid line gives the prediction by the full model. In this case the agreement is very good. For very short time the solid line nicely agrees with the simulation results. For the reaction considered the characteristic reaction time (here τ) is much longer than the time of ballistic flight. As a result, the inflow of the reactants is balanced by the outflow and the contribution to $k(t)$ coming from the ballistic motion is non-noticeable. The dashed and dotted lines give the results of the minimization for the simplified SFNL model with respect to a and D_{S} and for the simplified SCK model with respect to a and k_0, respectively. The dotted line does not fit the simulation results. It demonstrates that the SCK model is not universal. One should not expect that the parameters could be adjusted such that the model describes an arbitrary quenching process. The dashed line (SFNL) fits the simulation results nearly perfectly in spite of the model assumption (2.6). For the system considered, this assumption is completely false. The $g_{\mathrm{AB}}(r)$ function has a sharp maximum at $r \approx 1.06\sigma_{\mathrm{AB}}$ with the value of

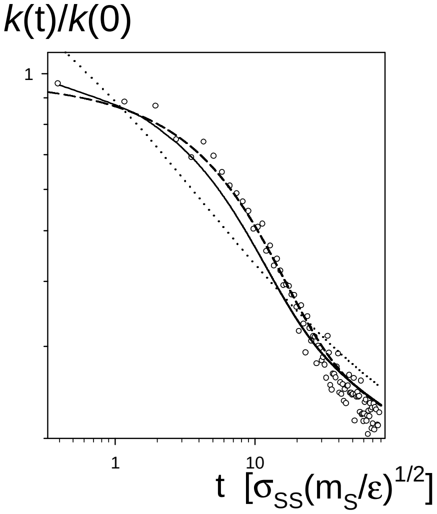

Fig. 3. $k(t)/k(0)$ as a function of time for the early phase of fluorescence quenching from: simulation of the SFNL reaction for $R = 1.0667\sigma_{\rm AB}$ and $\tau = 5.787\sigma_{\rm SS}(m_{\rm S}/\varepsilon)^{1/2}$ (circles), the prediction by the SFNL full model (solid line), the minimization with the SCK simplified model with respect to k_0 and $D_{\rm S}$ (dotted line), the minimization with the SFNL simplified model with respect to a and $D_{\rm S}$ (dashed line). Simulation: the mixture R6e, $\rho = 0.8594, k_{\rm B}T = 1.50$, $x_{\rm B} = 0.0005$ and, $D_{\rm S} = 0.0188$ (all in the reduced units of S).

about 3.0. As a result, according to (2.5) and the initial condition, the value of $k(0)$ resulted from simulation should be much larger than that calculated for the assumed structureless case. But the minimization performed within the simplified model has compensated this maximum by increasing non-physically the distance between R and a in the formula (2.10). As a result, the dashed curve fits the simulation data very well but a nonsense value for the distance of the minimum approach is obtained from the minimization (at fixed R): $a^{\rm fit} = 0.6\sigma_{\rm AB}$. The SFNL model enables us to describe the effect called the static quenching [10,17] even within the simplified model. This is possible because the model depends on many parameters and the first term on the right-hand side of (2.10) exactly fits the rate of static quenching. However, as it is shown above, some of the parameters which resulted from minimization may significantly disagree with the real ones.

3.2. Errors of the model for the long time stage

In this subsection we estimate the errors coming from the application of the Smoluchowski approach to describe the long time stage of fluorescence quenching. By fitting the $k(t)$ curve which resulted from the model with the computer data and taking the limit with $t_{\mathrm{D}} \to \infty$, we estimate the value of diffusion constant. The obtained $\mathrm{Lim}(D_{\mathrm{S}}^{\mathrm{fit}})$ is then compared with the value of D_{S} taken from the simulation. According to Szabo [1], the SFNL model becomes equivalent to the SCK model if $t \to \infty$. As a consequence, our analysis can be restricted only to the SCK model. The deviations in $\mathrm{Lim}(a^{\mathrm{fit}})$ from the real value of a are not analyzed since they are strongly correlated with that in $\mathrm{Lim}(D_{\mathrm{S}}^{\mathrm{fit}})$ [20]. We consider only the case when the reaction (here the SCK one) exactly corresponds to the model. Therefore, the value of $\mathrm{Lim}(D_{\mathrm{S}}^{\mathrm{fit}})/D_{\mathrm{S}} - 1$ can be treated as a measure of error resulted only from the description of the kinetics by the Smoluchowski equation. The test has been performed for a wide range of reaction parameters and different types of intermolecular interactions so we believe that random coincidences are absent. The fact that the conditions of our computer experiments are much closer to the assumptions of the models than it is for a real experiment, allows us to treat the scale of deviations between the simulation results and the model as a minimum level of errors expected in applications of the models based on the Smoluchowski approach to real experiments.

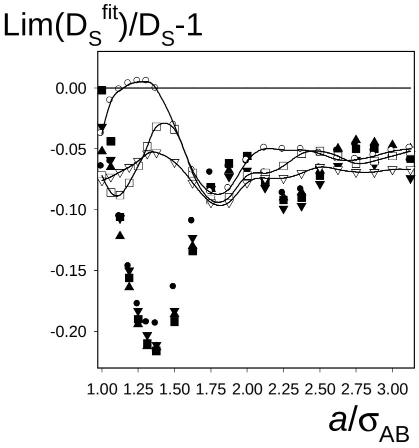

Fig. 4. The minimization — the SCK model at fixed a. $\mathrm{Lim}(D_{\mathrm{S}}^{\mathrm{fit}})/D_{\mathrm{S}} - 1$ as a function of a for the simple liquids at $\rho = 0.9358$, $k_{\mathrm{B}}T = 1.0$ and various interparticle potentials. Symbols: square — SS, $x_{\mathrm{B}} = 0.0015$, $D_{\mathrm{S}} = 0.0802$; triangle down — LJ, $x_{\mathrm{B}} = 0.00125$, $D_{\mathrm{S}} = 0.0560$; circle — R6e, $x_{\mathrm{B}} = 0.001$, $D_{\mathrm{S}} = 0.0266$. All in the reduced units of A. Filled symbols — the simplified model, empty symbols connected by a solid line — the full model ($g_{\mathrm{AB}}(r)$ from simulations).

$\mathrm{Lim}(D_{\mathrm{S}}^{\mathrm{fit}})/D_{\mathrm{S}}$ as a function of a for a number of the simple liquids for different interparticle potentials at fixed temperature and density is presented in Fig. 4. The same dependence for the mixtures for various temperatures and solute–solvent interaction parameters (η) is given in Fig. 5. The filled symbols show the results for the simplified model. The empty symbols, connected by a line, present the results obtained by using the full model.

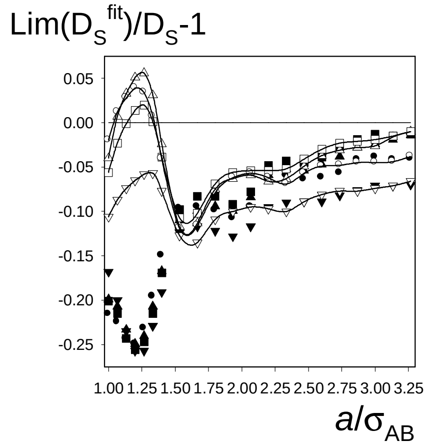

Fig. 5. The minimization — the SCK model at fixed a. $\mathrm{Lim}(D_{\mathrm{S}}^{\mathrm{fit}})/D_{\mathrm{S}} - 1$ as a function of a for the mixtures at $\rho = 0.8594$, various temperatures and solute–solvent interaction energy parameters (η). Symbols: triangle up — $x_{\mathrm{B}} = 0.0005$, $k_{\mathrm{B}}T = 1.0$, $D_{\mathrm{S}} = 0.0057$, $\eta = 1.0$; square — $x_{\mathrm{B}} = 0.0015$, $k_{\mathrm{B}}T = 1.25$, $D_{\mathrm{S}} = 0.0123$, $\eta = 1.1$; triangle down — $x_{\mathrm{B}} = 0.0005$, $k_{\mathrm{B}}T = 1.50$, $D_{\mathrm{S}} = 0.0188$, $\eta = 1.0$; circle — $x_{\mathrm{B}} = 0.0007$, $k_{\mathrm{B}}T = 1.50$, $D_{\mathrm{S}} = 0.0112$, $\eta = 1.5$; all in the reduced units of S. Remaining notations as in Fig. 4.

First, general conclusion from Figs. 4 and 5 agrees with the result of Zhou and Szabo [19]. An inclusion of real $g_{\mathrm{AB}}(r)$ significantly improves agreement between the simulation data and the model. Large number of N applied in our simulations enables us to estimate the errors quantitatively. For the simplified model, the maximum deviation in $\mathrm{Lim}(D_{\mathrm{S}}^{\mathrm{fit}})$ attain over 20% in the case of the simple liquid and 25% for the mixture. For the full model, the deviation does not exceed 10% level. In all cases presented in Figs. 4 and 5 the dependence of $\mathrm{Lim}(D_{\mathrm{S}}^{\mathrm{fit}})/D_{\mathrm{S}}$ on a is very similar in shape and is characterized by a deep minimum for a close to σ_{AB}. The minimum results from the screening by the first coordination shell (a sharp maximum in $g_{\mathrm{AB}}(r)$ for r close to σ_{AB}) that characterizes structure of real liquid. As a result, $D_{\mathrm{S}}^{\mathrm{fit}}$ calculated with the assumption $g_{\mathrm{AB}}(r) \equiv 1$ for values of a in the range where screening is effective is significantly reduced if compared with the real one. At very short distances the probability of collision with a screening particle decreases and the screening becomes less effective. This explains why, for simple liquids, the values of $\mathrm{Lim}(D_{\mathrm{S}}^{\mathrm{fit}})/D_{\mathrm{S}}$ are significantly higher for $a = \sigma_{\mathrm{AB}}$ than at the minimum. For the mixtures (Fig. 5) the increase in $\mathrm{Lim}(D_{\mathrm{S}}^{\mathrm{fit}})/D_{\mathrm{S}}$ for a approaching σ_{AB} is much less pronounced. We think that it is related to the presence of solvent. The S molecules, which are smaller than A (and B) ones, can efficiently screen the reactant molecules at distances very close to σ_{AB} (which is impossible for the simple liquids) and so reduce the increase of $D_{\mathrm{S}}^{\mathrm{fit}}$ at small a. It is confirmed by the shape of $g_{\mathrm{BC}}(r)$ function which has a sharp maximum for $r \approx 0.9\sigma_{\mathrm{AB}}$.

Basing on the results of the simulations for $a = \sigma_{\mathrm{AB}}$, Zhou and Szabo concluded [19] that the influence of $g_{\mathrm{AB}}(r)$ on the rate coefficient in long time limit is quite small. Figures 4 and 5 clearly show that the conclusion is true but only in a very special case of the particles of very similar sizes (here the simple liquid) and a equal or very close to σ_{AB} (Fig. 4 for $a \approx \sigma_{\mathrm{AB}}$). In general, the differences between the results of the simplified model (filled symbols) and the full model (empty symbols) are not low (Fig. 4 for a higher than about $1.15\sigma_{\mathrm{AB}}$ and Fig. 5 for all a).

4. Summary and final conclusions

In this work we have presented the results of molecular dynamics tests of the SCK and the SFNL models of diffusion controlled de-excitation process for spherical molecules. The simulations have been performed for various potentials describing interparticle interactions. We have found that in long time limit the shape of potential has a little influence on the results, thus we believe that the conclusions presented below can be generalized to other molecules of spherical or close to spherical shape. Our MD simulations were performed for the reaction cross sections exactly the same as that assumed by the models. As a result, we were able to extract the errors coming only from the description based on the Smoluchowski approach. The agreement of the diffusion coefficient, $D_{\mathrm{S}}^{\mathrm{fit}}$, obtained from the minimization, with the value from simulations was considered as a qualitative measure of the model accuracy for $t \to \infty$.

We demonstrated that a successful interpretation of experimental results with the models based on the Smoluchowski approach mainly depends on possibility of discarding the data coming from the early stage of fluorescence quenching. If this condition is fulfilled then the most important conclusions are the following: *(i)* if the simplified model is applied, the values of $\mathrm{Lim}(D_{\mathrm{S}}^{\mathrm{fit}})/D_{\mathrm{S}} - 1$ for a fixed a are almost always negative and can attain even 25% . The conclusion of Zhou and Szabo that the errors in the description of long time stage are quite small is true only for a very special case of the liquid consisting of very similar size particles and the reaction radius close to the particle diameter; *(ii)* The deviations in $\mathrm{Lim}(D_\mathrm{S}^\mathrm{fit})$ significantly decrease if the information on $g_\mathrm{AB}(r)$ is included in the model. However, the errors of about 10% may still occur.

The results presented in Sec. 3.1 show that the SCK model in the simplified version fails completely for short times (Figs. 1 and 2). Within the simplified model it is impossible to describe the initial stage of the process even qualitatively. As a result, if the initial stage data are not discarded (which is standard for describing experimental results), the parameters obtained from the minimization must be burdened with very high errors. If the full model is applied, the qualitative description is correct but, for very short time, there are still significant discrepancies between $k(t)$ from the model and from the simulation (Figs. 1 and 2). The reason of the inconsistency is ballistic motion of particles and the fact that the characteristic reaction time is very short (here, it is zero). If the characteristic time is larger (Fig. 3 — the SFNL model, solid line) the discrepancy vanishes. The SFNL model better fits the data than the SCK one (Fig. 3) and one can obtain a good fit even if the simplified model is applied. But this is only the result of the mathematical form of (2.10) and the parameters obtained from the minimization are usually nonphysical.

Both the SCK model and the SFNL model do not correspond to real processes because of oversimplified models for reaction cross section. But we believe that the conclusions from the work may be generalized also to more physical models which base on the Smoluchowski approach. The conclusions for the short time stage are in obvious agreement with physical intuition. Ignoring the liquid structure must lead to completely false description of the initial stage also for more reasonable sink terms. We expect also that the long time behavior of $k(t)$ does not depend on a particular form of the microscopic reaction cross section and its asymptotic form should be similar to an SCK model with "effective" k_0 and a. Therefore, our conclusions for errors in the description of the kinetics for long times should be more or less valid for any reaction.

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