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Non-Markovian transfer tensor method used in a chemical reaction in liquids

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Abstract. In this paper, the non-Markovian transfer tensor method (TTM) suggested by Cao's group was utilized in a real chemical reaction in liquids from a classical point of view. From the results of this numerical simulation, dramatic enhancement in speed of calculations and decrease in computational cost are shown by applying TTM method. It is wise to be used in complex systems with lots of degrees, such as the process of protein folding or in treating propagations with mountains of data. For some specific quantities we are interested in, how to find a map from complex systems to simple ones and from huge freedoms to a few ones, such as just to one freedom in this paper, it remains something for us to do in the future.

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Key words: non-Markovian effects, recombination, liquid, numerical simulation.

1 Introduction

The non-Markovian transfer tensor method (TTM) was initially proposed by Cao's group [1], and its basic idea relays on the thoughts that the initial stages of the evolution of one system encode the complete information of its underlying dynamical correlations. So one can extract these information from a short-time dynamics and compress it into non-Markovinan transfer tensors, which can be used to predict the long-time dynamics at later stages. A two-level open quantum system was studied in this method by Cao *et al.* in this paper, and it also shows that the relevant dynamical operators of the system such as the Hamiltonian and memory kernel could be reconstructed by using the transfer tensor method. Later, Mehraeen *et al.* [2] extended this method to a classical frame in studying of the barrier crossing kinetics with a double-well model. Dramatic enhancement in speed of calculations and decrease in computational cost are shown using TTM comparison with other methods [1,2].

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In probability theory and statistics, a Markov process is a stochastic process that the future state can be predicted solely based on its present state and it has nothing to do with its past states. In other words, Markov process can be thought of as memoryless. While in true life, most of the systems have to interact with environment, and as the fluctuation of the environment, it is hard to describe the evolutions of these system with this simple Markov model, thus the memory effect has to be taken into account. For example, early in 1973, Baus used a microscopic theory of the linearized plasma hydrodynamical equation to reveal the important non-Markovian effects on the plasma transport coefficients [3]; Recently, using non-equilibrium Green's function approach, Ribeiro and Vieira studied the non-markovian effects in electronic and spin transport [4]; Berrada examined the non-Markovian effect on the dynamics of the quantum Fisher information for a qubit system [5], etc..

Here, we continue to utilize the non-Markovian TTM to study a real reaction system in liquids, that is the two iodines recombine in liquid CCl_4. The recombination process has been studied for several decades since 1970s from both experimental and theoretical sides. The development of picosecond spectroscopy allowed the monitoring of the early dynamics of the recombination process and its dependence on a variety of solvents [6–9]. Langevin dynamics [10–12], generalized Langevin dynamics [13, 14] and molecular dynamics [15,16] were all used to describe solvent influence on chemical reactions at that time.

The paper is organized as follows: in Section 2, basic theory about TTM and details about its application in a classical frame are presented. Some information such as models and parameters used in the calculation about this recombination reaction will also be given in this section. Results and Discussions follow in Section 3. Finally, a brief summary of the present work is given in Section 4.

2 Theory

The realization of non-Markovian TTM can be simplified by assuming time-translational invariance and finite time correlation in the transfer tensors. Under certain assumptions, such as a time-independent Hamiltonian and finite time span of correlations in realistic systems, the transfer tensor is a function of time difference only and a limited number of transfer tensors is necessary [1]. The standard procedure of TTM is as a three-steps scheme:

1. Extract the dynamical maps $\{\varepsilon_k\}$ for a serial of short-time trajectories numerically or experimentally at the discretized times $t_k = k\Delta t$, where Δt is the time step of the simulation or the time resolution of the experiment,

$$\rho(t_k) = \varepsilon_k \rho(0), \tag{1}$$

$\rho(0)$ and $\rho(t_k)$ are density matrices of the system for $t = 0$ and $t = t_k$, respectively. Note that each dynamical map in a non-Markovian process needs to be generated independently, as the non-Markovianity violates the semigroup property, i.e., $\varepsilon_k \neq \varepsilon_1^k$, it contains correlations at the present time with all the previous time steps.

2. Derive the non-Markovian transfer tensors from these dynamical maps at each discretized time t_k according the following transformation

$$T_k = \varepsilon_k - \sum_{n=1}^{k-1} T_k \varepsilon_n, \tag{2}$$

and we define $T_1 \equiv \varepsilon_1$. Indeed T_k represents the time correlation between any pair of time steps with an interval of t_k under the assumption of time-translational invariance and it includes all correlations for time intervals $t \leq t_k$.

3. Evovle the density matrix to arbitrarily long time for times $t_m > t_K$ in a tensor multiplication fashion,

$$\rho(t_m) = \sum_{n=1}^{K} T_n \rho(t_{m-n}), \tag{3}$$

where K is a cutoff such that $T_m \to 0$, for $m > K$.

Now, it comes to the question how to define the structure of the density matrix $\rho(t)$. In the frame of classical mechanics, we discretize the phase space into several fine grids first. Taking a one-dimension problem for an example, assuming the grids are as follows, in the direction of position from x_1 to x_n, while in the direction of momentum from p_1 to p_m. There are $m \times n$ phase points $\{x_j p_k\}$ in the total space interested, then the density matrix used here is a matrix with dimension $(m \times n)^2$, as shown in Table 1. Each column of the density matrix $\rho(t)$ represents the densities of all phase points for a certain initial condition $(x_j p_k)$ at time t. Hence, the density matrix for $t=0$ is an identity matrix and it is straightforward to get the dynamical map at each time discretization, $\varepsilon_k = \rho(t_k)$. After the extraction of necessary transfer tensors, long time propagations could be issued visa a tensor multiplication method. This method can readily be applied to the process of protein folding, charge transport and chemical dynamics.

Table 1: Structure of density matrix for the initial stage, where $\mathbb{O}$ and $\mathbb{I}$ are zero and unit matrices.

$\rho(0)$	x_1p_1	$\cdots$	x_1p_m	$\cdots$	x_np_1	$\cdots$	x_np_m
x_1p_1	1	$\mathbb{O}$	0	$\mathbb{O}$	0	$\mathbb{O}$	0
$\vdots$	$\mathbb{O}$	$\mathbb{I}$	$\mathbb{O}$	$\mathbb{O}$	$\mathbb{O}$	$\mathbb{O}$	$\mathbb{O}$
x_1p_m	0	$\mathbb{O}$	1	$\mathbb{O}$	0	$\mathbb{O}$	0
$\vdots$	$\mathbb{O}$	$\mathbb{O}$	$\mathbb{O}$	$\mathbb{I}$	$\mathbb{O}$	$\mathbb{O}$	$\mathbb{O}$
x_np_1	0	$\mathbb{O}$	0	$\mathbb{O}$	1	$\mathbb{O}$	0
$\vdots$	$\mathbb{O}$	$\mathbb{O}$	$\mathbb{O}$	$\mathbb{O}$	$\mathbb{O}$	$\mathbb{I}$	$\mathbb{O}$
x_np_m	0	$\mathbb{O}$	0	$\mathbb{O}$	0	$\mathbb{O}$	1

Here we generalize the TTM in a real chemical reaction in liquids, that is I + I recombination in liquid CCl_4. Following the suggestion of Adelman *et al.* [17], the equations of motions for the two iodines deviating from their original positions could be describe by two generalized langevian equations (GLEs),

$$\ddot{x}_0(t) = -\frac{1}{m}\frac{\partial W(R)}{\partial x_0} - \omega_{e0}^2 x_0(t) + \omega_{c1}^4 \int_0^t \theta_1(t-\tau)x_0(\tau)d\tau + \omega_{c1}^2 F_x(t), \tag{4}$$

$$\ddot{y}_0(t) = -\frac{1}{m}\frac{\partial W(R)}{\partial y_0} - \omega_{e0}^2 y_0(t) + \omega_{c1}^4 \int_0^t \theta_1(t-\tau)y_0(\tau)d\tau + \omega_{c1}^2 F_y(t), \tag{5}$$

where $W(R)$ is the effective potential energy between the two atoms including the effects of liquids around them and R is their separation at time t. F_x and F_y are two independent random forces, which could be represents as two standard normal distributions with zero mean value and one variance value. Definitions of other parameters can be found in Ref. [17] and references in it. For this kind of problem, it involves two atoms with freedom of six. Here we only want to generalize the TTM, one restriction is added on the two atoms so that they can only move along the line between themselves, which reduces the degree of this problem to two. If only the relative motion between them is interested in, such as the process of recombination or dissociation, the problem could be further simplified as,

$$\ddot{r}_0(t) = -\frac{2}{m}\frac{\partial W(R)}{\partial r_0} - \omega_{e0}^2 r_0(t) + \omega_{c1}^4 \int_0^t \theta_1(t-\tau)r_0(\tau)d\tau + \omega_{c1}^2 F(t), \tag{6}$$

by subtracting Eq. (4) from Eq. (5). Note that the subtraction of two standard normal distribution is still a standard normal distribution, which is denoted by $F(t)$ here. And the relationship between R and r_0 satisfies $R = r_0 + r$, where r is the separation at initial time. As the form of solvent response function $\theta(t)$ is not determined, two atomic version of the harmonic chains heatbath model [17] is used in the numerical simulation,

$$\ddot{r}_0(t) = -\frac{2}{m}\frac{\partial W(R)}{\partial r_0} - \omega_{e0}^2(R) r_0(t) + \omega_{c1}^2(R) r_1(t), \tag{7}$$

$$\ddot{r}_1(t) = -\Omega_1^2 r_1(t) + \omega_{c1}^2(R) r_0(t) + \beta_2^2(R)\dot{r}_1(t) + f_2(R,t), \tag{8}$$

where the frictional and random forces are connected by the fluctuation-dissipation theorem:

$$\langle f_2(R,t) \cdot f_2(R,0) \rangle = \frac{2k_B T}{m} \beta_2(R) \delta(t). \tag{9}$$

Parameters used in Eq. (7), Eq. (8) and Eq. (9) are from literature [10, 13] for solvent number density being $6.303 \times 10^{-3}/\text{Å}^3$ and the average temperature $T = 305 \pm 4$K, however only components parallel to the molecular axis and their diagonal elements are used here.

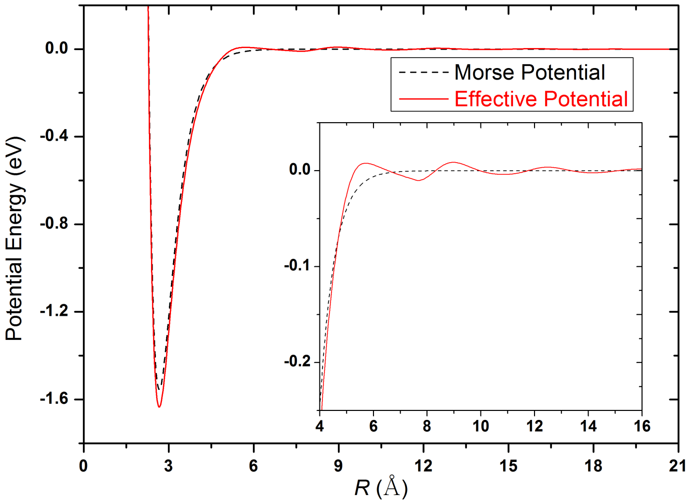

Figure 1: Plot of potential energy in eV vs R in Å. The Morse interaction potential is compared with the effective potential for I_2 in CCl_4. The insert shows part of enlarged details.

At the last part of this section, the potential energy curve used to describe iodines recombination in CCl_4 has to be mentioned. The effective potential energy $W(R)$ has two additive contributions: gas phase Morse diatomic potential [10] and cavity potential [18,19] which accounts for the influence of the solvent structure in the neighborhood of I atom. The effective potential $W(R)$ is displayed in Fig. 1. The most obvious influence of solvent structure is the barrier and well combinations introduced at the base of the Morse curve, which would effect the dynamical processes dramatically. Finally, the total phase space is coarse grained based on the feature of the potential energy curve into five states as in Fig. 2. They are state 1 for $R<5$Å, state 2 for R between 5 Å and 6 Å, state 3 for 6Å$<R<$9Å, state 4 for R between 9 Å and 12 Å and state 5 for $R>$12Å, respectively. And two absorption conditions are set at $R=3.5$Å and $R=12$Å, which means recombinations occur for $R<3.5$Å and dissociations occur for $R>12$Å. In this way, only a serial of 5-by-5 matrices are used to derived these transfer tensors according to the iterative relation in Eq. (1) and Eq. (2), and only trajectories initially from 3 states need to be sampled, it would save lots of computational memory space. However more attention needs to be paid on appropriately sampling momenta over the entire phase space.

3 Results

The initial conditions for numerically solving Eq. (7) and (8) are as follows: for each coarse grained state, $r_0=0, r_1=0$ and $\dot{r}_1=0$, while r and $\dot{r}_0$ are uniformly distributed. Remind you that r represents the distance between the two iodines at initial stage and $\dot{r}_0$ is their relative velocity at $t=0$. For each state, 10^5 trajectories are launched and a time step of 0.1 femtosecond is used for all internuclear distances. For those trajectories initially

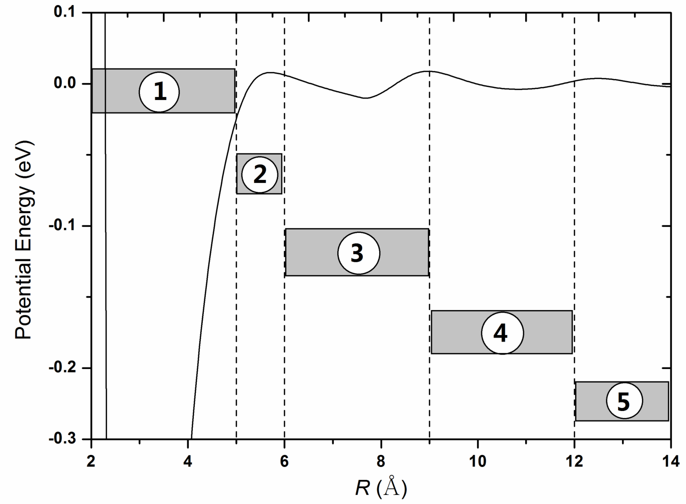

Figure 2: Five coarse grained states used in the simulation. They are divided by relative separation of the two iodines, state 1 for $R<5$Å, state 2 for 5Å$<R<$6Å, state 3 for 6Å$<R<$9Å, state 4 for 9Å$<R<$12Å and state 5 for $R>12$Å.

starting from state 3, about 10^6 time steps are needed to get converged results, while for others 5×10^5 time steps are enough. The recombination (dissociation) probabilities for trajectories initially starting from state 2 and state 3 are showed in Fig. 3. τ could be thought as the longest correlation time and $\tau = t_K = K\Delta t$, K is the cutoff for transfer tensors. So the correlations for time span with past stages beyond τ are neglected and accordingly we could find the correlation time, that is 3 picoseconds for state 2 and 10 picoseconds for state 3. It is also found that as long as the correlation time is determined, the time step Δt used to generate transfer tensors is not that important. A time step of $\Delta t = 0.02$ picosecond for both sates is used in the calculation.

First of all, the accuracy of TTM can easily be seen from the comparisons with results of numerically solving GLE. Both results fit very well along the entire time scale providing sufficient correlation time. Note that we don't intend to study the properties of this reaction system at present, only the utilization of TTM in a real reaction system is investigated. Also because of the simplification of this model, we do not expect a good fit with the experimental or theoretical results, which will not be shown here.

The efficiency of TTM depends on the number of states discretized and the longest simulation time used in one state. It is also found that if only specified initial conditions are interested in, i.e., the two iodines are separated between 6 Å and 9 Å initially (state 3), how to coarse grained other states do not effect final results much. From Fig. 2, it can be seen that there is a relatively deeper well in state 3, so longer simulation time is needed. According to the records, the wall-clock time used to finish numerically solving GLE is listed in Table. 2. As this model is relative simple, for large and complex systems, the

Table 2: Time used in numerically solving GLE for different initial states.

initial states	total wall-clock time used	ratio of time used for TTM
state 2	0 h 18 m	0.15
state 3	10 h 4 m	0.10
state 4	1 h 35 m	0.12

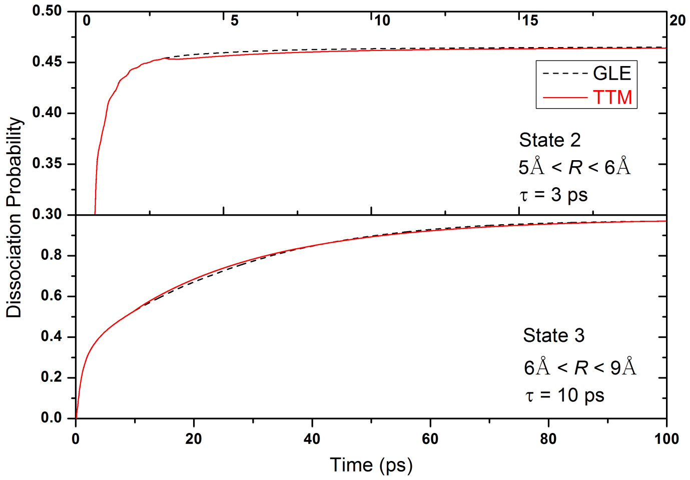

Figure 3: Dissociation probabilities for trajectories initially launching from different states. The top panel is for those from state 2, while the bottom panel is for those from state 3. The results from numerically solving GLE are plotted in black dashed line and the results from TTM are in red solid line. τ could be thought as correlation time.

cost would be dramatically increased. But the enhancement in speed of simulations can still be noticed. In TTM only one tenth of the simulation time is needed for trajectories initially projecting from state 3, considering that extra trajectories need to be launched from state 2 and state 4, the total time is less than one fifth. In other words, in this model it reduces at least four fifths simulation time using TTM instead of numerically solving GLE.

4 Conclusion

In this study, a non-Markovian transfer tensor method was used to simulate the process of recombination and dissociation for iodines in liquids. Comparing with the numerical evolution of pure generalized Langevin dynamics, using of the TTM can save computational resource and speed up the calculation several times by smart choosing the the physical quantities to be studied. It is wise to generalize this method to complex systems and to those with time consuming propagations, which are hard to do a complete time evolution at present.

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