

Solvent dynamics in a model system

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Abstract. We report herein a study of the solvent reorganization process in an electron transfer reaction. The calculations are based on a model consisting of 26 or 62 solvent particles. Molecular dynamics simulations are performed to calculate the electric field fluctuations during the orientational and translational motion of the solvent molecules. The changes in the electric fields at various points near the reacting sites in the system are evaluated as a function of time. From these electric fields, electric field time correlation functions are calculated. The main conclusion in this work is that it requires nearly 3 ps for the model solvent to reorient during the charge transfer. These results suggest ways of incorporating solvent dynamics based on molecular models into theoretical studies of electron transfer rates in condensed media.

Keywords. Solvent dynamics; model system; electron transfer reaction; electric field fluctuations; molecular dynamics simulations.

1. Introduction

The study of the influence of polarization fluctuations on electron transfer, proton transfer and heteronuclear bond cleavage reaction rates is being pursued actively for quite some time (Friedman and Newton 1982; Marcus 1960; Albery 1980). In both thermal and photochemical electron transfer reactions, the medium relaxation effects are extensively investigated experimentally as well as theoretically (Kosower *et al* 1983; Bagchi 1986). Many methods have been used in the past to study the dynamics of the medium fluctuations. From dielectric relaxation time measurements it is possible to deduce the reorientation times of solvent molecules in charge transfer processes (McQuarrie 1976). Hertz and coworkers (Hertz 1973) studied the dielectric relaxation of water using an NMR relaxation technique and found that the dielectric relaxation time in water is about 2.5 ps. If the aqueous medium is strongly coupled to the reaction coordinate for a fast electron transfer then this time scale will influence the dynamics of electron transfer significantly. Another example of electron transfer rate control by medium relaxation is the study of the effect of solvent on the photochemical intramolecular electron transfer

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rates in (phenylamino)naphthalene sulphonate derivatives (Kosower *et al* 1978, 1983). Nuclei with $I \geq 1$ possess an electric quadrupole moment which interacts with electric field gradients at the position of the nucleus (Hertz 1973b). In dilute electrolyte solutions, quadrupole relaxation becomes more important than the electric field calculations due to interionic motions (Hertz 1973b; Wolynes 1980). Hynes and Wolynes (1981) studied the electric field gradient fluctuations and calculated the quadrupole relaxation times based on the continuum model analogous to Zwanzig's mobility theory and these values for relaxation times (0.3–0.5 ps) were about 10 times shorter than that of Hertz's experiments (2.5 ps). The continuum model underestimates the solvent correlation times in the vicinity of ions. In the continuum model the dynamical relaxation is overemphasized while the Hertz's method seems to neglect it (Hynes and Wolynes 1981). In a molecular model, there is normally a distance of closest approach which is absent in the continuum model and this will correct for the overemphasis of the dynamical relaxation in the continuum model.

In an earlier study of electron exchange kinetics to account for the dynamical fluctuations in a medium surrounding the reactants, the relaxation time for the solvent was explicitly included in the expression for the rate constant for electron transfer (Tembe *et al* 1982),

$$k = \exp(-A^\ddagger/k_B T) / 2(\tau^e + \tau^\ddagger), \quad (1)$$

where A^\ddagger is the activation free energy for the reaction, k_B , the Boltzmann constant, T , the absolute temperature, τ^e is the characteristic time for the primary electron transfer in the absence of solvent (0.16 ps) and τ^\ddagger is relaxation time for the activation process. The activation process for the aqueous electron transfer has an inner-sphere contribution due to the vibrational relaxation of the reactants and an outer-sphere contribution due to the relaxation of the solvent (bath) degrees of freedom (Tembe *et al* 1982). The overall relaxation rate can be written as the sum of the relaxation rates for the inner-sphere modes $(\tau_{in})^{-1}$ and the relaxation rate for the solvent reorganization $(\tau_{out})^{-1}$,

$$(\tau^\ddagger)^{-1} = (\tau_{in})^{-1} + (\tau_{out})^{-1}. \quad (2)$$

In this report we evaluate the solvent reorganization time, τ_{out} explicitly based on two simple models for the solvent (Vijaya Kumar 1985). The method and the results and discussions are given in the following sections.

2. Method

In our molecular dynamics (MD) simulations we consider a system with a donor and an acceptor separated by 5 Å enclosed in a solvent consisting of 26 particles (system A) or 62 particles (system B). All the particles in the system interact with each other by a Lennard-Jones plus a Coulombic interaction given by

$$U_{ij}(r_{ij}) = U_{LJ}(r_{ij}) + q_i q_j / r_{ij}. \quad (3)$$

The system is enclosed in a spherical shell of radius 8 Å (26 particles) or 14 Å (62 particles) and the movement of the particles is restrained within the sphere by a

harmonic wall potential with a force constant, 5700 Joules/mole/Å². The time step for the simulation is 0.02 ps and the temperature is held constant by stochastic collisions (Andersen 1980). During each time step, velocities of 5 particles are reassigned from a Gaussian distribution at the system temperature, $T = 298$ K. The parameters for the LJ potential are $\epsilon/k = 120$ K and $\sigma = 3.4$ Å. The charges on the solvent particles are taken as 0.05 electronic charge and for the solutes (donor and acceptor or the reactants) as -0.1 and $+0.1$ electronic charge respectively. The above values of charges on the reactants and the solvent were chosen so that the electrostatic interactions are similar in strength to the Lennard-Jones interaction and that the clustering of +ve charges around -ve charges (and vice versa) will be avoided during the simulation. These parameters correspond to a charge transfer of $1e$ in a medium of dielectric constant greater than 10. We use the Verlet algorithm to integrate the equations of motion (Verlet 1967).

To study the dynamical correlations in the solvent we calculate the electric fields at a few points in the vicinity of the reactants (see figure 1). Electric fields (EF) are calculated using the equation

$$EF_{pi} = q_{sol}(X_p - X_i)/r_{pi}^3 \quad (4)$$

where q is the charge on the solvent particles, r_{pi} is the distance from point p to the i th particle, and X refers to the coordinate x , y or z . From the variation of electric fields with time, the time correlation functions (EF tefs) for the components of the electric field are calculated from

$$C(\tau) = \langle EF(0) EF(\tau) \rangle / \langle EF(0)^2 \rangle. \quad (5)$$

The simulations are done for a duration of 400 ps after an equilibration period of 30 ps.

3. Results and discussions

The various points in the vicinity of the reactants at which the electric fields are evaluated are shown in figure 1. The time dependence of the electric fields in x , y and z directions at a point midway between the ions (print no. 8 of figure 1) are shown in figure 2. The magnitude of the fluctuations in the electric fields in these plots (as well as in others not reported in this work) are typically about $10^{-3} e/\text{Å}^2$. The energies corresponding to these fluctuations are of the same order of magnitude as the thermal energies at 298 K. The average time required for a peak to peak fluctuation in the electric fields ranges from 2 to 5 ps. There is no significant dependence of these electric field fluctuations on the direction chosen, namely along the axis containing the reacting ions or perpendicular to this axis. This is due to the frequency of stochastic collisions per time step of the simulation.

In figure 3 we show the electric field time correlation functions. In figure 3a, the EF tefs for x , y and z components of the electric field in system A at point no. 8 of figure 1 are shown. In figure 3b, the same functions for system B are shown. The time dependence is quite similar in the two cases. For example, in system A, the x , y and z components of EF tefs have the values 0.62, 0.66 and 0.7, respectively, after

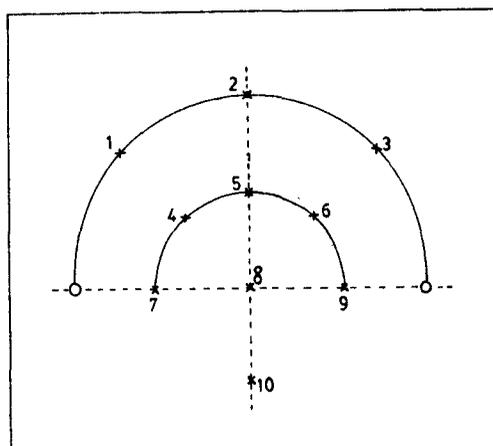


Figure 1. Coordinates of the points at which electric fields (EF) are calculated. The points are numbered from 1 to 10 and are indicated by X. The positions of reactants are denoted by circles.

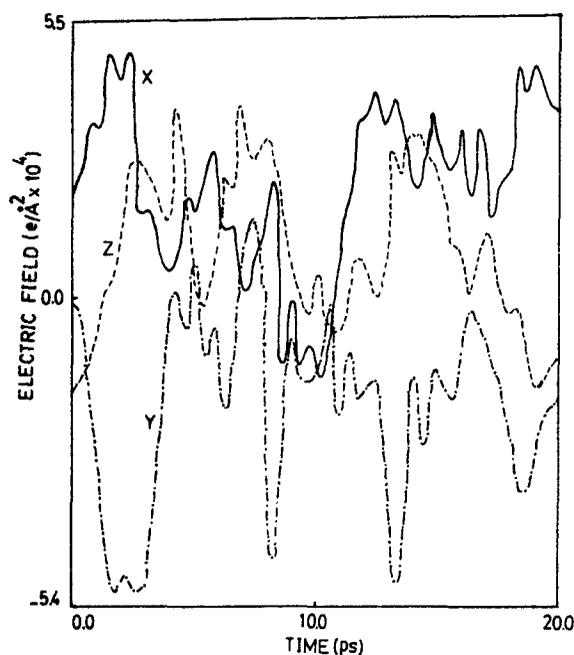


Figure 2. Electric fields ($10^4 \times$ electronic charge/ \AA^2) as a function of time (ps) at point no. 8 (x, y and z directions) for system A.

3 ps. The same values in system B are 0.7, 0.67 and 0.71 respectively. In figures 3c and d we show the EF tcf's for two points not along the line joining the two ions, namely, points 1 and 4 in figure 1 for system A. In figure 3e, we show the EF tcf's at point no. 7 of system B. In figure 3f, the EF tcf's at the ions are shown. In all the cases, the z component seems to decay more rapidly. None of the EF tcf's can be fitted as a single exponential. In order to assess the relative initial decay rates, we fit the logarithm of the initial 1 ps part of the EF tcf's as straight lines and from the

slopes obtain the correlation times. The correlation times obtained in this manner for different components of the electric fields at various points in the cavity region surrounding the ions are shown in tables 1 and 2 for system A and system B respectively. These times range from 1.13 to 6.13 ps. The average values of the relaxation times are 2.82, 2.84 and 3.39 for the x , y and z components of the electric field for system A.

The behaviour of EF tcfs at large times in a specific case (i.e., for point no. 8 which is the midpoint between the ions) in system A is shown in figure 4a. The values of

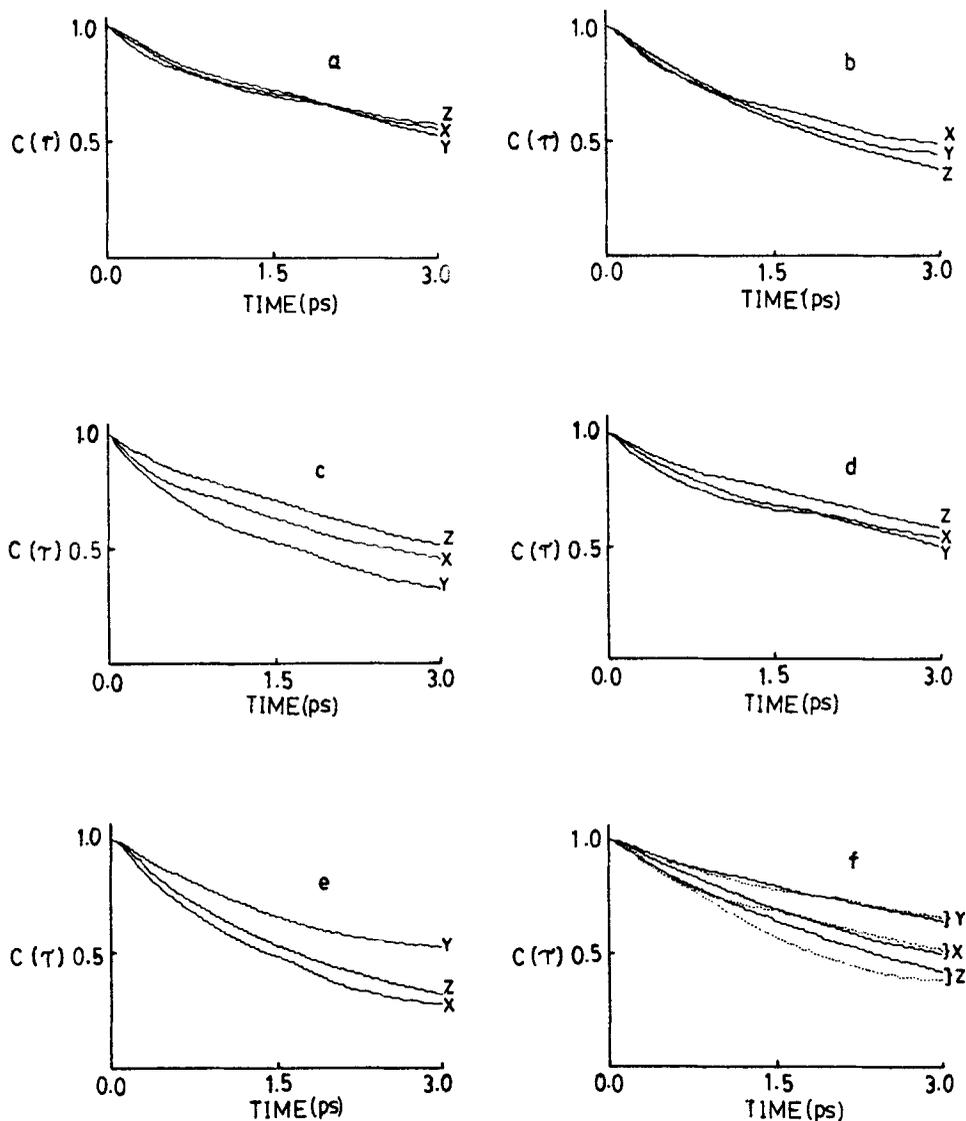


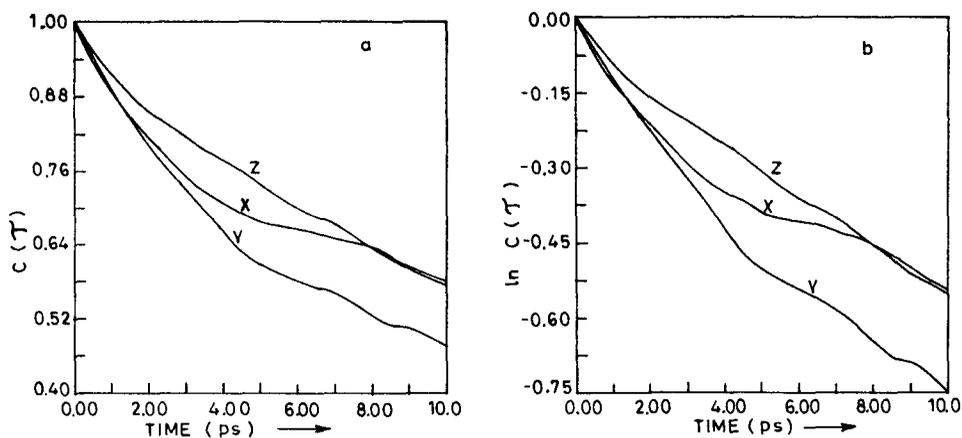
Figure 3. Correlation functions $C(\tau)$ s for the x , y and z components of the electric field as a function of time (ps). (a) at point no. 8 for system A, (b) at point no. 8 for system B, (c) at point no. 1 for system A, (d) at point no. 4 for system A, (e) at point no. 7 for system B, and (f) at the ions in system B (---- for -ve ion and for +ve ion).

Table 1. Relaxation times (ps) of the EF tcfs in *x*, *y* and *z* directions at various points in figure 1 for system A.

Point no.	<i>X</i>	<i>Y</i>	<i>Z</i>
1	3.04	2.02	4.13
2	1.13	1.39	2.43
3	2.60	2.30	3.11
4	2.94	3.41	4.43
5	1.72	2.16	2.28
6	2.20	2.30	3.24
7	4.12	3.70	4.60
8	3.68	3.85	3.50
9	3.18	4.10	4.18
10	3.63	3.25	2.02
Average	2.82	2.84	3.39

Table 2. Relaxation times (ps) for the EF tcfs in *x*, *y* and *z* directions at various points in figure 1 for system B.

Point no.	<i>X</i>	<i>Y</i>	<i>Z</i>
7	1.90	3.54	2.24
8	2.89	2.96	2.74
9	2.30	2.67	2.24
at -ve ion	6.13	3.52	4.17
at +ve ion	2.70	4.56	3.85

**Figure 4.** (a) Correlation functions $C(\tau)$ s for the *x*, *y* and *z* components of the electric field as a function time (ps) at point no. 8 for system A. (b) Logarithm of $C(\tau)$ as a function of time (ps) at point no. 8 for system A.

the $\ln C(\tau)$ are plotted in figure 4b. Since it is not a single exponential we fitted EF tcfs in this range assuming a multi-exponential of the form,

$$C(\tau) = A_1 e^{-\tau/\tau_1} + A_2 e^{-\tau/\tau_2} + A_3 e^{-\tau/\tau_3}. \quad (6)$$

The values of the coefficients A_1 , A_2 and A_3 of the above multi-exponential function for the EF tcfs in the x , y and z directions are 0.2, 0.3 and 0.5 respectively. The same values of A_1 , A_2 and A_3 are used for all the three components for ease in interpreting the values of the relaxation times. The values of the relaxation times τ_1 , τ_2 and τ_3 appearing in the multi-exponential form that fit the EF tcfs obtained in the simulations (and which are shown in figure 4a) up to 10 ps are given in table 3. The standard deviations between the actual EF tcfs and the fitted functions are also shown in the table. The EF tcf in the y -direction decays most rapidly and this is reflected in the smaller values of the three relaxation times for this function. The value of τ_1 for the EF tcfs in the x - and y -directions are nearly the same because the two tcfs have the same initial slopes. The values of τ_3 for the x - and z -components are also nearly the same due to the tcfs having the same values after about 7.5 ps. The values of τ_2 increases as we go from the y -, x - and z -directions. We are investigating further the asymmetry of the EF tcfs in the y and z -directions.

In our simulations we find that there is no significant dependence of the results on the size of the systems (26 or 62 solvent particles). This is in agreement with the previous work by Engström *et al* (1984). They have calculated quadrupolar relaxation of ions like Li^+ , Na^+ and Cl^- in dilute solutions. The electric field gradient at the nuclei of these ions is responsible for the quadrupolar relaxation of the nuclei with spin quantum number $I > 1$. It was shown in their calculations (Engström *et al* 1984) that the correlation times for the diffusive decay of reorientational motions of the solvent around the ions range from 2 to 6 ps. It was also found in their study that the choice of boundary conditions used in the simulations and the number of solvent particles used in the simulations did not have any significant effect on their results. The rapid decay of the electric field gradient tcfs was attributed partly to a correlated motion of water in the first hydration shell, and the complex time dependence of the tcfs indicated a non-exponential decay of correlations. Friedman and Newton (1982) have discussed a dynamical theory for the solvent reorganization process and found that the experimental (e.p.r.) measurement of the electric field gradient correlation time combined with a relation in the continuum model gives a value of τ_{out} equal to about 2 ps.

One would expect the electron to traverse a region in which the relaxation times are shortest. As we find that there are no significant deviations in the relaxation times at the points in the neighbourhood of the ions and the locations of the ions themselves, we may use an *average* value of relaxation time (3 ps) in (1). The EF correlation times obtained in our model as well as the reorientational correlational times for dipole moment vector in the first hydration shell of Li^+ using an MCY model (Matsouka *et al* 1976) for water are similar in magnitude (3–6 ps). If we take

Table 3. Relaxation times (ps) for the EF tcfs (shown in figure 4a) in x , y and z directions at point no. 8 for system A obtained from a multi-exponential fit (6).

Ef tcfs in direction	τ_1	τ_2	τ_3	Standard Deviation
x	3.5	13.0	39.5	0.007
y	3.4	6.5	30.0	0.009
z	4.1	19.5	39.0	0.007

these values to represent the solvent relaxation times in the aqueous electron exchange reaction, their effect on the rate constants is within a factor of 2 of the values reported by Tembe *et al* (1982).

The correlation times obtained in our work may be compared with some of the relaxation times commonly used in literature. The simplest is the Debye relaxation time, $\tau_D = \zeta/2kT$ (Debye 1929). This is obtained from a model wherein a dipolar molecule is considered to be a sphere of radius a which is moving in a continuous fluid of viscosity η . Here ζ is the frictional constant given by $\zeta = 8 \pi \eta a^3$. In this model the dipole reaches equilibrium by frictional reorientation. The value of τ_D for H₂O was found to be 8.2 ps at 298 K. Another relaxation time, reported recently by van der Zwan and Hynes (1985) is the longitudinal relaxation time (τ_L). In their work a dipole is assumed to be in a spherical Onsager cavity with a dielectric constant of unity. The dipole in this model experiences a reaction field \mathbf{R} , which is given by

$$\mathbf{R} = (B_{op} + B_{or})\boldsymbol{\mu}. \quad (7)$$

Here, B_{op} and B_{or} are optical and orientational solvent response functions. The solvent orientational response function, B_{or} is related to the time dependent dielectric friction coefficient, $\zeta(t)$, which relates the torque \mathbf{T} experienced by the dipole to its angular velocity Ω (Nee and Zwanzig 1970).

$$\mathbf{T}(t) = - \int_0^t ds \zeta(t-s) \Omega(s). \quad (8)$$

This $\zeta(t)$ is related to τ_L by

$$\zeta(t) = \zeta(t=0) \exp(-t/\tau_L). \quad (9)$$

This relaxation time (τ_L) is a measure of the nonlocal effects in the dielectric friction coefficient. The relation between τ_L and τ_D for a continuum Debye-Onsager model ignoring solvent polarizability is

$$\tau_L = \tau_D (2\epsilon_\infty + 1/2\epsilon_0 + 1), \quad (10)$$

where ϵ_0 and ϵ_∞ are static and high frequency dielectric constants.

In highly polar solvents τ_L is much smaller than τ_D . For water τ_L was found to be 0.24 ps at 298 K as against a value of zero implied in the Debye model. A calculation has been reported for the quadrupole relaxation time, τ_Q , by Hynes and Wolynes (1981) which was referred to in §1. In their model a quadrupole is placed in a spherical Onsager cavity. In this case a reaction field gradient is experienced by the quadrupole. An electrical torque is experienced by the rotating quadrupole due to the lagging response of the solvent polarization. The torque in this case is related to the quadrupole dielectric friction coefficient, ζ_Q , which is proportional to quadrupolar relaxation tcf $C_Q(t)$,

$$C_Q(t) \propto \zeta_Q(t) \propto e^{-t/\tau_Q}. \quad (11)$$

The quadrupole relaxation time is also related to τ_D by

$$\tau_Q = \tau_D(2 + 3\epsilon_\infty/2 + 3\epsilon_0). \quad (12)$$

For water τ_Q was found to be of the same order as τ_L (0.26 ps).

The relaxation times calculated in our work are based on central force models with translational and overall rotational motions of the solvent. To calculate relaxation times like τ_L and τ_Q we need to change from a central force model without internal rotations to molecular models in which internal rotations of molecules are also a part of the overall dynamics. In calculating τ_L and τ_Q we need to freeze the translational motions allowing only rotational motions. Since rotational motions are more rapid than translational motions, we expect that the resulting relaxation times will be smaller than what we obtained in our calculations. We are now looking at the extension of our model to include point dipoles in rigid spheres and are also investigating the effect of the size and the strength parameters of the potentials on the dynamical fluctuations. When the $\text{Fe}^{2+}-\text{H}_2\text{O}$ and $\text{Fe}^{3+}-\text{H}_2\text{O}$ interactions become available, the simulations can be performed on the actual molecular models.

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