

CONDENSED-MATTER
SPECTROSCOPY

Luminescence Quenching Kinetics upon Diffusion-Accelerated Dipole–Dipole Energy Transfer for a Realistic Condensed-Matter Model

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Abstract—The hard-sphere model is considered as a more realistic condensed-matter model. In this model, the radial distribution function of molecules in a medium, used for calculations of luminescence decay kinetics, takes into account the short-range order in fluids and has the shape of damped oscillations. It is assumed that the motion of donor and acceptor molecules in a solution for the lifetime of the excited state of the donor is described by the diffusion equation, while the luminescence quenching occurs due to the long-range dipole–dipole energy transfer. It is shown that, if diffusion coefficients are small, the kinetics determined in this study hardly differs at all from the traditional kinetics. At intermediate and large diffusion coefficients, this difference becomes significant and should be taken into account in estimating the Förster energy transfer radius and diffusion coefficients from experimental luminescence decay curves.

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INTRODUCTION

The theory of luminescence quenching in fluids and solids due to resonance energy transfer (RET) from energy donors (excited molecules) to energy acceptors (quenchers), starting with the pioneering studies by Förster [1] and Dexter [2], is based on the assumption that molecules are point particles homogeneously distributed in the medium. In this case, the radial distribution function of molecules $g(r)$ does not depend on the distance r between the particles and is equal to unity for $0 \leq r < \infty$; i.e., quenchers are homogeneously and independently distributed around an excited molecule. The luminescence kinetics in the presence of quenchers (normalized to unity at the initial time instant) has the form

$$I(t) = \exp(-t/\tau_0) \times \exp\left(-4\pi n_q \int_0^\infty (1 - e^{-k(r)t}) g(r) r^2 dr\right), \quad (1)$$

where τ_0 is the lifetime of the excited state of the donor in the absence of quenching, n_q is the concentration of quenchers (the number of molecules per unit volume), and $k(r)$ is the RET rate. This equation was derived under the assumption that the concentration of donor

molecules is very small and that the donors and acceptors are immobile. In the case of dipole–dipole RET [1],

$$k(r) = \frac{1}{\tau_0} \left(\frac{R_0}{r}\right)^6, \quad (2)$$

where R_0 is the Förster radius determined by the overlap of the donor luminescence and acceptor absorption spectra, by the quantum yield of the donor, and by the refractive index of the medium. The parameter R_0 varies from 10 to 70 Å [3, 4].

In the case of the exchange mechanism of RET [2],

$$k(r) = k(0) \exp(2r/L), \quad (3)$$

where $k(0)$ is the quenching rate at the zero distance between the donor and acceptor and L is the effective Bohr radius.

Eqs (2), (3) are approximate. The true rate of RET depends not only on the distance between particles but also on their mutual orientation. (For simplicity, below, we will consider only the isotropic mechanism of RET.)

Molecules are not point particles. The problem of RET between particles of finite sizes was considered in [5, 6] (see also review [7]). Molecules were modeled by spherical particles, the distance of closest approach between the donor and acceptor (the collision radius) d was introduced into consideration, and the radial distri-

bution function in Eq. (1) was represented by the unit step function (SF)

$$g_{\text{SF}}(r) = \begin{cases} 0, & r < d, \\ 1, & r > d. \end{cases} \quad (4)$$

Taking into account the distance of closest approach, Eq. (1) can be rewritten in the form

$$I(t) = \exp(-t/\tau_0)\exp(-cH(t)), \quad (5)$$

$$H(t) = 4\pi \int_1^{\infty} (1 - e^{-k(x)t})g(x)x^2 dx, \quad (6)$$

where $c = n_q d^3$ and $x = r/d$. In [5], the dipole–dipole RET was studied within the framework of this approximation. Note that the acceptors are still assumed to be independently distributed. This means that the model proposed is inapplicable in the case of large concentrations of acceptors.

As is known, taking into account the closest approach distance leads to the exponential decay (5) at short times ($k(d)t \ll 1$). At large times, the kinetics shows no noticeable difference for $d = 0$ and $d > 0$.

In reality, the radial distribution function is a more complex function of distance than SF (4). There exists a long-range order in crystals and a short-range order in fluids, because of which the radial distribution function has the shape of damped oscillations. If the fluid density decreases, the radial distribution function approaches the SF (the gas phase). A number of models of fluids were proposed for calculating $g(r)$. The simplest of them is the hard-sphere (HS) model [8]. This model was used in [9, 10] to calculate the rate $K(t)$ of a diffusion-controlled reaction. It was shown that the time dependence of the reaction is the same as for SF (4), $K(t) = \alpha + \beta\sqrt{t}$, but the α and β parameters have more realistic values.

In this work, we study the kinetics of the luminescence decay caused by the dipole–dipole RET taking into account the short-range order and diffusion of molecules in fluids. The same problem in the absence of diffusion of molecules was considered in our studies [11, 12].

BASIC EQUATIONS

In fluids, molecules can move within the time τ_0 at a distance exceeding R_0 , because of which the donor and acceptor molecules can approach each other and thus enhance the luminescence decay. The motion length depends on the solvent viscosity, and the motion process in the RET theory is usually described by the diffusion equation. The inclusion of diffusion leads to

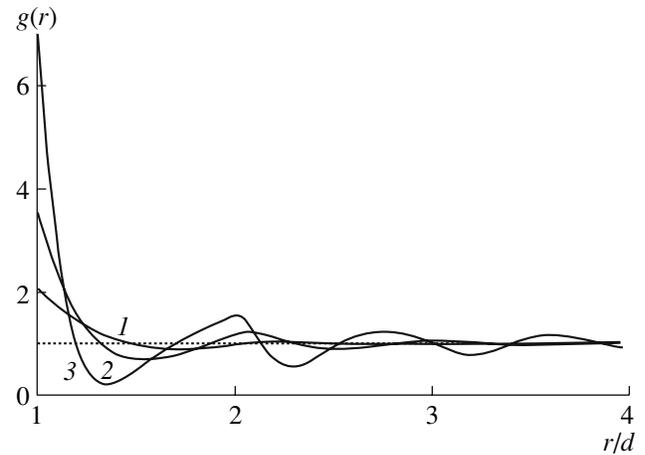


Fig. 1. Radial distribution function (the HS fluid model) for the fluid densities $\rho = (1) 0.5$, $(2) 0.8$, and $(3) 1.1$.

replacement of the function $H(t)$ in Eq. (5) by the function [3, 4, 13, 14]

$$H(t) = 4\pi \int_0^t dt \int_1^{\infty} k(x)g^*(x, t)x^2 dx. \quad (7)$$

Here, $g^*(r, t)$ is the radial distribution function of donor–acceptor pairs in which the donor is in the excited state and the acceptor is in the ground state. This distribution function is the solution of the diffusion equation

$$\frac{\partial g^*(r, t)}{\partial t} = D\Delta g^*(r, t) - k(r)g^*(r, t), \quad (8)$$

where D is the diffusion coefficient equal to the sum of the diffusion coefficients of donor and acceptor molecules and Δ is the Laplace operator. Equation (8) is solved under the initial and boundary conditions

$$g^*(r, 0) = g(r), \quad \left. \frac{\partial g^*(r, t)}{\partial x} \right|_{r=d} = 0. \quad (9)$$

To calculate the function $g^*(x, t)$ and, hence, the luminescence kinetics in fluids (by formulas (5), (7)–(9)), we should know the radial distribution function $g(r)$. This function was studied for several fluid models. We chose the HS model for $g(r)$ [8] due to the following reasons. First, this model is the natural next step in the RET theory after SF (4). Second, the HS fluid was studied in detail; thus, analytical solutions [15, 20] and the Laplace transform [15] for $g(r)$ were obtained, and tables for $g(r)$ at various densities of fluids are available [18, 21, 22]. Third, the $g(r)$ function for the HS model agrees well with the computer simulation data, although some discrepancies exist mainly in the region of high densities [21, 23].

In this study, we use the detailed tables of [18]. The HS distribution function for several dimensionless fluid densities ρ ($\rho = n_f d^3$, where n_f and d are the density and

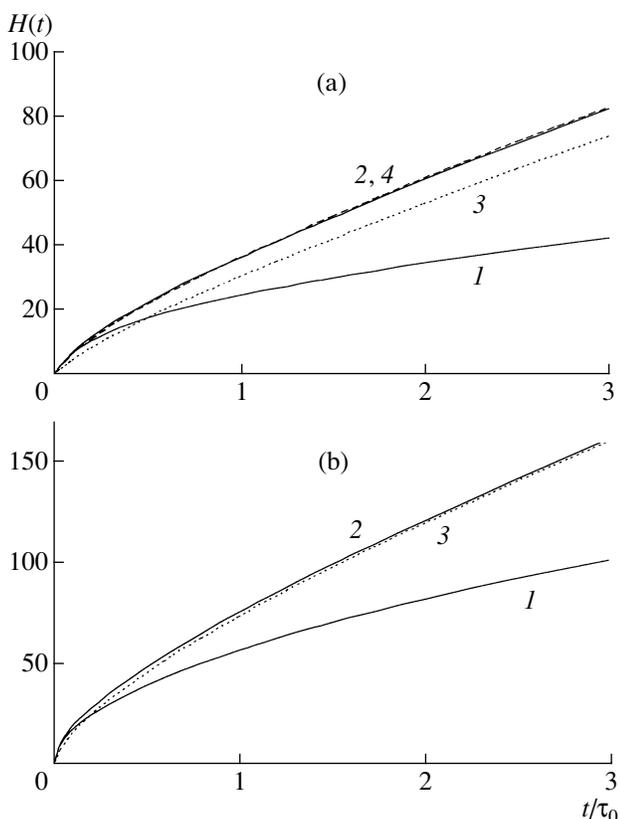


Fig. 2. Luminescence decay kinetics in the case of small diffusion coefficients, $\rho = 0.8$, and $c = 1$, calculated by the (curves 1) HS model, static quenching, with $D = 0$ and $R_0/d =$ (a) 1.5 and (b) 2; (solid curves 2) HS and (dotted curves 3) SF models with $D\tau_0/d^2 = 1$ and $R_0/d =$ (a) 1.5 and (b) 2; and (dashed curves 4) SF model with $R_0/d = 1.6$ and $D\tau_0/d^2 = 0.75$.

HS diameter of fluid molecules) is shown in Fig. 1. Note that there is a very simple analytical solution for $g(r)$ at $r = d$ [17],

$$g(d) = \frac{1 + \xi/2}{(1 - \xi)^2}, \quad \xi = \frac{\pi\rho}{6}. \quad (10)$$

To simplify the calculation, hereafter we assume that the donors, acceptors, and fluid molecules are spherical particles of the same diameter d . In this case, the radial distribution functions for the donor-acceptor pairs in (6) and (9) and for the HS fluid molecules coincide with each other. For our calculations, we will use $g(r)$ for $\rho = 0.8$. There are two reasons for this. First, the difference between SF (4) and $g(r)$ for the HF fluid at this density is the most pronounced (according to formula (10) and data of [18], at the distance of closest approach, $g(d) \approx 3.58$ for $\rho = 0.8$). Second, in the density range from 0.943 to 0.104 [22, 24], the solid and liquid phases are in thermodynamic equilibrium.

Below, the luminescence kinetics calculated using the HS radial distribution function and SF (4) will be called HS and SF kinetics, respectively.

CALCULATION RESULTS

Small diffusion coefficients ($D\tau_0/d^2 < 1$). Our calculations show that the HS luminescence kinetics in the time interval $0 < t/\tau_0 < 3$ is nonexponential ($H(t)$ in formula (5) is a nonlinear function of time) and noticeably differs from the SF kinetics only if $R_0/d < 2$ (Figs. 2a and 2b, where $R_0/d = 1.5$ and 2, respectively; $D\tau_0/d^2 = 1$; and $\rho = 0.8$). The difference in the HS and HF kinetics in Fig. 2a almost vanishes if the SF kinetics is calculated using R_0/d increased from 1.5 to 1.6 and $D\tau_0/d^2$ simultaneously decreased from 1 to 0.75. This is understandable, because the luminescence decay in the case of weak diffusion is determined mainly by the static quenching, which occurs only at a short distance between the donors and acceptors, where the HS distribution function noticeably exceeds SF (4). The effect of diffusion of molecules becomes noticeable only at large times when quenching occurs at large distances, at which the HS function nearly coincides with function (4).

Intermediate diffusion coefficients $D\tau_0/R_0^2 \sim 1$. In this case, the luminescence decay is determined both by the static quenching and by the diffusion of molecules. At the initial stage, the luminescence decays nonexponentially (the static quenching) and then the decay becomes exponential (the quenching changes from static to diffusion-accelerated and, in formula (5), $cH(t) = kt$) (Fig. 3),

$$I(t) = \exp(-t/\tau_0)\exp(-kt). \quad (11)$$

As is known [3, 4, 25, 26], at $(D\tau_0/R_0^2)(t/\tau_0)^{2/3} \gg 1$, the decay rate constant k for the SF kinetics in Eq. (11) has the form ($k = k_{\text{SF}}$)

$$k_{\text{SF}} = 0.676 \times 4\pi c \left(\frac{D\tau_0}{d^2}\right)^{3/4} \left(\frac{R_0}{d}\right)^{3/2} \quad (12)$$

and depends on the product $D^{3/4}R_0^{3/2}$.

The calculations show a noticeable difference between the HS and SF kinetics (and between the corresponding functions $H(t)$) not only at $R_0/d < 2$, but also at $R_0/d \geq 2$. Figure 3a shows these kinetics calculated for $R_0/d = 1.5$ and $D\tau_0/d^2 = 5$. The difference in the curves is almost absent in the whole time interval $0 \leq t/\tau_0 \leq 3$ if, calculating the SF kinetics, we increase the parameter R_0/d from 1.5 to 1.61 (simultaneously decreasing $D\tau_0/d^2$ to 4.5) or to 1.57 (increasing $D\tau_0/d^2$ from 5 to 7.5 (Fig. 3a)).

Figure 3b demonstrates analogous calculation results for $R_0/d = 2$ and $D\tau_0/d^2 = 10$. The HS and HF kinetics almost do not differ from each other if R_0/d in

calculating the SF kinetics is increased from 2 to 2.8 (with an unchanged diffusion coefficient, i.e., $D\tau_0/d^2 = 10$) or to 2.11 (with $D\tau_0/d^2$ decreased from 10 to 9).

Extremely large diffusion coefficients ($D\tau_0/R_0^2 \gg 1$). In this case, the luminescence decay is determined mainly by the diffusion of molecules, the luminescence kinetics being exponential in the whole time interval $0 \leq t/\tau_0 \leq 3$ and described by formula (11). The HS and SF kinetics are different for all the values of the Förster energy transfer radius.

For the HS kinetics, the decay rate constant in (11) (at $D\tau_0/R_0^2 \rightarrow \infty$) has the form ($k = k_{HS}$)

$$k_{HS} = 4\pi c \int_1^\infty k(x)g(x)x^2 dx, \quad (13)$$

and the decay constant for the SF kinetics ($k = k_{SF}$) is [3]

$$k_{SF} = 6 \frac{4\pi}{3} c \left(\frac{R_0}{d}\right)^6 \frac{1}{y^{3/4}} \frac{I_{3/4}(0.5\sqrt{y})}{I_{-3/4}(0.5\sqrt{y})}, \quad (14)$$

where $y = \left(\frac{R_0}{d}\right)^6 \frac{d^2}{D\tau_0}$ and $I_{\pm 3/4}$ is the Bessel function of the imaginary argument. Formula (14) together with (11) is valid at $R_0^3/(D\tau_0)^{3/2} \ll 2$ [3].

At rather large diffusion coefficients, formula (14) can be expanded in a series in the small parameter y . As a result, we obtain

$$k_{SF} = 6 \frac{4\pi}{3} c \left(\frac{R_0}{d}\right)^6 \left\{ \frac{\Gamma(1/4)}{8\Gamma(7/4)} + \left[-\frac{\Gamma^2(1/4)}{128\Gamma(5/4)\Gamma(7/4)} + \frac{\Gamma(1/4)}{128\Gamma(11/4)} \right] y + \left[\frac{\Gamma(1/4)}{8\Gamma(7/4)} \left(\frac{\Gamma^2(1/4)}{256\Gamma^2(5/4)} - \frac{\Gamma(1/4)}{512\Gamma(9/4)} \right) - \frac{\Gamma^2(1/4)}{2048\Gamma(5/4)\Gamma(11/4)} + \frac{\Gamma(1/4)}{4096\Gamma(15/4)} \right] y^2 + O(y^3) \right\}.$$

Substituting the numerical values for the Γ function, we finally have

$$k_{SF} = \frac{4\pi}{3} c \left(\frac{R_0}{d}\right)^6 \left(1 - \frac{3}{14}y + \frac{21}{440}y^2 + O(y^3) \right). \quad (15)$$

As follows from formulas (13) and (15), at $D\tau_0/R_0^2 \rightarrow \infty$, the constants k_{HS} and k_{SF} do not depend on the diffusion coefficient D and, in addition, their ratio k_{HS}/k_{SF} does not depend on R_0 and is approximately 1.655. This means that the difference between

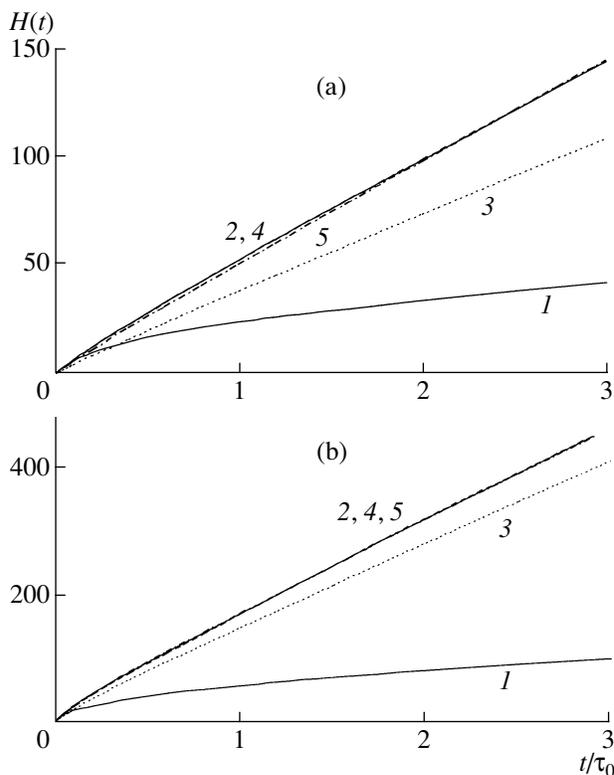


Fig. 3. Luminescence decay kinetics in the case of intermediate diffusion coefficients, $\rho = 0.8$, and $c = 1$, calculated by the (curves 1) HS model, static quenching, with $D = 0$ and $R_0/d =$ (a) 1.5 and (b) 2; (solid curves 2) HS and (dotted curves 3) SF models with $R_0/d =$ (a) 1.5 and (b) 2 and $D\tau_0/d^2 =$ (a) 5 and (b) 10; (dashed curves 4) SF model with $R_0/d =$ (a) 1.61 and (b) 2.8 and $D\tau_0/d^2 =$ (a) 4.5 and (b) 10; and (dashed-and-dotted curves 5) SF model with $R_0/d =$ (a) 1.57 and (b) 2.11 and $D\tau_0/d^2 =$ (a) 7.5 and (b) 9. Curves 2 and 4 in Fig. 3a and curves 2, 4, and 5 in Fig. 3b virtually coincide.

the HS and FS kinetics can be eliminated in only one way; namely, when calculating the SF kinetics, it is necessary to increase the Förster radius by $1.655^{1/6} \approx 1.088$ times, i.e., less than by 10%; variations in the diffusion coefficients cannot eliminate this difference.

CONCLUSIONS

In this study, the radial distribution function for the HS fluid model was used to calculate the luminescence decay due to the dipole–dipole RET. This model takes into account the short-range order in fluids, because of which the radial distribution function of molecules has a shape of damped oscillations.

The cases of small, intermediate, and large diffusion coefficients of molecules are considered. It is shown that, in all these cases, the luminescence decay for the dipole–dipole RET obtained within the framework of the HS model hardly differs at from the traditional

kinetics (the SF model) calculated with R_0 increased by less than 10%; the diffusion coefficient in this case may vary within a wide range. These variations can be most significant in the case of extremely large diffusion coefficients. Naturally, the largest diffusion coefficient corresponds to the smallest R_0 .

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