

Polar solvation dynamics: A combination of the reference interaction-site model and mode-coupling theories*

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Abstract: We employ the reference interaction-site model (RISM) theory for solvation dynamics of simple ions in acetonitrile. For the description of time evolution of solvent relaxation, we apply the mode-coupling theory recently developed by Yamaguchi and coworkers [*Mol. Phys.* **101**, 1211 (2003)]. The combination of the RISM/mode-coupling theory is used for the calculation of the dynamic response function, $S_S(t)$, which measures the relaxation of average energy of the solute–solvent system. $S_S(t)$ decays with the Gaussian plus underdamped curves in the time duration of first 1 ps, followed by slow, long-tailed components down to tens of picoseconds. We show that the RISM/mode-coupling framework is applicable rather well for the detailed description of solvation dynamics at the molecular level.

INTRODUCTION

The time-dependent response of solvent molecules owing to instantaneous changes of the electronic structure of solute has been a target of intensive research, because of their tight connection with chemical reaction dynamics in solution. This type of solvent response, usually referred to as solvation dynamics, has been understood in relation to the solvent fluctuation. The time duration of solvent fluctuation that is responsible for solvation dynamics varies from tens of femtoseconds to some hundreds of picoseconds at room temperature. Time-resolved methodologies, covering the time domain mentioned above, have thus been utilized to reveal molecularity of the solvent fluctuation. In particular, femtosecond–picosecond laser spectroscopy [1–10], molecular dynamics simulations [11–15], and various series of theories [16–27] have been regarded as useful devices to make us accessible to such ultrafast phenomena. In this sense, we have performed transient hole-burning (THB) and time-resolved fluorescence (TRF) spectroscopy of dye molecules in various polar solvents [7,8,10]. On the basis of the spectra observed, we can define the dynamic response function of the average-energy relaxation of the solute–solvent system:

$$S_e(t) = \frac{\tilde{v}(t) - \tilde{v}(\infty)}{\tilde{v}(0) - \tilde{v}(\infty)} \quad (1)$$

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where $\tilde{v}(t)$ denotes the first moment of the spectral function at time t when the solute is excited at $t = 0$. In a conventional analysis, the maximum of the THB or TRF spectra is chosen as $\tilde{v}(t)$.

By virtue of studies particularly targeting at the ultrafast time domain reported elsewhere [1,2,6,11], we may accept a general scenario concerned with relaxation processes as follows: Within 100 fs after the excitation, some solvent molecules in the vicinity of solute fluctuate with small angles, which we call the librational motion. This fast relaxation process is responsible for the essential component (>70 %) for $S_e(t)$. The other part followed by the fast process explained above has slow components up to picoseconds, which is commonly ascribed to diffusive motions. Our interests are how chemical and physical properties of solute and solvent characterize the entire relaxation picture.

For this purpose, some of the present authors have developed the theoretical approach by means of the reference interaction-site model (RISM) theory as published elsewhere [19,23,27]. Relying on the RISM theory, one can especially obtain molecular view regarding the static description of solute and solvent. In our previous handling, we have coupled the RISM theory with the site–site Smoluchowski–Vlasov (SSSV) equation proposed by Hirata [28], for the sake of description of time evolution of solvent relaxation. In the scheme of the RISM/SSSV theory, we solve a Smoluchowski-type equation for atoms with a Vlasov-type mean-field term, incorporated with the RISM representation. Hirata and coworkers [19] have applied the RISM/SSSV framework to the solvation dynamics of simple ions in polar solvents, and have found that the theory is applicable to capture essential view of solvation processes. Nishiyama and coworkers [22,23,27] have extended this treatment toward more realistic solute–solvent systems employed in actual laser experiments. Even though the RISM/SSSV handling works suitably for solvation dynamics, however, we indeed need a more authentic procedure covering the non-Markovian region of solvent motions, which has not been accessible very well by the previous works. Such an update of the theory can help us discuss more practical snapshots concerning the solvation profile.

In the present contribution, we use a mode-coupling theory for the purpose of more realistic description of time evolution of solvent relaxation. Chong and Hirata [29,30] have developed the mode-coupling theory incorporated with the RISM theory, and they have proven that the combination of the two theories can be applicable well for the description of dynamics of molecular liquids. Followed by their reports [29,30], two of the present authors, Yamaguchi and coworkers have recently applied the mode-coupling theory to more realistic mechanisms of chemical phenomena; the shear molecular viscosity coefficient [31], reorientation of molecular liquids [32], or the dielectric relaxation spectrum [33]. Hereafter, we call the last publication [33] “Paper I”. In particular, in Paper I they have presented that the combination of the site–site generalized Langevin equation and mode-coupling theory is applicable fairly well. In this report, we employ the mode-coupling theory for the solvent dynamics under the framework presented by Paper I, whereas for the static part we keep relying on the RISM theory used in our previous works [19,22,23,27].

RISM/MODE-COUPLING THEORY

We just outline the theoretical formulation for solvation dynamics employed in the present work. For the details regarding the general description of solvation dynamics by the RISM theory, the reader is referred to our previous publication [19,27] and the references therein.

As a common practice for theories and simulations, the corresponding quantity of eq. 1, which is measured by experiments can be defined as:

$$S_S(t) = \frac{\overline{\delta\epsilon(t)} - \overline{\delta\epsilon(\infty)}}{\overline{\delta\epsilon(0)} - \overline{\delta\epsilon(\infty)}} \quad (2)$$

where $\delta\epsilon(t)$ stands for the solvation-energy change at time $t = t$, and the overbars denote an average concerning solutes under the experimental observation. The physical meaning of $S_S(t)$ is identical to $S_e(t)$

in eq. 1, which indicates the time-dependent relaxation of average energy of the solute–solvent system. We replace the subscript only for the sake of clarifying the method used to obtain these functions. Within the linear response approximation, we reduce eq. 2 to:

$$S_S(t) = \frac{\langle \delta\varepsilon(t)\delta\varepsilon(0) \rangle}{\langle \delta\varepsilon(0)\delta\varepsilon(0) \rangle} \quad (3)$$

where $\langle \bullet \rangle$ expresses an ensemble average over the solvent configuration around solute in the electronic ground state. By means of the surrogate approximation, a site–site description of eq. 3 is given as [18]:

$$S_S(t) = \frac{\int_0^\infty dk k^2 \sum_{jj'} \mathbf{F}_{jj'}(k,t) \mathbf{B}_{jj'}(k)}{\int_0^\infty dk k^2 \sum_{jj'} \mathbf{F}_{jj'}(k,t=0) \mathbf{B}_{jj'}(k)} \quad (4)$$

where k is the wave vector. $\mathbf{F}(k,t)$ means the intermediate scattering function of neat solvent, from which the entire dynamic response of solvent can be characterized. The crucial point of the present paper is that we employ the generalized Langevin equation/mode-coupling theory to obtain $\mathbf{F}(k,t)$ as reported in Paper I. Here, let us step onto the explanation of $\mathbf{B}_{jj'}(k)$ concerned with the solute–solvent coupling:

$$\mathbf{B}_{jj'}(k) = \sum_{\lambda\lambda'} \Delta\phi_{\lambda j}(k) \boldsymbol{\omega}_{\lambda\lambda'}(k) \Delta\phi_{\lambda j'}(k) \quad (5)$$

where $\boldsymbol{\omega}_{\lambda\lambda'}$ represents the intramolecular correlation function with the solute-sites λ and λ' . $\Delta\phi(k) = \phi_{\lambda j}^E(k) - \phi_{\lambda j}^G(k) - \phi_{\lambda j}^D(k)$ where $\phi_{\lambda j}^D(k)$ ($D = G$ or E) means the solute–solvent coupling. Regarding the photo-excited states of solute, the labels G and E specify the ground and excited states, respectively. The subscript j denotes the solvent site. For the sake of simplicity, we can replace the vertical energy gap of the ground and excited states of solute with the solute–solvent direct correlation function, $\mathbf{c}_{\lambda j}(k)$, which leads to [18,19]:

$$\phi_{\lambda j}(k) = -k_B T \mathbf{c}_{\lambda j}(k) \quad (6)$$

with k_B and T the Boltzmann constant and temperature, respectively. We employ the extended RISM theory to define $\mathbf{c}_{\lambda j}(k)$ [34]:

$$\mathbf{h}_{\lambda j} = \sum_{\lambda'j'} \left(\omega_{\lambda\lambda'} * \mathbf{c}_{\lambda'j'} * \omega_{j'j} + \rho \omega_{\lambda\lambda'} * \mathbf{c}_{\lambda'j'} * \mathbf{h}_{j'j} \right) \quad (7)$$

where $\mathbf{h}_{\lambda j}$ and $\mathbf{h}_{jj'}$ are the pair correlation functions labeled by the solute and solvent sites λ and j , respectively. In eq. 7, we use asterisks to express the convolution integrals. ρ stands for the bulk density of solvent. As a closure relation for eq. 7, we employ the hypernetted-chain (HNC) approximation.

RESULTS AND DISCUSSION

We first describe our system investigated in this study. We employ acetonitrile as a representative of polar aprotic solvent, employing a model description proposed by Edwards and coworkers [35]. We use two types of solutes: one is a chloride ion “Cl⁻”, keeping neutral in electronic charge before $t < 0$ and put $-1.0 e$ at $t = 0$. Another is a model solute “S⁺” using for the sake of comparison with the results by molecular dynamics simulation reported by Maroncelli [11], where we change the charge as $S \rightarrow S^{+1.0}$ at $t = 0$. As the intermolecular site–site interaction, we choose an additive pairwise potential function of the Lennard–Jones plus Coulomb term, $u_{\alpha\beta}$:

$$u_{\alpha\beta} = 4\varepsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 \right] + \frac{q_\alpha q_\beta}{r} \quad (8)$$

where α and β represent the interaction-site of either solute or solvent. q_γ ($\gamma = \alpha$ or β) stands for the charge put on the corresponding site. ε and σ have usual meaning. $T = 298$ K is chosen throughout the calculation. Precisely, we use the Lorentz–Berthelot combination rule for interaction between the different species. On the other hand, the parameters for interactions between the same species are chosen as listed in Table 1.

Table 1 Solute and solvent models used for the RISM theory.

		$(\varepsilon_{\alpha\beta} / k_B)/K$	$\sigma_{\alpha\beta}/\text{\AA}$	Charge/ e
Solutes	Cl \rightarrow Cl $^-$	60	4.41	0 \rightarrow -1.0
	“S” \rightarrow “S $^+$ ”	38	3.1	0 \rightarrow +1.0
Solvent (acetonitrile)	Me	191	3.6	0.269
	C	50	3.4	0.129
	N	50	3.3	-0.398

Figure 1 depicts $S_S(t)$ obtained by the mode-coupling theory in the present work, associated with Cl \rightarrow Cl $^-$ in acetonitrile. With the mode-coupling theory, $S_S(t)$ starts to decay with the Gaussian-like curve, which is responsible for >80 % of the relaxation achieved in 150 fs. Followed by the fast relaxation, the underdamping component emerges with the period around 300 fs, decreasing the amplitude with time evolution. Within 1 ps, 90 % of the decay is achieved, but this is not the very end of the relaxation process. We also find the slower curve with the lifetime in a couple of picoseconds. Such a time profile of $S_S(t)$, in particular in the earlier stage up to 1 ps, agrees with a conventional view of solvation

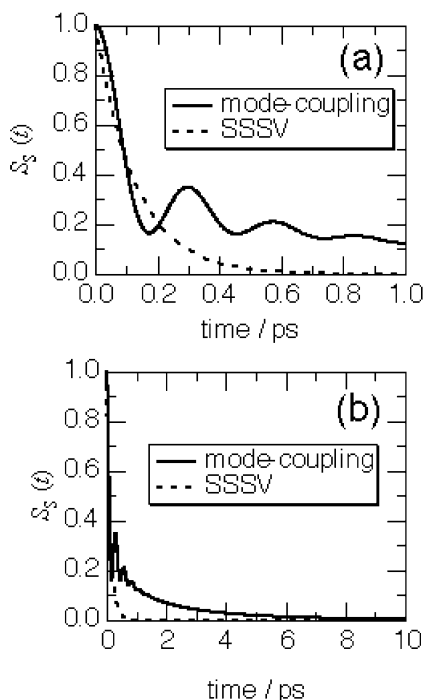


Fig. 1 The relaxation processes of $S_S(t)$ for Cl \rightarrow Cl $^-$ in acetonitrile. The solid and dashed lines indicate the mode-coupling theory (this work) and SSSV equation [23], respectively, which are used along with the RISM theory. The identical data-sets obtained by both theories are illustrated, changing the time domain focused as: (a) from 0 ps down to 1 ps, and (b) to 10 ps.

processes. The Gaussian plus underdamping decays are attributed to libration of solvent, as discussed elsewhere [1,2,6,11]. The slower component for the duration of picoseconds is assigned to be a diffusive origin.

As a comparison, Fig. 1 also illustrates our previous result by means of the SSSV equation [23]. In this case, $S_S(t)$ misses the Gaussian decay and the underdamping profile in the very first stage of the relaxation. In the RISM/SSSV framework we employed previously, we took a diffusion constant matrix as an empirical parameter [19,22,23,27]. As most of nondiffusive origins are not reflected in the $S_S(t)$ curve calculated by the SSSV equation, characteristic features for the decay regarding solvent libration can be lost. This is a plausible explanation for the outstanding differences of the curves, by their appearances, depending on the methods concerning the dynamics part we have used.

Regarded as one of the benchmarking work of this research field, Maroncelli has performed molecular dynamics simulations of various simple solutes [11]. Figure 2 compares our present work with the nonequilibrium simulation by Maroncelli [11], keeping the solute–solvent system identical. Our result using the mode-coupling theory reproduces the simulation well, especially in the time domain earlier than 200 fs. From a quantitative point of view, general features of the rest part are similar to each other, even though our curve emphasizes the amplitude of the damping.

So far, we have revealed that the combination of the RISM and mode-coupling theory is appropriate for the description of solvation dynamics. Having in mind that the theoretical combination used presently works well, we should revisit Fig. 1. Although the mode-coupling theory drastically upgrades $S_S(t)$ in more realistic manner, the curve obtained by the RISM/SSSV theory captures essential characters of relaxation. Within the time region of first 200 fs, the SSSV-work decays quantitatively close to the present result, irrespective of the Gaussian plus underdamping nature. Even more, the SSSV-work has reproduced the slower relaxation with the lifetime in picoseconds, apart from the numerical discrepancy in the amplitude [23]. At the present point of the investigation, we suggest that the memory of solvent friction which is not incorporated in the RISM/SSSV theory causes the deviation between the decays obtained by two different theories.

In the present study we have used very simple solute–solvent systems, demonstrating the applicability of the RISM/mode-coupling theory. Various investigations [14,27] have shown that the geometrical shape and charge distribution of solute largely affect $S_S(t)$. Because experimentalists generally do not choose simple ions as solutes, further studies using more realistic model solutes are indeed desirable. Such a development in the RISM/mode-coupling scheme is really straightforward. On the other

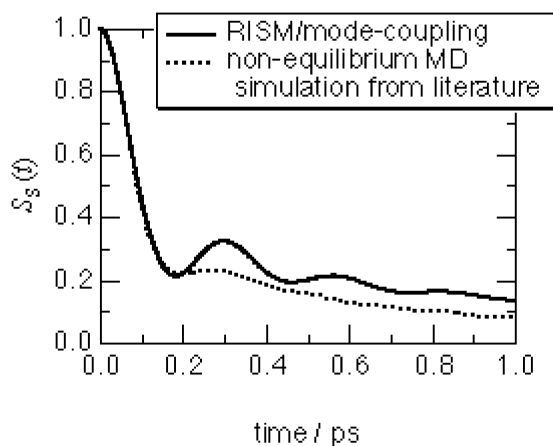


Fig. 2 $S_S(t)$ for the model solute “S” \rightarrow “S⁺” in acetonitrile. The solid line stands for the result of the RISM/mode-coupling theory. Also shown in the dotted line is the literature data obtained by nonequilibrium molecular dynamics simulation, performed by Maroncelli [11].

hand, the chemical variety of solvent has been very much to the point in solvation dynamics. The extension of solvents toward water and alcohols, for example, is also in our concern [36].

CONCLUDING REMARKS

In this publication, we have applied the combination of the RISM and mode-coupling theories to solvation dynamics. We have chosen acetonitrile as a representative of a polar aprotic solvent, and have used simple model ions as solute. The RISM/mode-coupling theory turns out to be a powerful tool for realistic descriptions of solvation dynamics in femtosecond-picosecond regions. The dynamic response function $S_S(t)$, which gauges the relaxation of average energy of the solute–solvent system, has been calculated. Within 1 ps, $S_S(t)$ decays by 90 % with the Gaussian type followed by underdamping curve. The general profile of the decay is in agreement with other investigations published elsewhere [1,2,6,11].

In the conventional context, the mode-coupling theory has been developed for investigation concerned with “slow” phenomena, say, glass dynamics. Yamaguchi and Hirata [32] have recently applied the RISM/mode-coupling theory for reorientational relaxation of molecular liquids, and in the present paper we have further extended the use of this framework to solvation processes.

As a perspective of our investigation, we are now extending the present theoretical formula toward more realistic solute–solvent systems employed in laser experiments. By varying the chemical nature of solute and solvent, we can obtain further molecular view concerning the decay profile of $S_S(t)$. On the other hand, in our recent reports [22,27] we have decoupled $S_S(t)$ into the acoustic mode, or translational motion of solvent, and the optical mode, or solvent rotation, respectively, under the RISM/SSSV theory. This decomposition has made us access to detailed molecular origin of the solvent dynamics. Powered by the theoretical formula we have developed in this work, we are also decoupling $S_S(t)$ into each solvent mode. These efforts mentioned above will be published as our next report [36].

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REFERENCES

1. S. J. Rosenthal, X. Xie, M. Du, G. R. Fleming. *J. Chem. Phys.* **95**, 4715 (1991).
2. M. Cho, S. J. Rosenthal, N. F. Scherner, L. D. Ziegler, G. R. Fleming. *J. Chem. Phys.* **96**, 5033 (1992).
3. H. Murakami, S. Kinoshita, Y. Hirata, T. Okada, N. Mataga. *J. Chem. Phys.* **97**, 7881 (1992).
4. C. F. Chapman, R. S. Fee, M. Maroncelli. *J. Phys. Chem.* **99**, 4811 (1995).
5. M. L. Horng, J. A. Gardecki, A. Papazyan, M. Maroncelli. *J. Phys. Chem.* **99**, 17311 (1995).
6. J. Ma, D. V. Bout, M. Berg. *J. Chem. Phys.* **103**, 9146 (1995).
7. K. Nishiyama, Y. Asano, N. Hashimoto, T. Okada. *J. Mol. Liq.* **65/66**, 41 (1995).
8. K. Nishiyama and T. Okada. *J. Phys. Chem. A* **101**, 5729 (1997).
9. C. Chudoba, E. T. J. Nibbering, T. Elsaesser. *Phys. Rev. Lett.* **81**, 3010 (1998).
10. K. Nishiyama and T. Okada. *J. Phys. Chem. A* **102**, 9729 (1998).
11. M. Maroncelli. *J. Chem. Phys.* **94**, 2084 (1991).
12. M. Maroncelli, P. U. Kumar, A. Papazyan, M. L. Horng, S. J. Rosenthal, G. R. Fleming. In *Ultrafast Reaction Dynamics and Solvent Effects*, Vol. 298, Y. Gauduel and P. J. Rossky (Eds.), p. 310, AIP Press, New York (1994).
13. P. V. Kumar and M. Maroncelli. *J. Chem. Phys.* **103**, 3038 (1995).
14. B. M. Ladanyi and M. Maroncelli. *J. Chem. Phys.* **109**, 3204 (1998).

15. B. Bagchi and R. Biswas. In *Advances in Chemical Physics*, Vol. 109, I. Prigogine and S. A. Rice (Eds.), p. 207, Wiley, New York (1999).
16. L. E. Fried and S. Mukamel. *J. Chem. Phys.* **93**, 932 (1990).
17. A. Yoshimori. *Chem. Phys. Lett.* **184**, 76 (1991).
18. F. O. Raineri, H. Resat, B.-C. Perng, F. Hirata, H. L. Friedman. *J. Chem. Phys.* **100**, 1477 (1994).
19. F. Hirata, T. Munakata, F. Raineri, H. L. Friedman. *J. Mol. Liq.* **65/66**, 15 (1995).
20. B. M. Ladanyi and R. M. Stratt. *J. Phys. Chem.* **100**, 1266 (1996).
21. A. Yoshimori. *J. Chem. Phys.* **105**, 5971 (1996).
22. K. Nishiyama, F. Hirata, T. Okada. *J. Chin. Chem. Soc.* **47**, 837 (2000).
23. K. Nishiyama, F. Hirata, T. Okada. *Chem. Phys. Lett.* **330**, 125 (2000).
24. F. O. Raineri and H. L. Friedman. *Z. Phys. Chem.* **7**, 929 (2000).
25. K. Nishiyama, F. Hirata, T. Okada. *J. Mol. Liq.* **90**, 251 (2001).
26. A. Yoshimori. *J. Phys. Soc. Japan* **70**, 4201 (2001).
27. K. Nishiyama, F. Hirata, T. Okada. *J. Chem. Phys.* **118**, 2279 (2003).
28. F. Hirata. *J. Chem. Phys.* **96**, 4619 (1992).
29. S.-H. Chong and F. Hirata. *Phys. Rev. E* **57**, 1691 (1998).
30. S.-H. Chong and F. Hirata. *Phys. Rev. E* **58**, 6188 (1998).
31. T. Yamaguchi and F. Hirata. *J. Chem. Phys.* **115**, 9340 (2001).
32. T. Yamaguchi and F. Hirata. *J. Chem. Phys.* **117**, 2216 (2002).
33. T. Yamaguchi, S.-H. Chong, F. Hirata. *Mol. Phys.* **101**, 1211 (2003).
34. F. Hirata, P. J. Rossky, B. M. Pettitt. *J. Chem. Phys.* **78**, 4133 (1983).
35. D. M. Edwards, P. A. Madden, I. R. McDonald. *Mol. Phys.* **51**, 1141 (1984).
36. K. Nishiyama, T. Yamaguchi, F. Hirata, T. Okada. To be submitted.