J. At. Mol. Sci.
doi: 10.4208/jams.050416.081916a

Vol. **7**, No. 4, pp. 155-162
November 2016

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

Huan Yang*

*School of Physics, Shandong University, Jinan 250100, China*

Received 4 May 2016; Accepted (in revised version) 19 August 2016
Published Online 10 November 2016

**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.

**PACS**: 02.50.Cw, 34.10.+x

**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].

*Corresponding author. *Email address:* h.yang@sdu.edu.cn (H. Yang)

 

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 $\Delta t$ 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