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A One-Dimensional Energy Diffusion Approach to Multidimensional Dynamical Processes in the Condensed Phase

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We propose a generalized one-dimensional energy diffusion approach for describing the dynamics of multidimensional dynamical processes in the condensed phase. On the basis of a formalism originally due to Zwanzig, we obtain a one-dimensional kinetic equation for a properly selected relevant dynamical quantity and derive new analytical results for the dynamics of a multidimensional electron-transfer process, nonequilibrium solvation, and diffusive escape from a potential well. The calculated results for electron-transfer reactions in solvent-separated and contact ion pair systems are found to be in good agreement with the experimental results. We are able to explain the rate of the electron-transfer reaction using much smaller and reasonable values of the solvent reorganization energy in contrast to earlier works that had to use a much larger value. The proposed theory is not only conceptually simpler than the conventional approaches but is also free from many of their limitations. More importantly, it provides a single theoretical framework for describing a wide class of dynamical phenomena.

1. Introduction

Dynamical processes in the condensed phase such as electron-transfer (ET) reactions,[1] diffusive escape from potential wells,[2] activated barrier crossing, nonequilibrium solvation,[3] etc. are of immense and long standing importance in various frontier areas of research in physics, chemistry, and biology. A theoretical description of these phenomena is, however, severely hindered by the multidimensional nature of the collective motion involved and also the difficulty in evaluation of the nonequilibrium time correlation functions for proceeding beyond linear response theory. The objective of the present work is to bypass these difficulties by developing alternative simpler approaches for describing condensed phase dynamics. We obtain here a new simple one-dimensional theoretical framework by identifying a proper reaction co-ordinate (or the relevant dynamical variable) and deriving a kinetic equation for its probability distribution function, which is shown to provide a generalized approach for describing a wide class of dynamical phenomena. Specifically, we consider its application to the dynamics of three important multidimensional dynamical problems, viz. two-dimensional electron transfer, nonequilibrium solvation, and escape of a particle from a potential well.

The description that we propose is based on a kinetic equation for the probability distribution of a microscopic phase space function A constrained to have a value γ at time t that was proposed originally by Zwanzig[4] and can be written, in a modified form,[5] as

$$\frac{\partial P(\gamma,t|\gamma_0,0)}{\partial t} = \frac{\partial}{\partial \gamma}\left\{\int_0^t D(\gamma,\tau)\,\mathrm{d}\tau \left[\frac{\partial P(\gamma,t-\tau|\gamma_0,0)}{\partial \gamma} + \frac{\partial}{\partial \gamma}\{\beta V_{\mathrm{eff}}(\gamma)\}P(\gamma,t-\tau|\gamma_0,0)\right]\right\} \quad (1)$$

where γ_0 is the value of γ at $t = 0$ and the time-dependent as well as γ-dependent diffusivity is defined as $D(\gamma,t) = \langle \dot{A}(t)\dot{A}(0)\delta(A(t) - \gamma)\rangle/\langle\delta(A(t) - \gamma)\rangle$, with the broken brackets denoting an equilibrium ensemble average and the dot corresponding to the time derivative. The effective potential $V_{\mathrm{eff}}(\gamma)$ is defined as $V_{\mathrm{eff}}(\gamma) = \ln\langle\delta(A(t) - \gamma)\rangle$ where β $(= 1/k_{\mathrm{B}}T)$ denotes the inverse temperature. Zwanzig's derivation of eq 1 assumes that $\mathrm{d}A(t)/\mathrm{d}t$ is small, which has been discussed by him in detail.[4]

2. Theory of Electron Transfer

In an ET process, the system moving initially on a multidimensional reactant potential energy surface (PES) crosses to the product PES at the intersection point. The ET reactions do occur with an intrinsic rate k_0 corresponding to $\gamma = 0$, i.e., when the reactant and product potential energies are equal.[1] Hence, the kinetic equation for $P(\gamma,t|\gamma_0,0)$ given by eq 1 should be modified for ET reactions by introducing a delta sink with strength k_0 to its right side. The modified kinetic equation, for ET reactions, thus becomes

$$\frac{\partial P(\gamma,t|\gamma_0,0)}{\partial t} = \frac{\partial}{\partial \gamma}\left\{\int_0^t D(\gamma,\tau)\,\mathrm{d}\tau \left[\frac{\partial P(\gamma,t-\tau|\gamma_0,0)}{\partial \gamma} + \frac{\partial}{\partial \gamma}\{\beta V_{\mathrm{eff}}(\gamma)\}P(\gamma,t-\tau|\gamma_0,0)\right]\right\} - k_0\delta(\gamma)P(\gamma,t|\gamma_0,0) \quad (2)$$

Here the sink strength (k_0) can be expressed in terms of an electron-transfer integral as $k_0 = (4\pi^2/h)J^2$, where h denotes the Planck constant. A simple theoretical model that we consider here consists of a multidimensional space spanned by the low-frequency solvent polarization (X) and the vibrational coordinate[6] (Q) or two low-frequency solvent collective coordinates.[7] In Figure 1, the PES of the system is drawn in the two-dimensional space spanned by the coordinates X and Q, with the curve ABC representing the intersection of the reactant and product PES, and ET takes place when the reactant reaches the intersection point. The dynamical effects in ET reactions can be investigated theoretically using this model for which the

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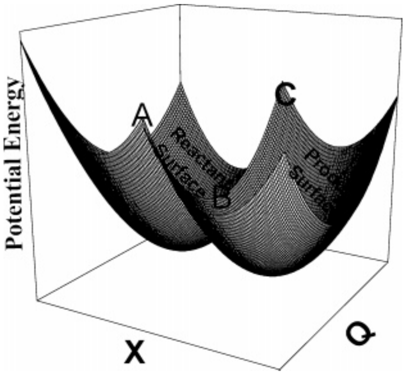

Figure 1. Typical potential energy surface of a two-dimensional electron-transfer reaction. The two surfaces intersect on the curve ABC.

conventional Smoluchowski equation[6,7] approach is cumbersome and highly involved, thus making the simpler one-dimensional description, as proposed here, very important and significant. When specialized to the standard low-frequency harmonic oscillator model[6,7] for the reactant and product PES defined as, respectively, $V^{R}(Q,X) = (^1/_2)Q^2 + (^1/_2)X^2$ and $V^{P}(Q,X) = (^1/_2)(Q - Q_0)^2 + (^1/_2)(X - X_0)^2 + \Delta G$, the modified generalized kinetic equation (eq 1), in the Markovian limit, for ET reactions becomes

$$\frac{\partial P(\gamma,t|\gamma_0,0)}{\partial t} = D_{\text{eff}}\frac{\partial}{\partial \gamma}\left[\frac{\partial P(\gamma,t|\gamma_0,0)}{\partial \gamma} + \frac{\beta}{2(\lambda + \lambda_0)}[\gamma - (\lambda + \lambda_0 + \Delta G)]P(\gamma,t|\gamma_0,0)\right] - k_0\delta(\gamma)P(\gamma,t|\gamma_0,0) \quad (3)$$

where $D(\gamma,t)$ of eq 1 has been replaced by the effective diffusivity $D_{\text{eff}} = \int_0^\infty \mathrm{d}t\,[X_0^2\langle \dot{X}(t)\dot{X}(0)\rangle + Q_0^2\langle \dot{Q}(t)\dot{Q}(0)\rangle]$ within the Markovian approximation and assumption of weak γ-dependence of $D(\gamma,t)$. It is also assumed that the cross-velocity contribution is zero. Here, the low-frequency vibrational reorganization energy λ and solvent reorganization energy λ_0 are given by $\lambda = (^1/_2)Q_0^2$ and $\lambda_0 = (^1/_2)X_0^2$, respectively, while ΔG represents the free energy of the ET reaction. Equation 3 also can be rewritten as

$$\frac{\partial P(z,t|z_0,0)}{\partial t} = D_{\text{eff}}\frac{\partial}{\partial z}\left[\frac{\partial P(z,t|z_0,0)}{\partial z} + \frac{\beta}{2(\lambda + \lambda_0)}zP(z,t|z_0,0)\right] - k_0\delta(z - z^*)P(z,t|z_0,0) \quad (4)$$

using the variables $z = \gamma + z^*$, $z_0 = \gamma_0 + z^*$, and $z^* = -(\lambda + \lambda_0 + \Delta G)$. This is an important result because it provides a one-dimensional energy diffusion equation of the reactive system and can be numerically solved much more easily than the two-dimensional Smoluchowski equation involving X and Q coordinates. It may be noted that the present one-dimensional description of a two-dimensional ET is analogous to the Zusman equation[8] proposed earlier for a one-dimensional ET process. The formal solution of eq 4 is given by

$$P(z,t|z_0,0) = P_0(z,t|z_0,0) - k_0\int_0^t \mathrm{d}\tau\, P_0(z,t - \tau|z^*,0)P(z^*,\tau|z_0,0) \quad (5)$$

where the function $P_0(z,t|z_0,0)$ is the solution of eq 4 in the absence of any sink term. The probability of finding the system at time t within the reactant surface is defined as $P(t) = \int_{-\infty}^{\infty} \mathrm{d}z\, P(z,t|z_0,0)$, and the average rate constant k of the ET reaction can be expressed as $k^{-1} = \int_0^\infty \mathrm{d}t\, P(t)$, which also can be written as

$$k^{-1} = (k_{\text{TST}})^{-1} + k_{\text{D}}^{-1} \quad (6)$$

Here, k_{TST} represents the transition state theory (TST) result obtained by Marcus,[1] which can be expressed as

$$k_{\text{TST}} = k_0(4\pi k_{\text{B}}T(\lambda_0 + \lambda))^{-1/2}\exp\left[-\frac{(\Delta G + \lambda + \lambda_0)^2}{4k_{\text{B}}T(\lambda_0 + \lambda)}\right] \quad (7)$$

while k_{D} represents the rate constant for the well dynamics and can be expressed in terms of the nonequilibrium distribution function $P_0(z,t|z_0,0)$ in the absence of sink (i.e., solution of eq 4 with $k_0 = 0$) as

$$k_{\text{D}}^{-1}(z^*,z_0) = \frac{\int_0^\infty \mathrm{d}t\,[(P_0(z^*,t|z^*,0) - P_0(z^*,t|z_0,0))]}{P_0(z^*,\infty|z^*,0)} \quad (8)$$

One can have an analytical expression for this quantity by using the standard expression of $P_0(z^*,t|z_0,0)$ and evaluating a line integral with a gradient of k_{D}^{-1} in two-dimensional space (x,y) from (0,0) to (z^*,z_0), using a suitable path $(0,0) \rightarrow (z^*,0) \rightarrow (z^*,z_0)$ because the integral is path-independent. The analytical expression for k_{D}^{-1} thus obtained is given by

$$k_{\text{D}}^{-1}(z^*,z_0) = (\pi)^{1/2}(k_{\text{B}}T(\lambda_0 + \lambda))^{1/2}D_{\text{eff}}^{-1} \times \sum_{n=0}^{\infty}\frac{1}{n!}\left[\frac{1}{2n + 1}(A_2^{2n+1} - A_1^{2n+1}) + 2(\pi)^{-1/2} \times \sum_{m=0}^{\infty}\frac{(-1)^m}{m!(2m + 1)X_{\text{mn}}}(A_2^{X_{mn}} - A_1^{X_{mn}})\right] \quad (9)$$

where $X_{mn} = 2m + 2n + 2$ with A_1 and A_2 (for $A_1 < A_2$) given by $A_1 = z_0/(4k_{\text{B}}T(\lambda_0 + \lambda))^{1/2}$ and $A_2 = z^*/(4k_{\text{B}}T(\lambda_0 + \lambda))^{1/2}$. The effective diffusivity can be approximated in terms of the solvent relaxation time τ_{T} as $D_{\text{eff}} = 2k_{\text{B}}T(\lambda_0 + \lambda)/\tau_{\text{T}}$. If the system evolves from an initial equilibrium state, then the corresponding rate constant is given by

$$k_{\text{d}}^{-1} = \tau_{\text{T}}[\ln 2 + (2\pi)^{1/2}\int_0^{A_0}\mathrm{d}x\,\exp[x^2/2]\,\mathrm{erf}(x/2)] \quad (10)$$

where $A_0 = (\lambda_0 + \lambda + \Delta G)/(2k_{\text{B}}T(\lambda_0 + \lambda))^{1/2}$. Equations 4, 9, and 10 are the new results of the present work. An analogous expression has been derived by Tachiya and Murata[9] for one-dimensional ET reactions. It may be noted that analytical results for the ET rate constant k cannot be obtained[10] by directly solving the two-dimensional Smoluchowski equation, and in fact the difficulty for numerical evaluation through this equation increases drastically with an increase in dimensionality. The investigation of two-dimensional ET as a one-dimensional problem leading to an analytical expression for the rate constant, as shown here, is only illustrative, and it is straightforward to use the present approach to formulate the treatment of ET reactions involving higher-dimensional (more than two) space as a one-dimensional problem and obtain analogues of eqs 4, 9, and 10. In the case of a delocalized sink, one should replace the localized $\delta(\gamma)$ sink of eq 3 by a generalized sink function[11] $S(\gamma)$.

As an illustrative example, we now consider a typical ET reaction, where a molecule DA is excited from the ground state, leading to ion pair formation and the system then relaxes downward along the PES of the resulting D^+A^- system until it meets the PES of the ground state DA, when the back ET reaction takes place. Considering the potential energy for the system DA and D^+A^- to be given by $V^{DA}(Q,X) = (^1/_2)Q^2 + (^1/_2)X^2$ and $V^{D^+A^-}(Q,X) = (^1/_2)(Q - Q_0)^2 + (^1/_2)(X - X_0)^2 - \Delta G$, respectively, where ΔG represents the free energy of back-ET (charge recombination reaction), the rate constant $k_D{}^{-1}$ is given by eq 9 with $Z_0 = -2(\lambda + \lambda_0)$.

3. Nonequilibrium Solvation Dynamics

Another very important dynamical process is the nonequilibrium solvation of a newly created charge or dipole that provides[3] a microscopic understanding of the relaxation of the solvent molecules around a newly created ion or dipole at different time domains. The calculation of the nonequilibrium solvation time (NEST) through simulation, however, requires harvesting of the nonequilibrium trajectories and is, therefore, computationally demanding. One of the most common approximations in theoretical studies of solvation dynamics is based on the assumption of linear response, which permits the replacement of NEST by the equilibrium solvation time correlation function, the theoretical calculation of which is rather simple. Computer simulation[12] as well as experimental studies show that in many situations the linear response theory breaks down, and hence a good theoretical method for the evaluation of NEST is in demand. The relevant quantity of interest is the NEST, which is defined as

$$S(t) = \frac{\overline{\Delta E(t)} - \overline{\Delta E(\infty)}}{\overline{\Delta E(0)} - \overline{\Delta E(\infty)}} \tag{11}$$

and is directly accessible via time-dependent fluorescence. Here $\overline{\Delta E(t)}$ is the nonequilibrium ensemble average of the energy gap between the ground and the excited states of the solute. We propose here a simple one-dimensional dynamical equation for its evaluation. Many optical and rate processes involving molecules in solution can be described by considering a two (electronic) level system coupled to collective harmonic bath coordinates representing the solvent, which was first proposed by Zwanzig[13] and is widely used for the study of barrier crossing dynamics,[14] many ultrafast nonlinear techniques,[15] Landau diamagnetism[16] in a dissipative and confined system, etc. The generalized form of the potential energy of the system in multidimensional space in this model for the ground and excited states of the solute is given, respectively, by

$$V_g = V_s{}^g(Q_1...Q_N) + \sum_{j=1}^{N_s}\sum_{i=1}^{N} \frac{1}{2} m_i\left(\omega_i q_i + \frac{C_i^j}{m_i\omega_i} Q_j\right)^2 \tag{12}$$

and

$$V_e = V_s{}^e(Q_1...Q_N) + \sum_{j=1}^{N_s}\sum_{i=1}^{N} \frac{1}{2} m_i\left(\omega_i q_i + \frac{C_i^j}{m_i\omega_i} Q_j\right)^2 \tag{13}$$

In eqs 12 and 13, the first terms represent the potential energy of the solute (consisting of N_s vibrational degrees of freedom) in the ground and excited states, respectively, and are assumed to be given by $V_s{}^g(Q_1...Q_N) = (^1/_2)M\sum_{j=1}^{N_s}\Omega_j{}^2Q_j{}^2$ and $V_s{}^g(Q_1...Q_N) = (^1/_2)M \sum_{j=1}^{N_s}\Omega_j{}^2(Q_j - d_j)^2$ with Ω_j and M denoting the frequency and mass of the solute particle, while m_i, ω_i, and q_i represent, respectively, the mass, frequency, and positions of the ith bath oscillator and the coefficient C_i^j couples the ith bath oscillator to the system coordinate Q_j. The excited state of the solute here corresponds to a displaced harmonic oscillator with d_j denoting the displacement for the jth oscillator. It is clear from eq 11 that the relevant microscopic phase space function A can be considered to be $A = V_s^e - V_s^g$, and the probability of this phase space function to have the value ΔE satisfies the equation

$$\frac{\partial P(\Delta E,t|\Delta E_0,0)}{\partial t} = \int_0^t C_v(\tau)\,d\tau\,\frac{\partial}{\partial \Delta E}\left[\frac{\partial P(\Delta E,t-\tau|\Delta E_0,0)}{\partial \Delta E} + (C + D\Delta E)P(\Delta E,t-\tau|\Delta E_0,0)\right] \tag{14}$$

where $C = (1/2k_BT)$, $D = (2\lambda_{or}k_BT)^{-1}\lambda_{or} = (^1/_2)M \sum_{j=1}{}^{N_s}\Omega_j{}^2d_j{}^2$, and $C_v(t)$ is the collective velocity correlation function of the solute particle in the excited state. In the Markovian limit, as is clear from eq 14, the probability distribution $P(\Delta E,t|\Delta E_0,0)$ of the energy gap between the electronic states of the solute are Gaussian throughout the dynamics of nonequlibrium solvation. These remarkable energy gap statistics also have been observed[17] in real systems through simulation studies, such as nonequilibrium relaxation following the dipolar transition of solute in water. Now, defining the nonequilibrium solvation energy as $\overline{\Delta E(t)} = \int_{-\infty}^{\infty} d\Delta E P(\Delta E,t|\Delta E_0,0)$, using eqs 14 and 11, one obtains, after some algebra, the result

$$S(t) = L^{-1}\left(s + \frac{1}{2\lambda_{or}k_BT} C_v(s)\right)^{-1} \tag{15}$$

where L^{-1} represents the inverse Laplace transform and $C_v(s)$ is the Laplace transform of $C_v(t)$. Equations 14 and 15 represent new important results of the present work and provide an important relation between the solvation time correlation function and the velocity correlation function $C_v(t)$ of the solute in the excited state. To obtain an analytical expression for $S(t)$, we assume that the frequency of oscillation for different modes of the solute particle are identical ($\Omega_i = \Omega_j = \Omega$), and in the overdamped limit, the velocity correlation function decays exponentially with a decay constant $1/\xi$, where ξ is the friction exerted on the solute particle by the solvent particles. Within these approximations, after some algebra, we obtain the expression for $S(t)$ given by

$$S(t) = \frac{\exp[-(\xi/2)t]}{2P}[(1 + P)\exp[(P\xi/2)t]] - (1 - P)\exp[-(P\xi/2)t] \tag{16}$$

with $P = (1 - 4(\Omega/\xi)^2)^{1/2}$.

4. Diffusive Escape from a Potential Well

The escape of a particle[2] from a potential well in the condensed phase is another important dynamical phenomenon that we consider here. The motion of the particle is coupled to the solvent motion, thus requiring a description of the dynamics to be multidimensional. We employ a model potential similar to the one defined in eq 12 and assume the solute particle to escape from the potential well on attaining the energy E_d, i.e., $V_s^g(Q_1...Q_{N_s}) = E_d$. Thus the obvious choice for the phase space function is $A = V_s^g(Q_1...Q_{N_s})$, and the dynamical equation for the probability that this potential energy function A is constrained to have the value E as obtained from eq 1 is given, in the Markovian limit, by

$$\frac{\partial P(E,t|E_0,0)}{\partial t} = 4D\frac{\partial}{\partial E}\left[E\frac{\partial P(E,t|E_0,0)}{\partial E} + \left(\frac{E}{k_B T} + 1 - \frac{N_s}{2}\right)P(E,t|E_0,0)\right] \quad (17)$$

Here, D is the diffusion constant corresponding to the motion along the hyperspherical coordinate of the solute particle. A similar equation for a one-dimensional problem ($N_s = 1$) was derived by Kramers[18] based on a different approach. The present generalized one-dimensional energy diffusion equation, however, corresponds to a multidimensional problem. The rate constant k for the escape process can be evaluated[19] by solving eq 17 using the reflecting boundary condition at $E = 0$ and a perfectly absorbing boundary condition at $E = E_d$. The resulting expression for k is obtained as

$$k = \frac{4\beta D \int_0^{\beta E_d} dz\, z^{n-1} \exp[-z]}{\int_0^{\beta E_d} dz\, z^n \exp[z][\int_0^1 dt\, t^{n-1} \exp[-zt]]^2} \quad (18)$$

where $n = N_s/2$. Equations 17 and 18 represent important results of the present work. The diffusion constant D appearing in eq 18 can be calculated using suitable approaches including the scaling laws proposed recently.[20,21] It is clear from this equation that the rate of escape of a particle from the potential well decreases with an increase of barrier height E_d as expected.

5. Results and Discussion

The one-dimensional energy diffusion approach to multidimensional dynamical processes developed here and applied to understand three important dynamical processes, viz. ET reactions, nonequilibrium solvation dynamics, and diffusive escape from the potential well, is now illustrated through numerical results. Our first consideration is the example of ET reactions for which we consider two different types of specific examples, viz. solvent-separated ion pair (SSIP), where the ion pair is separated by solvent molecules, and the case of ET for contact ion pair (CIP), where the ion pair is in contact with each other. To explain the experimental results, Tachiya and Murata[9] had considered only single-mode diffusive motion in the X coordinate and used the parameters: $J = 0.003$ eV (for SSIP), $J = 0.3$ eV (for CIP),[9] and $\lambda_0 = 1.5$ eV. But this value of the reorganization energy λ_0 is quite high and cannot be easily rationalized. However, the ET process is multidimensional in nature, and the reorganization energy might be contributed by different modes and not necessarily from one single mode as they have considered in their investigation. In the present theory, we have developed a one-dimensional description of two-dimensional motion where the total reorganization energy is contributed by two modes. For simplicity, we consider here the reorganization energy for the two modes X and Q to be the same, and the best fitted value of λ_0 is found to be 0.75 eV, which is much less than the value taken by Tachiya and Murata.[9] The calculated values of the rate constant k for the ET process in the SSIP and CIP cases are plotted along with the available experimental results[22,23] as a function of ΔG in Figures 2 and 3, respectively. It is observed that for the SSIP case k_D has very little effect on the overall ET reaction rate constant k, which is mainly controlled by k_{TST} as predicted by Marcus in his landmark work.[1] In this case, the electronic coupling strength J is very small, as a result only a small fraction of the reactant undergoes the ET reaction, the rest relaxes downward toward the minimum along the PES of the excited state, and further reaction occurs via the activated Marcus mechanism. This observation of the ET reaction proceeding always via the activated mechanism for small J values is quite general because the system has to relax after excitation, reach the population minimum, and then overcome the reaction barrier. As a result, the total rate of the ET reaction is independent of the initial nonequilibrium configuration, and Marcus theory does work quite well. However, in the case of CIP, the value of J is large as expected, and the back-ET reaction occurs with almost unit probability during the course of the relaxation as the reactant population reaches the reaction zone. Thus, the reaction can occur from a completely nonequilibrium condition, and an interplay between k_{TST} and k_D leads to a non-Marcus energy-gap-dependent rate of ET reactions, as is clear from Figure 3. As a result, the rate of the ET reaction is strongly dependent on the initial nonequilibrium configuration as well as the solvent relaxation dynamics. As already mentioned, the experimental results are reproduced with much lower values of the solvent reorganization energy λ_0 (= 0.75 eV), in contrast to the higher value ($\lambda_0 = 1.5$ eV) used by Tachiya and Murata.[9] Although Gayathri and Bagchi[10] did predict earlier the rate of the same ET reactions using smaller values of λ_0, they evaluated the rate

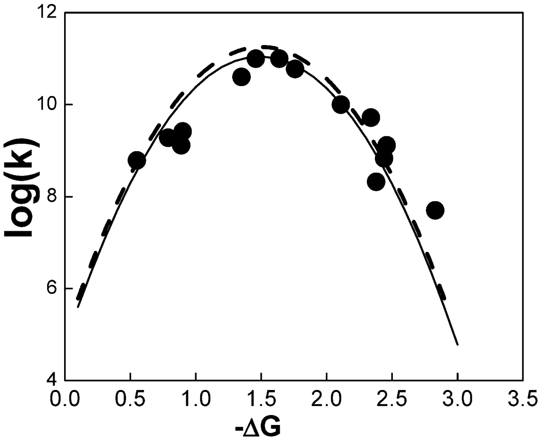

Figure 2. Plot of the electron-transfer rate constant k vs the free energy change ΔG for the solvent-separated ion pair for the parameter values $\lambda_0 = 0.75$ eV, $\tau_T = 0.3$ ps, $T = 300$ K, and $J = 0.003$ eV. The solid line represents the present calculated results, the dashed line represents results based on Marcus theory (eq 7), and the circles represent the experimental results.[22]

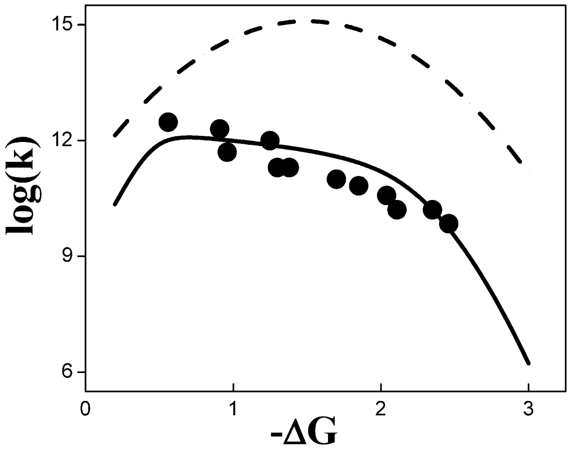

Figure 3. Plot of the electron-transfer rate constant k vs the free energy change ΔG for the contact ion pair for $J = 0.3$ eV. Other parameters and the key are the same as in Figure 2 except that the source of the experimental results is different.[23]

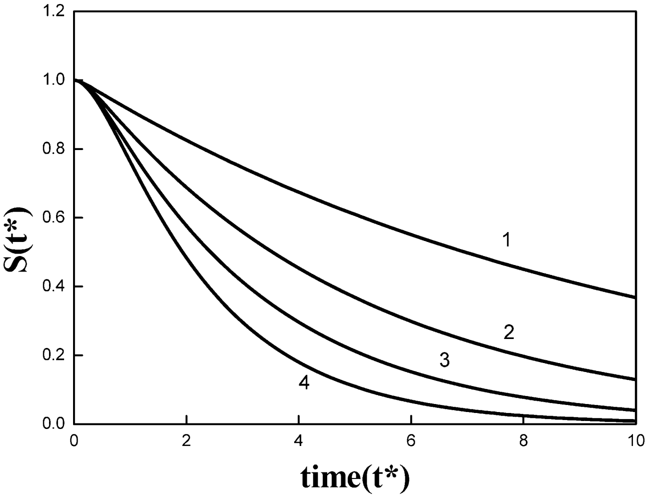

Figure 4. Plot of the nonequilibrium solvation time correlation function $S(t)$ vs scaled time t^* ($= \Omega t$) for the parameter values: Frequency $\Omega = 10^{12}$ s^{-1}, friction coefficient $\xi = 10\Omega$ for curve 1, $\xi = 5\Omega$ for curve 2, $\xi = (^{10}/_{3})\Omega$ for curve 3, and $\xi = 2.5$ for curve 4.

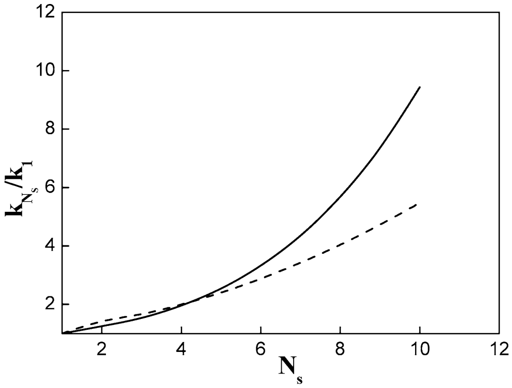

Figure 5. Plot of the ratio of the rate of escape of a solute particle having N_s degrees of freedom to the same for one degree of freedom vs the number of degrees of freedom N_s. The solid line corresponds to the calculated results for $\beta E_d = 3$, and the dashed line corresponds to $\beta E_d = 2$.

numerically using the multidimensional Smoluchowski equation, which is cumbersome, whereas we have obtained here an analytical expression for the rate of electron transfer, which is easy to evaluate.

The next problem that we consider involves nonequilibrium solvation dynamics in the overdamped limit, i.e., $\Omega/\xi \ll 1$. It is clear from eq 16 that the solvation time is not of a single-exponential form, whereas, in the Markovian limit, it can be expressed in the simple exponential form $\exp[-\Omega^2 t/\xi]$. In Figure 4, we have plotted the nonequilibrium solvation time correlation function, $S(t)$, as a function of time for different values of the friction experienced by the solute particle. We have considered here the frequency of the solute particle to be $\Omega = 10^{12}$ s^{-1}. It is clear from the figure that the solvation becomes faster, with a decrease of the friction coefficient, which agrees with the intuition that the solute can readjust itself along with the solvent molecules to reach the equilibrium faster. While the discussion here is based on a model system, it is also observed in many realistic systems. Finally, we investigate the problem of dynamics of escape of a particle from a potential well, for which we have calculated the ratio of the escape (k_{N_s}/k_1) of a particle for different degrees of freedom (N_s) of the solute particle as well as different barrier heights and plotted the results in Figure 5. From the figure, it is clear that the escape rate increases with an increase in the solute degree of freedom for a given value of the barrier height. This increase in rate is due to a decrease of βV_{eff} of the solute particle in the energy space.

6. Concluding Remarks

In this work, we have presented, for the first time, using Zwanzig's generalized kinetic equation and the proper selection of the multidimensional reaction co-ordinate or the relevant dynamical variable, a kinetic equation for its probability distribution function, which is shown to provide a generalized approach for describing a wide class of dynamical phenomena. Specifically, we have considered its application to the dynamics of three important multidimensional dynamical problems, viz. two-dimensional electron transfer, nonequilibrium solvation, and escape of a particle from the potential well. The one-dimensional energy diffusion equation proposed here is conceptually simple, computationally economic, and also free from many of the bottlenecks of the conventional approaches. As illustrative examples, we have considered ET reactions in nonequilibrium situations and derived an analytical expression for the rate of ET where the overall rate constant is explicitly dependent on various physical parameters of the system. We are able to explain the rate of the electron-transfer reaction using much smaller and reasonable values of the solvent reorganization energy, in contrast to earlier works that had to use much larger values for the same. This has been possible in our theory as the total reorganization energy considered here is contributed by two modes of motion in contrast to the earlier consideration of only a single mode. It may be mentioned that a prediction[10] of the rate of the same ET reactions using smaller values for the solvent reorganization had been reported earlier, but it involved numerical solution of the multidimensional Smoluchowski equation, whereas the present work provides analytical results. We also have provided a scheme to study the nonequilibrium solvation without invoking the linear response theory. Numerical results based on the harmonic oscillator model show that with a decrease of the friction experienced by the solute particle the nonequilibrium solvation becomes faster, which is observed in many realistic systems. We also have studied the dynamics of escape of a particle moving in a multidimensional space through the one-dimensional approach presented here.

Although we have adopted here some generic model to derive the analytical results, an analytical expression for the rate of ET reactions and escape of a particle from a potential well for arbitrary potential $V_{\mathrm{eff}}(\gamma)$ and γ-dependent diffusivity also has been possible to obtain. In the case of nonequilibrium solvation dynamics, however, for arbitrary potential $V_{\mathrm{eff}}(\gamma)$ one has to solve the one-dimensional equation (eq 1) numerically with the initial value $\gamma_0 = \langle V_s^e - V_s^g \rangle$, which can be calculated using equilibrium theory. Because the equation is a one-dimensional one, it is rather easy to solve it in comparison to other conventional methods. Most interestingly, in the present theory, it is easy to incorporate the effect of the initial nonequilibrium configuration through γ_0, whereas the same is not easy for the conventional approaches that are based on linear response theory. Moreover, in many situations, the linear response theory breaks down, but our theory provides a simple method to evaluate the nonequilibrium solvation time correlation function. We will address a detailed discussion on all of these issues in future work.

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