

## Ion Solvation Dynamics in Supercritical Fluids

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We present a theoretical study of ion solvation dynamics in a supercritical solvent. Molecular dynamics simulations show a significant difference between equilibrium and nonequilibrium solvent response functions, especially pronounced at medium and low solvent densities. We propose a simple analytical theory for the nonequilibrium solvation function based on the generalized nonlinear Smoluchowski-Vlasov equation. The theory is shown to be in excellent agreement with simulation over a wide range of supercritical solvent densities.

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Supercritical fluids (SCFs) have stimulated much industrial and scientific interest as a result of their unique physical properties, including the pronounced solvent clustering around strongly interacting solutes [1–3]. While the static aspects of this solvent clustering are reasonably well understood [3], its dynamic ramifications are far less clear. Given that the motions of individual solvent particles directly affect the rates of various physical and chemical processes in solution, such as energy relaxation, electron transfer, and chemical reactions [4–6], it is important to develop a microscopic understanding of solvation dynamics in supercritical media.

The solvation dynamics experiment monitors the response of the solvent molecules to an optical excitation of the solute, which typically involves a sudden change in the solute charge distribution [6,7]. The normalized nonequilibrium solvent response function is defined by

$$S(t) = \frac{\overline{\Delta E}(t) - \overline{\Delta E}(\infty)}{\overline{\Delta E}(0) - \overline{\Delta E}(\infty)}, \quad (1)$$

where  $\Delta E(t)$  is the energy gap between the ground and excited states of the solute, which changes in time due to the solvent reorganization following the solute excitation. The overbars denote a nonequilibrium ensemble average, where the solute is promoted to the excited state at  $t = 0$ , with the initial solvent distribution corresponding to the solute in its ground state and the solvent dynamics after  $t = 0$  evolving according to the solute-solvent excited state interaction potential.

One of the most common approximations in theoretical studies of solvation dynamics is based on the idea of linear response, according to which  $S(t)$  can be replaced by the corresponding equilibrium solvation time correlation function (TCF):

$$C(t) = \frac{\langle \delta \Delta E(0) \delta \Delta E(t) \rangle}{\langle (\delta \Delta E)^2 \rangle}, \quad (2)$$

where the angled brackets represent the equilibrium ensemble average with the solute either in its ground or excited state, and  $\delta \Delta E = \Delta E - \langle \Delta E \rangle$ .

The validity of linear response has been investigated in numerous simulation studies of solvation dynamics. In the case of *pure* dense liquids,  $S(t)$  was generally found to agree reasonably well with  $C(t)$  [8,9], although a few exceptions have been observed [10–12]. The situation is quite different in the case of liquid mixtures, where the change in the solute charge distribution can strongly affect the preferential solvation of the solute by one of the components, leading to the breakdown of linear response. This phenomenon was observed in several simulation studies [13–16] and was analyzed theoretically [17–20].

We now note that liquid mixtures and supercritical solvents exhibit certain similarities in the context of solvation, in a sense that preferential solvation in mixtures plays a role similar to the solvent clustering in SCFs. Accordingly, one could also expect a breakdown of linear response in SCFs, especially in the low density regime, where a significant change in the solute-solvent interaction can lead to a dramatic reorganization of the solvent microstructure around the solute. Indeed, the simulation studies of ionic solvation in a model polar supercritical solvent [21] and in supercritical water [22] have both shown large differences between  $S(t)$  and  $C(t)$ , especially pronounced at medium and low solvent densities, where  $S(t)$  exhibited significantly *slower* long-time decay compared to  $C(t)$ . This finding is hardly surprising, since the long-time diffusive behavior of nonequilibrium solvent response reflects gradual clustering of solvent molecules around a newly created ionic solute, which involves solvent density fluctuations much larger in size compared to spontaneous fluctuations of the local solvent density around a neutral solute. By contrast, the short-time inertial behavior of  $S(t)$  and  $C(t)$ , which is dominated by rotational solvent motions in polar media, was found to be rather similar in polar supercritical solvents [21,22].

In the present work, we consider ion solvation dynamics in a nonpolar supercritical solvent, where only translational motions contribute to the solvation process, and the nonequilibrium solvent response function *at all times*

reflects the clustering of solvent around an excited solute. We simulate both equilibrium and nonequilibrium solvation correlation functions and show that there is a pronounced difference between  $S(t)$  and  $C(t)$  at all times, especially at low and medium solvent densities. However, the main goal of our study goes beyond a simple demonstration of a breakdown of linear response. As already mentioned, the calculation of  $S(t)$  from simulation requires harvesting multiple nonequilibrium trajectories and therefore is much more demanding compared to  $C(t)$ . Hence, it would be very useful to develop an analytical theory for computing  $S(t)$ . While equilibrium solvation TCFs for polar [23] and nonpolar [24] supercritical solvents have been calculated on the basis of the mode-coupling theory, no theoretical framework is yet available for the treatment of nonequilibrium solvent response at

supercritical conditions. The major goal of the present Letter is to present such a theory.

We consider a single dilute solute in a bath of spherical solvent particles. Solvent molecules interact with each other via isotropic pairwise additive potential  $\phi(r)$ , and the solute-solvent interaction potential is denoted by  $\phi_0(r)$  [ $\phi_1(r)$ ] when the solute is in its ground (excited) state, respectively. Our goal is to compute the nonequilibrium solvent response  $S(t)$  following the excitation of the solute at  $t = 0$ . The time-dependent energy gap between the ground and excited states can be written as  $\Delta E(t) = \int d\vec{r}(\phi_1(r) - \phi_0(r))\rho(r, t)$ , where  $\rho(r, t)$  is the nonequilibrium solvent density profile around the solute.

Most previous theoretical studies of nonequilibrium solvent response in dense polar liquids were based on the Smoluchowski-Vlasov equation [25–27] for  $\rho(r, t)$ :

$$\frac{\partial \rho(r, t)}{\partial t} = D(t) \left[ \nabla^2 \rho(r, t) + \beta \nabla \rho(r, t) \nabla w_1(r) - \nabla \rho(r, t) \nabla \int d\vec{r}' c(|\vec{r} - \vec{r}'|) (\rho(r', t) - \rho_1(r')) \right], \quad (3)$$

with  $D(t) = \int_0^t d\tau [C_v(\tau) + C_v^s(\tau)]$ , where  $C_v(t)$  and  $C_v^s(t)$  are the solute and solvent velocity TCFs,  $\beta = 1/k_B T$ ,  $w_1(r)$  is the excited state solute-solvent potential of mean force,  $\rho_1(r) \equiv \rho(r, t = \infty)$  is the *equilibrium* solvent density profile around the excited state solute, and  $c(r)$  is the solvent direct correlation function evaluated at the bulk solvent density  $\rho_b$  [note that we have replaced the anisotropic direct correlation function for an inhomogeneous system,  $c(\vec{r}, \vec{r}')$ , with the isotropic (two-body) one,  $c(|\vec{r} - \vec{r}'|)$ , which should be a reasonable approximation for low- and medium-density fluids studied here]. The right-hand side of Eq. (3) thus involves three familiar terms: a diffusion term, a potential of mean force term, and a mean-field term due to other solvent molecules. Note that Eq. (3) is the *generalized* Smoluchowski-Vlasov equation [28], since it contains the time-dependent relative diffusion coefficient,  $D(t)$ , which makes it possible to properly account for the inertial short-time behavior of the solvent response. In previous applications of the Smoluchowski-Vlasov equation to solvation dynamics [18,25,26],  $D(t)$  was replaced by its long-time limit, which would make its applicability in the subpicosecond regime somewhat questionable. In addition, earlier studies of nonequilibrium solvation employed a *linearized* version of the Smoluchowski-Vlasov equation [25,26], whereby  $\rho(r, t)$  in the first factor in the mean-field term was replaced by the equilibrium profile  $\rho_1(r)$ . While this linearization approximation could be appropriate for dense liquids with relatively small density fluctuations, it is unlikely to be acceptable for SCFs, where the solvent density profiles around the ground and excited state solutes differ dramatically. In view of that, we chose to work with the nonlinear form of the Smoluchowski-Vlasov equation. However, while the linearized equation can be solved using standard Laplace transform techniques, the nonlinear equation presents significant numerical challenges due to the fact that the mean-field term is both

nonlinear in  $\rho(r, t)$  and contains the spatial convolution involving  $c(r)$ . In order to make further progress, we have adopted the following approximation. We introduce functions  $\Delta w_0(r)$  and  $\Delta w_1(r)$  according to  $\beta \Delta w_0(r) = - \int d\vec{r}' c(|\vec{r} - \vec{r}'|) (\rho_0(r') - \rho_b)$  and  $\beta \Delta w_1(r) = - \int d\vec{r}' c(|\vec{r} - \vec{r}'|) (\rho_1(r') - \rho_b)$ , where  $\rho_0(r) \equiv \rho(r, t = 0)$  is the equilibrium solvent density profile around the ground state solute. Note that within the hypernetted chain approximation [29],  $\Delta w_0(r)$  and  $\Delta w_1(r)$  are the solvent mediated components of the ground and excited state solute-solvent potentials of mean force,  $w_0(r)$  and  $w_1(r)$ , respectively. In other words,  $w_0(r) = \phi_0(r) + \Delta w_0(r)$  and  $w_1(r) = \phi_1(r) + \Delta w_1(r)$ . The above observation suggests combining the second and third terms in Eq. (3) into a single term with a *time-dependent* potential of mean force:

$$\frac{\partial \rho(r, t)}{\partial t} = D(t) [\nabla^2 \rho(r, t) + \beta \nabla \rho(r, t) \nabla w(r, t)], \quad (4)$$

where we have introduced  $w(r, t)$  according to the following approximation:  $w(r, t) = w_1(r) + (\Delta w_0(r) - \Delta w_1(r))S_w(t)$ , where  $S_w(t)$  is a “switching function,” which interpolates between initial and final solute-solvent potentials of mean force. By comparing Eqs. (3) and (4), one sees that an appropriate form for  $S_w(t)$  would be a function that is equal to unity at  $t = 0$  and then decays to zero on the same time scale as  $\rho(r, t)$  approaches its equilibrium value. We have adopted the following form, which satisfies the above requirements:

$$S_w(t) = \frac{\rho(r_{\max}, t) - \rho_1(r_{\max})}{\rho_0(r_{\max}) - \rho_1(r_{\max})}, \quad (5)$$

where  $\rho(r_{\max}, t)$  is the value of the first peak of the time-dependent solute-solvent density profile. Since  $\rho(r, t)$  is itself the solution of the generalized Smoluchowski-Vlasov equation, it is clear that Eqs. (4) and (5) must

be solved simultaneously and iteratively, until a self-consistent solution for  $\rho(r, t)$  is obtained.

In order to test the accuracy of the proposed approach, we next compare theoretical results with molecular dynamics (MD) simulations. We consider solvation of a positive Xe ion in supercritical xenon. Ionic mobilities in supercritical rare gases have been extensively studied experimentally [30,31] and theoretically [32], and there exists a wealth of structural and dynamical data on these systems. We assume that the solvent atoms interact via the familiar Lennard-Jones (LJ) potential:  $\phi(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$ , where  $\epsilon$  is the well depth and  $\sigma$  is the effective solvent diameter. The dimensionless density and temperature of the solvent are defined by  $\rho^* = \rho\sigma^3$  and  $T^* = k_B T/\epsilon$ ; the best estimates for the critical density and temperature of a LJ fluid are [33]  $\rho_c^* = 0.316$  and  $T_c^* = 1.312$ . We choose the LJ parameters for xenon by requiring that the reduced experimental critical density and temperature of Xe coincide with the corresponding critical constants of a LJ fluid. The experimental values for the critical point of Xe are as follows:  $\rho_c = 8.454$  mol/L and  $T_c = 289.74$  K [34]. Using these values, one obtains  $\epsilon/k_B = 220.8$  K and  $\sigma = 3.96$  Å.

When the solute is in its ground (neutral) state, it is identical to the solvent, and therefore  $\phi_0(r) = \phi(r)$ . The excited state solute-solvent (ion-atom) potential contains an additional long-range charge-induced dipole component, which has the form  $-e^2\alpha/2r^4$ , where  $\alpha$  is the solvent atom polarizability [34] (note that we take into account ion-induced dipole interactions but neglect the induced dipole-induced dipole term in the solvent potential [35]). Taking  $\sigma$  and  $\epsilon$  parameters for Xe<sup>+</sup> to be the same as for Xe, we write the excited state solute-solvent potential as follows [36]:  $\phi_1(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6] - \gamma\epsilon(\frac{\sigma}{r})^4$ , where  $\gamma = e^2\alpha/2\epsilon\sigma^4$ . The experimental value for the Xe polarizability [37] ( $\alpha = 4.02 \times 10^{-24}$  cm<sup>3</sup>) yields  $\gamma = 6.19$ .

We now compute from MD simulations both the non-equilibrium solvent response function given by Eq. (1) and the equilibrium solvation TCF (for the excited state solute) given by Eq. (2). In performing the equilibrium MD simulations, the velocity-Verlet algorithm is used to integrate the equations of motion for a liquid of 2047 solvent particles and one ion in a cubic box employing periodic boundary conditions and the minimum image convention. The dimensionless box length is equal to  $(2048/\rho^*)^{1/3}$ , and the pair potentials are truncated at half of this value. The system is propagated with a time step of  $\delta t = 0.007$  ps.

In order to compute the nonequilibrium solvent response function, we have obtained long equilibrium trajectories with the neutral solute, from which we generated 5000 initial configurations. For each of these configurations, the solute charge was changed instantaneously from 0 to +1, and the energy gap was monitored as the solvent relaxed to its equilibrium with the ionic solute. By performing an average over 5000 nonequilibrium trajec-

tories, we have obtained  $\overline{\Delta E}(t)$ , from which  $S(t)$  was computed according to Eq. (1).

The calculations were performed along the supercritical isotherm  $T^* = 1.37$ , which corresponds to the reduced temperature  $T_r = T/T_c = 1.05$ . We considered three solvent densities ( $\rho^* = 0.17, 0.316, \text{ and } 0.57$ ), which covers the range from dilute gaslike to dense liquidlike regime. Our simulation results for  $C(t)$  and  $S(t)$  are shown in Fig. 1. We see that at all densities the equilibrium solvation TCFs exhibit very rapid initial decay with a time constant of approximately 0.5 ps (essentially density independent), which accounts for  $\sim 70\%$  of the total decay of  $C(t)$ . This initial dropoff is followed by a small bump and slowly decaying long-time tail (with a time constant on the order of 10 ps), whose amplitude increases somewhat with decreasing solvent density. Since the major focus of the present study is the theory of *nonequilibrium* solvent response, we defer a detailed theoretical analysis of  $C(t)$  to a later publication. For the present time, we simply note that both the bump and the long-time tail can be explained within the mode-coupling theory as arising due to the coupling of the solute energy gap to the solvent (equilibrium) density fluctuations [24].

Turning next to the simulation results for the nonequilibrium solvent response function, we note first of all that  $S(t)$  differs from  $C(t)$  at all times, with the difference being especially dramatic at medium and low densities. One can still discern fast and slow components of the

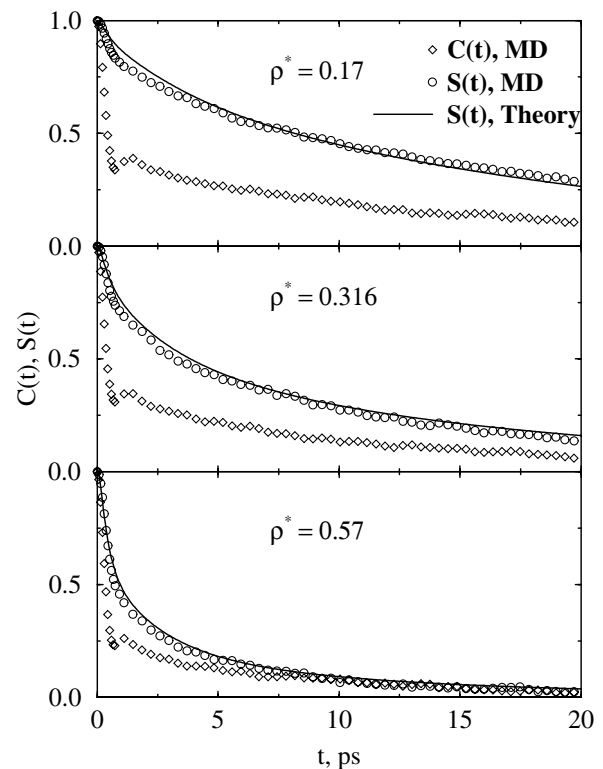


FIG. 1. Simulation and theoretical results for equilibrium and nonequilibrium solvent response functions at  $T^* = 1.37$  at three solvent densities.

solvent response in  $S(t)$ , although the separation between the two time scales is less clear-cut compared to  $C(t)$ . In sharp contrast to the equilibrium solvation TCF, the amount of the decay provided by the faster component of the nonequilibrium solvent response depends very strongly on the solvent density, ranging from  $\sim 60\%$  at the high-density point to only  $\sim 20\%$  at the low-density point. As a result, the amplitude of the long-time tail of  $S(t)$  increases dramatically with decreasing solvent density. Overall,  $S(t)$  decays substantially slower than  $C(t)$ , especially at medium and low densities (the same trend was observed in the study of ion solvation dynamics in supercritical water [22]).

We now perform theoretical calculations of the non-equilibrium solvent response function by solving Eqs. (4) and (5) simultaneously. As input, the theory requires the ground and excited state solute-solvent potentials of mean force and the solute and solvent velocity TCFs. We compute the former from the inhomogeneous integral equation theory with Percus-Yevick closure [38] and the latter from the mode-coupling theory [32]. The accuracy of both these treatments has been thoroughly assessed in our earlier study of Xe ion diffusion in supercritical xenon [32]. Our theoretical results for  $S(t)$  are also shown in Fig. 1, and one sees that theory is in excellent agreement with simulation at medium and high densities and deviates only slightly from simulation at the low density point. The latter discrepancy is likely due to our approximate form of the switching function [Eq. (5)], which is taken to be spatially independent. While choosing a more sophisticated form for  $S_w(t)$  (e.g., incorporating some form of  $r$  dependence into it) could help reduce the remaining discrepancy, it would also make the theory more demanding computationally. We believe that the proposed form achieves a reasonable compromise between accuracy and computational simplicity.

In conclusion, we have proposed a simple but accurate analytical theory for  $S(t)$  based on the generalized non-linear Smoluchowski-Vlasov equation. This is an important result, since the calculation of nonequilibrium solvent response function from simulations is very demanding, and a robust theory for  $S(t)$  can significantly reduce the computational cost of the studies of solvation dynamics.

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