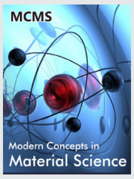
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Research Article

Chemical Rate Constant Using the Generalized Langevin Equation with Hydrodynamic and Dielectric Memory in Relation to Molecular Solar Thermal Energy Storage

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Abstract

Molecular solar thermal (MOST) systems, such as norbornadiene–quadricyclane, azobenzenes, and dihydroazulenes, offer promising pathways for solar energy storage via photoinduced isomerization, energy storage and subsequent thermal energy release. A key challenge in optimizing these systems lies in accurately modeling the coupled electronic and conformational transitions within condensed phases. We present a rigorous theoretical framework based on the Generalized Langevin Equation (GLE) that captures essential features of solute–solvent interactions, including memory effects and non-Markovian friction arising from slow environmental relaxation. The GLE formalism incorporates a time-dependent memory kernel $\Gamma(t)$ to describe temporally correlated noise and friction over a broad range of timescales. This approach is especially well-suited for modeling MOST systems in polar and structured solvents where dielectric relaxation, hydrogen bonding, and hydrodynamic interactions critically influence the dynamics of transition states and thermal back-reaction rates.

Introduction

Harnessing and storing solar energy at the molecular level is one of the most exciting frontiers in chemistry and materials science. As the need for renewable and sustainable energy technologies increases, the conversion of sunlight into a storable chemical form without the need for intermediate electrical or mechanical energy is a very desirable approach [1-9].

It involves photochemical systems that are capable of reversibly storing solar energy through structural or electronic rearrangements. This provides a method to obtain scalable, sustainable, and efficient solar-to-chemical energy conversion systems. Current investigations focus on the use of photo-switchable molecules that perform a transformation upon photoexcitation and so one is able to store solar energy in the form of chemical bonds. The chemical transformations enable reversible storage of solar energy in the form of metastable chemical bonds and this is the basic principle for molecular solar thermal (MOST) energy storage systems [1-9].

Understanding the dynamics of MOST systems requires modeling the influence of the solvent environment, molecular friction, and energy dissipation pathways on reaction dynamics. The timescales involved in these processes span from femtosecond electronic transitions to nanosecond-to-millisecond conformational relaxations. Therefore, one needs a framework that goes beyond simple Markovian dynamics. The Generalized Langevin Equation (GLE) is able to incorporate memory-dependent friction and correlated noise and we can model solvent-coupled dynamics [10-27]. The GLE is:

$$m\ddot{x}(t) = -\frac{dV}{dx}(x) - \int_o^t \Gamma(t-t')\dot{x}(t')\,dt' + R(t), \qquad (1)$$

where $\Gamma(t)$ is a memory kernel and R(t) is a stochastic force satisfying the fluctuation-dissipation relation:

$$\langle R(t)R(t')\rangle = k_B T\Gamma(|t-t'|). \qquad (2)$$

The reaction coordinate is given by x, the mass of the reacting system is m and the potential is denoted V. This allows one to analyze how the effects of solvent viscosity and polarization relaxation are able to modify energy conversion efficiency and reaction dynamics in MOST systems [10-27].

The GLE has become a foundational tool for investigating the dynamics of chemical reactions in condensed-phase environments. Unlike its Markovian counterpart, the GLE is able to include non-Markovian dynamics by accounting for memory effects through time-dependent friction kernels. Thereby it is possible for the method to model more accurately the dynamical correlations between a reactive system and its complex environment [10-27].

Traditional rate theories given by Transition State Theory (TST) and Kramers' theory assume instantaneous dissipation and uncorrelated noise. For realistic condensed-phase systems, the response of the solvent to the chemical reaction is delayed and frequency-dependent. This is due to the following:

(i) Hydrodynamic memory related to diffusion in the solvent, (ii) dielectric relaxation due to reorientation of solvent molecules. [10-27] The time-dependent interactions related to these two effects can significantly alter reaction rates and the GLE gives a microscopical extension to Kramers' theory by incorporating these features. We are able to compute generalized transmission coefficients and predict how frequency-dependent friction modifies barrier-crossing dynamics [10-27]. Generally, GLE-based methods have been applied to study a broad range of processes including (i) Proton and electron transfer reactions in polar solvents, (ii) isomerization in molecular switches and biological systems, (iii) barrier crossing in enzyme active sites, and (iv) solvent-controlled reaction dynamics, where the solvent friction determines the dominant time scale.

Overall, the GLE framework allows for accurate predictions of rate constants, transmission coefficients, and reaction coordinate dynamics with the possibility to investigate non-equilibrium molecular reaction dynamics [10-27]. It is crucial for the theoretical understanding of chemical kinetics in realistic systems that one is able to connect microscopic solvent dynamics and macroscopic reaction rates [10-27].

Molecular solar thermal energy storage systems offer significant advantages since they are closed-loop, relying only on light and heat. One is able to store energy without moving parts and it offers modular scalability from the molecular to the materials level. However, practical application of MOST systems is still limited by several challenges i) obtaining long storage lifetimes without unwanted thermal degradation, ii) improving the quantum yield and spectral overlap with the solar spectrum, iii) ensuring molecular back-conversion to release heat on demand, and iv) keeping thermal stability and reversibility over many cycles [3].

Some of the most studied MOST systems include norbornadiene-quadricyclane systems, azobenzenes, and dihydroazulenes, each system is capable of storing energy in a metastable high-energy form after photoisomerization. These photochromic molecules have turned out to be ideal candidates for MOST systems where energy is stored during the light-induced transition and later released as heat through thermal or catalytic back-conversion [1,2].

Norbornadiene derivatives undergo a photoinduced [2+2] cycloaddition to form quadricyclane which is a highly strained cage-like structure. This reaction absorbs a photon in the UV or visible range and the system is able to store more than 100 kJ/mol of energy. The stored energy is released by the reverse reaction as heat upon thermal or catalytic stimulation. The transition from QC to NBD is governed by a well-defined reaction coordinate and can be modeled as a barrier crossing process. It is possible to change the energy landscape significantly by including substituents on the NBD ring. Generally the substituents can tune the absorption spectrum, quantum yield, and back-conversion barrier. Quantum chemical calculations and ultrafast spectroscopy studies revealed that substituent effects change significantly the excited-state lifetimes and vibrational relaxation pathways [2,4]. Appropriate molecular designs can improve the thermal half-life of QC while keeping reversibility and eliminating side reactions.

Azobenzenes exhibit cis–trans isomerization upon irradiation and the trans isomer is thermodynamically favored. On the other hand, the cis form obtained via UV or blue-light excitation, is a metastable higher-energy state.

$$trans - Azobenzene \xrightarrow{hv} cis - Azobenzene \xrightarrow{\Delta,\, Catalyst} trans - Azobenzene$$

The energy stored per molecule (around 50 kJ/mol) is lower than that for the NBD–QC systems, whereas azobenzenes benefit from high quantum yields, rapid and reversible switching. The azobenzenes can be functionalized to absorb across different parts of the solar spectrum by substituting electron-donating and withdrawing groups on the aromatic rings [5]. Furthermore, azobenzenes have been widely integrated into polymeric back-bones, liquid crystals, and even self-assembled monolayers for responsive materials and optomechanical actuation.

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The DHA–VHF pair is another promising MOST candidate. The absorption of UV-Vis radiation initiates ring-opening of DHA to form VHF which is a structure stabilized by resonance. This MOST system is able to store about 55–70 kJ/mol of energy, and it reverts to DHA while releasing heat.

$$DHA \xrightarrow{h\nu} VHF \xrightarrow{\Delta} DHA$$

Generally, DHA-VHF systems offer improved fatigue resistance and reduced photochemical degradation. Rearrangements of the electronic structure via substitution make it possible to design molecules with thermal half-lives ranging from minutes to days. The reversion barrier related to the heat releasing reaction is often modeled using transition state theory corrected by frictional dynamics and it is sensitive to both solvent polarity and viscosity [6].

It is crucial to balance energy density, cycling stability, and spectral tuning while minimizing side reactions. Therefore, understanding the underlying rate processes by including how friction, hydrodynamics, and dielectric effects impact back-conversion is essential. This knowledge will provide critical insight into designing next-generation MOST molecules.

The rate of a chemical reaction is given by how reactive compounds cross energy barriers and this is often modeled as escape from a potential well. Classical transition state theory (TST) provides a rate estimate based on equilibrium distributions while ignoring friction and memory effects. However, real systems exhibit non-Markovian dynamics due to solvent interactions. It is important to utilize the GLE in order to obtain a more accurate model by accounting for time-dependent friction and as-sociated colored noise as required by the fluctuation-dissipation theorem (FDT) [10-27].

The next step is to derive the chemical reaction rate constant from the GLE framework incorporating two realistic memory contributions: hydro-dynamic (due to unsteady fluid flow) and dielectric (due to polarization relaxation).

The Generalized Langevin Equation

The GLE for a particle in a potential U(x) under non-Markovian friction is given by [10-27]:

$$m\ddot{x}(t) = -\frac{dU}{dx}(x) - \int_o^t \Gamma(t-t')\dot{x}(t')\,dt' + R(t), \tag{3}$$

where m is the mass of the particle, the function Γ(t) is the memory (or friction) kernel, describing how the medium exerts a history-dependent drag, and R(t) is a stochastic force representing thermal fluctuations.

The noise term satisfies:

$$\langle R(t)\rangle = 0, \tag{4}$$

$$\langle R(t)R(t')\rangle = k_B T\Gamma(|t-t'|), \tag{5}$$

which reflects the fluctuation-dissipation theorem (FDT) [10-18,24] and this ensures thermodynamic consistency by coupling the dissipative and fluctuating forces.

We stress that the application of the GLE is based on the following physical assumptions [10-27]:

- The particle is immersed in a thermal bath. The temperature T of the bath is constant and the noise strength is given by $k_B T$.
- The memory kernel Γ(t) and the noise R(t) depend on time differences.
- Furthermore, the friction kernel is causal and Γ(t) = 0 for t smaller than 0[19].

Hydrodynamic memory relates to inertia and viscous diffusion in the surrounding fluid. The hydrodynamic memory kernel is modeled as:

$$\Gamma_{hydro}(t) = \left[\delta(t) + \frac{1}{\sqrt{\pi t/\tau_H}}\right], \tag{6}$$

where $\gamma = 6\pi\eta a$ is the Stokes friction coefficient for a spherical particle of radius a in a fluid of viscosity η. The hydrodynamic relaxation time is $\tau_H = \frac{a^2}{v}$ where $v = \eta/\rho$ is the kinematic viscosity and ρ the fluid density.

The delta-function term represents instantaneous (Markovian) drag, while the $t^{-1/2}$ tail accounts for the [20,21] long-time tails in the velocity autocorrelation function [22]. Dielectric memory comes from the relaxation of the electric polarization field in a dielectric medium. The dielectric memory kernel is:

$$\Gamma_{diel}(t) = \gamma_D e^{-t/\tau_D} \tag{7}$$

and we have that i) γ_D is the amplitude of the dielectric friction, and ii) τ_D is the dielectric relaxation time. This provides an exponential decay of the polarization response. This behavior is related to Debye relaxation [23] and is crucial when modeling the motion of charged particles and dipoles in polar solvents [10-18,24].

Including both hydrodynamic and dielectric contributions into the GLE gives a physically grounded description of Brownian motion in complex environments. The fluctuation-dissipation relation ensures thermodynamic consistency and the memory kernels reflect the slow relaxation dynamics of the medium.

The total kernel is given by

$$\Gamma(t) = \Gamma_{hydro}(t) + \Gamma_{diel}(t). \tag{8}$$

We use Fourier transforms to solve the GLE analytically and we define

$$\tilde{x}(\omega) = \int_{-\infty}^{\infty} x(t)e^{i\omega t}\,dt. \tag{9}$$

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In the frequency domain we get:

$$-m\omega^2\tilde{x}(\omega) = -i\omega\tilde{\Gamma}(\omega)\tilde{x}(\omega) + \tilde{R}(\omega) \quad (10)$$

and this gives the following solution

$$\tilde{x}(\omega) = \frac{\tilde{R}(\omega)}{-m\omega^2 - -i\omega\tilde{\Gamma}(\omega)} \quad (11)$$

where we have defined the mobility $\mu(\omega)$ as

$$\mu(\omega) = \frac{1}{-m\omega^2 - -i\omega\tilde{\Gamma}(\omega)}. \quad (12)$$

Our next step is to perform Fourier transforms of the kernels and for the hydrodynamic kernel we have that

$$\tilde{\Gamma}_{hydro}(\omega) = \gamma\left[1+(1-i)\sqrt{\frac{\omega H}{2\omega}}\right], \quad (13)$$

Where $\omega_H = 1/\tau_H$. for the dielectric kernel, we find

$$\tilde{\Gamma}_{diel}(\omega) = \frac{\gamma_D}{1+i\omega\tau_D} \quad (14)$$

and the total friction is given

$$\tilde{\Gamma}(\omega) = \tilde{\Gamma}_{hydro}(\omega) + \tilde{\Gamma}_{diel}(\omega). \quad (15)$$

Hereby we have introduced the GLE including both hydrodynamic and dielectric friction and the next step is to utilize the GLE for investigating a chemical reaction in solution.

Chemical rate constants for MOST systems using the generalized Langevin equation

Chemical reaction rates in condensed phase systems are significantly influenced by the couplings between the reactive coordinate and its influenced. Classical transition state theory assumes memoryless (Markovian) dynamics and does not capture the complex temporal correlations introduced by realistic solvents. We introduce non-Markovian theories by including memory kernels that encode frictional retardation effects [10-27]. The GLE is a powerful framework for describing such dynamics since it gives a systematic and physically grounded framework for modeling reaction dynamics in complex environments [10-27].

We begin by formulating the GLE for a one-dimensional reaction coordinate q(t) which represents the progress along the reaction pathway [10-27]:

$$m\ddot{q}(t) = +\int_o^t \gamma(t-t')\,\dot{q}(t')\,dt' + \frac{dU(q)}{dq} = \eta(t), \quad (16)$$

where we have that [10-27].

- m is the mass of the reacting molecular system along the reaction coordinate,
- $\gamma(t)$ is the memory kernel,
- $U(q)$ is the potential energy surface,
- $\eta(t)$ is a stochastic force with correlations given by the fluctuation-dissipation theorem:

$$\langle\eta(t)\eta(t')\rangle = k_B T\gamma\left(\left|t-t'\right|\right). \quad (17)$$

We make several assumptions in order to derive reaction rates using the GLE [10-27]:

- We use a single, suitably chosen reaction coordinate that captures the essential progress of the system along the reaction pathway. We assume that the full dynamics of a high-dimensional molecular or condensed-phase system is projected onto this coordinate. Thereby we have one degree of freedom for describing the slow, collective degree of freedom governing barrier crossing or conformational transitions. All the other degrees of freedom are treated as a thermodynamic environment or thermal bath [10,24].
- The thermal bath for the fast microscopic degrees of freedom (e.g., solvent molecules, intramolecular vibrations, or phonon modes) is modeled as a collection of independent harmonic oscillators that are linearly coupled to the reaction coordinate. By using the harmonic approximation we are able to perform an exact integration of the bath dynamics and this gives a memory kernel and a fluctuation force acting on the reaction coordinate [25].
- The potential energy near the reactant minimum is approximated as a harmonic well. For modeling the transition state, two common approximations are used: an inverted harmonic potential to represent the parabolic barrier top, or a Morse potential to account for finite barrier height and anharmonicity [26,27].
- For time t = 0, the system is assumed to be in thermal equilibrium within the reactant well. Thereby the initial distributions of coordinates and momenta follow the Boltzmann distribution and it is restricted to the stable region of configuration space. This is standard initial conditions used in rate theory to for thermally activated transitions [24].
- The coupling between the system and bath satisfies the fluctuation-dissipation theorem (FDT). Therefore we ensure that the random (fluctuating) forces and the dissipative (memory) kernel are consistent with each other and with the bath temperature T. In the absence of external driving forces, the FDT guarantees that the system will relax toward thermal equilibrium and maintain detailed balance. This is a requirement for thermodynamic consistency and is satisfied when the bath consists of harmonic oscillators, that for t = 0 are in thermal equilibrium [10-27].

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We consider two types of potential energy surfaces:

i. the harmonic potential near the reactant well,

$$U(q)=\frac{1}{2}m\omega_0^2q^2, \qquad (18)$$

ii. and the Morse potential to model anharmonicity near the transition state:

$$U(q)=D_e\left(1-e^{-a(q-q_0)}\right)^2, \qquad (19)$$

where D_e is the dissociation energy, a the range parameter, and q_0 the minimum.

The derivation of the reaction rate constant within transition state theory (TST) is without dissipation and the TST rate k_{TST} is given by [10-27]:

$$k_{TST}=\frac{\omega_0}{2\pi}e^{-\beta\Delta U}, \qquad (20)$$

where ΔU is the barrier height and ω_0 is the frequency in the reactant well. The inclusion of dissipation gives a transmission coefficient k and a modification of the TST rate k_{TST}

$$k=\kappa\cdot k_{TST}. \qquad (21)$$

Grote and Hynes extended Kramers' theory to include memory effects. Kramers' theory describes the rate of barrier crossing under thermal fluctuations and friction. However, it assumes Markovian dynamics with instantaneous friction. Grote and Hynes extended this theory by incorporating memory effects using the GLE [10-27]. Utilizing the harmonic approximation near the barrier we have that near the barrier top $(x=0)$, the potential is approximated as:

$$V(x)\approx-\frac{1}{2}m\omega_b^2x^2, \qquad (22)$$

where ω_b is the (imaginary) frequency of the unstable mode/reaction co-ordinate. Therefore, we have the following GLE for a chemical reaction

$$m\ddot{x}(t)=m\omega_b^2x(t)-\int_o^t\Gamma(t-t')\dot{x}(t')\,dt'+R(t). \qquad (23)$$

Taking the Laplace transform of the GLE gives the following

$$ms^2\tilde{x}(s)-msx(0)-m\dot{x}(0)=m\omega_b^2\tilde{x}(s)-s\tilde{\Gamma}(s)\tilde{x}(s)+\tilde{R}(s) \qquad (24)$$

and this can be rearranged to

$$\tilde{x}(s)=\frac{msx(0)+m\dot{x}(0)+\tilde{R}(s)}{m\left(s^2-\omega_b^2\right)+s\tilde{\Gamma}(s)}. \qquad (25)$$

We note that the poles of $\tilde{x}(s)$ determine the long-time dynamics and are found from the denominator:

$$D(s)=m\left(s^2-\omega_b^2\right)+s\tilde{\Gamma}(s). \qquad (26)$$

We let $s=\lambda$ be the pole with Re $(\lambda)>0$ dominating the barrier escape.

The transmission coefficient κ_{GH} modifies the Transition State Theory (TST) rate:

$$k_{GH}=\kappa_{GH}k_{TST}=\left(\frac{\lambda}{\omega_b}\right)\left(\frac{\omega_0}{2\pi}\right)e^{-\beta\Delta V}, \qquad (27)$$

where:

- ω_0 is the frequency at the bottom of the reactant well.
- λ satisfies:

$$m\lambda^2+\lambda\tilde{\Gamma}(\lambda)=m\omega_b^2. \qquad (28)$$

This equation must be solved numerically or analytically for specific expressions of $\Gamma(t)$.

For an exponential memory kernel, we have that $\Gamma(t)=\gamma\tau^{-1}e^{-t/\tau}$, we find the Laplace transform to be given as

$$\tilde{\Gamma}(s)=\frac{\gamma}{1+s\tau}. \qquad (29)$$

Thereby we obtain the following equation:

$$m\lambda^2+\lambda\frac{\gamma}{1+\lambda\tau}=m\omega_b^2 \qquad (30)$$

and this can be solved numerically for λ.

Grote and Hynes extended Kramers' theory to include non-Markovian memory effects by analyzing the GLE near the barrier top [13]. They found that the resulting rate includes a transmission coefficient $k_{GH}=\lambda/\omega_b$, where λ incorporates the effects of frictional memory via the Laplace trans-form of the kernel [13].

The effective barrier frequency ω_b satisfies:

$$\omega_b^2+\omega_b\tilde{\gamma}(\omega_b)=\omega_\ddagger^2, \qquad (31)$$

where $\omega_\ddagger$ is the curvature of the inverted potential at the barrier top, and $\tilde{\gamma}(\omega)$ is the Laplace transform of the friction kernel.

The transmission coefficient becomes:

$$\kappa=\frac{\omega_b}{\omega_\ddagger}. \qquad (32)$$

Hydrodynamic and Dielectric Memory Kernels

The total memory kernel is modeled as a sum of the hydrodynamic and dielectric memory kernels:

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$$\gamma\left(t\right)=\gamma_H\left(t\right)+\gamma_D\left(t\right), \qquad (33)$$

with:

$$\gamma_H\left(t\right)=\frac{\varsigma}{\sqrt{\pi t}}, \qquad (34)$$

$$\gamma_D\left(t\right)=\gamma_0 e^{-t/\tau_D}, \qquad (35)$$

where ς is a hydrodynamic coefficient and τ_D the dielectric relaxation time.

We note that the Laplace transform $\tilde{\gamma}(s)$ of the total kernel is given by:

$$\tilde{\gamma}\left(s\right)=\frac{\varsigma}{\sqrt{s}}+\frac{\gamma_0}{1+s\tau_D}. \qquad (36)$$

Solving for ω_b

We numerically solve the self-consistent equation:

$$\omega_b^2+\omega_b\tilde{\gamma}\left(\omega_b\right)=\omega_\ddagger^2. \qquad (37)$$

This can be solved iteratively or graphically for specific parameters.

Numerical Example

We take the following parameters:

- ω_0 = 1 THz
- $\omega_\ddagger$ = 0.5 THz
- ς = 0.1 kg/s1/2
- γ_0 = 0.2 kg/s
- τ_D = 0.1 ps
- T =300K

Solving the Grote-Hynes equation numerically yields $\omega_b\approx 0.42$ THz.

Then:

$$\kappa=\frac{0.42}{0.5}=0.84, \qquad (38)$$

and the rate constant is:

$$k=0.84\cdot\frac{1}{2\pi}\cdot 1\cdot e^{-\beta\Delta U}. \qquad (39)$$

For another case, we simulate the system using the following parameters:

- $m=1,\ \omega_b=1$
- $\gamma=1,\ \gamma_D=0.5,\ \tau_D=1$

and solving the Grote-Hynes equation numerically we find for this case:

$$\omega_{GH}\approx 0.63\Rightarrow\kappa_{GH}=\frac{1}{0.63}\approx 1.59. \qquad (40)$$

We have derived the chemical rate constant in a system with non-Markovian dynamics using the GLE framework and incorporating both hydrodynamic and dielectric memory effects into the friction kernel. Thereby, we obtained corrections to TST via the Grote-Hynes theory. These corrections are crucial in molecular systems embedded in polar solvents or viscous media, especially for photoisomerization reactions in MOST applications.

We expect that future work may explore multidimensional GLE systems, non-linear friction kernels, or stochastic embedding methods to simulate dynamics directly [10-27].

Numerical Solver for GH Equation

Using a numerical root-finding algorithm (e.g., Newton-Raphson or bisec-tion), we solve:

$$\omega^2+\frac{1}{m}\omega\tilde{\Gamma}\left(\omega\right)-\omega_b^2=0 \qquad (41)$$

with:

$$\tilde{\Gamma}\left(\omega\right)=\gamma\left(1+\frac{\left(1=i\right)}{\sqrt{2}}\sqrt{\frac{\omega_H}{\omega}}\right)+\frac{\gamma_D}{1+i\omega\tau_D}. \qquad (42)$$

Simulating GLE Trajectories

To simulate trajectories, we discretize the GLE:

$$m\ddot{x}_n=V'\left(x_n\right)-\sum_{j=0}^{n}\Gamma\left(t_n-t_j\right)\dot{x}_j\Delta t+R_n, \qquad (43)$$

using synthetic random force samples Rn with appropriate correlation. The numerical integration can be done with a predictor-corrector scheme or fractional Langevin integrators.

Conclusion and Outlook

For efficient solar energy storage, molecular systems capable of photoin-duced energy capture and long-term thermal stability have gained significant attention including systems such as norbornadiene–quadricyclane, azobenzenes, and dihydroazulenes. For these systems the conversion of photon energy into chemical energy followed by controlled release depends on the dynamics of conformational and electronic transitions in molecular systems in condensed phases.

We have presented a rigorous theoretical framework needed for describing the dynamics of energy storage and release in MOST systems including solvent interactions, slow environmental relaxation, and memory effects. The GLE provides a natural and powerful tool for capturing these features by incorporating both deterministic and stochastic components of friction and noise that are non-Markovian in nature.

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The influence of the solvent spans a wide range of timescales, from ultrafast inertial and librational motions to slow collective reorganizations, rotational diffusion, and long-range hydrodynamic interactions. Markovian approaches based on the Langevin equation model solvent friction as instantaneous with white-noise stochastic forces and deltafunction damping. Thereby, these methods neglect the complex temporal correlations often exhibited by real environments.

On the other hand the GLE method extends this framework by including a memory kernel $\Gamma(t)$, that takes care of time-delayed frictional effects. The GLE method is particularly well suited for modeling dynamical processes in polar solvents, structured fluids, and complex media where one encounters significant memory effects due to phenomena such as dielectric relaxation, hydrogen bonding, and hydrodynamic coupling.

The method presented will be used for investigations of MOST systems where energy is stored in metastable photoisomers formed by light-induced transitions along with energy release over activation barriers. It is clear that both the rate of thermal back-conversion and the stability of the high-energy form are strongly modulated by solvent dynamics. Furthermore, at the transition state frictional forces due to solvent response significantly affect the effective barrier crossing rate.

For molecular solar thermal systems and other energy storage technologies GLE models provide information that can be used for predicting how solvation dynamics affect energy storage lifetimes and efficiency. In our future work we will combine GLE-based theory with atomistic simulation and enhance our ability to engineer high-performance molecular switches.

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Conflict of Interest

None.

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