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Solvation dynamics of a charge bubble in water

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Abstract. A microscopic theory is used to calculate the solvation-time correlation function, ($S(t)$), of a light, non-stationary charge bubble in water. The calculated correlation function is found to be similar to the energy-time correlation function of a solvated electron. The ionic mobility of a charge bubble of the size of the hydrated electron is also calculated. It is found that the mobility of the charge plays a very important role in its own solvation.

Keywords. Solvation dynamics; ultrafast spectroscopy; ionic mobility; electron solvation.

1. Introduction

In this work we present a microscopic calculation of the solvation dynamics of a light (nearly massless) non-stationary charge bubble in water. The bubble is characterized by a spherical shape which is uniformly filled by a charge of 1 esu. The bubble interacts with water molecules (which are assumed to be dipoles) through charge–dipole interaction. This model has been introduced to mimic some aspects of an electron in water and has been partly motivated by the interesting electro-hydrodynamic model of electron solvation introduced recently by Rips (1995). We have calculated the solvation-time correlation function ($S(t)$) of this system. The new aspect of the present study is the systematic incorporation of the self-motion of the solute. The calculated $S(t)$ is surprisingly similar to the solvation energy correlation function of a solvated electron obtained via quantum simulations by Rossky and coworkers (Schwartz and Rossky 1994). While it is probable that this similarity is purely fortuitous and that the present fully classical calculation has no connection with electron solvation dynamics, there is still the possibilty that it is the same long wavelength dynamics that contributes to initial solvation in both the systems. The present theoretical calculation incorporates the long wavelength polarization response of the liquid correctly.

2. Theoretical formulation

Both in experiments and in computer simulation studies the time-dependent progress of solvation of a probe solute is described either in terms of the solvation time correlation function ($S(t)$) or the solvation energy–energy time correlation function

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($C_{EE}(t)$). The solvation time correlation function, $S(t)$ is defined as usual by the following expression (Bagchi *et al* 1984),

$$S(t) = \frac{E_{\text{solv}}(t) - E_{\text{solv}}(\infty)}{E_{\text{solv}}(0) - E_{\text{solv}}(\infty)}, \tag{1}$$

where $E_{\text{solv}}(t)$ is the time-dependent solvation energy of the probe at time t and $E_{\text{solv}}(\infty)$ is the solvation energy at equilibrium. The energy–energy time correlation function, $C_{EE}(t)$ is defined by the following expression (Nandi *et al* 1995),

$$C_{\text{EE}}(t) = \frac{\langle \Delta E(t) \Delta E(0) \rangle}{\langle |\Delta E(0)|^2 \rangle}, \tag{2}$$

where $\Delta E(t)$ is the fluctuation in the energy difference between two levels. It is usually stated that $S(t)$ and $C_{\text{EE}}(t)$ are the same *within the linear response* of the liquid. However, for solvation of electron, $S(t)$ and $C_{\text{EE}}(t)$ can be considerably different. Here we calculate $C_{\text{EE}}(t)$.

In order to study the time-dependent progress of solvation in liquids like water, we need a theory that properly includes the dynamic response of the liquid and also the coupling of the probe solute to the solvent. The present theoretical formulation is based on the well-known density functional theory (DFT) and has been discussed many times earlier (Nandi *et al* 1995; Biswas and Bagchi 1996), so we give only the bare essentials here. Let us consider a system where the charge bubble is translationally mobile and the surrounding dipolar molecules are free to rotate and translate. All these motions can contribute to the process of solvation of the charge bubble. One can then use the DFT to obtain a general free energy functional (of density) from statistical mechanics. The free energy functional leads to the following expression for the time-dependent solvation energy (Nandi *et al* 1995)

$$E_{\text{sol}}(r,t) = -k_B T n_b(\mathbf{r},t) \int \mathrm{d}\mathbf{r}' \mathrm{d}\Omega' c_{b-d}(\mathbf{r},\mathbf{r}',\Omega') \delta\rho(\mathbf{r}',\Omega',t), \tag{3}$$

where $n_b(\mathbf{r},t)$ is the probability that the charge bubble is at position $\mathbf{r}$ at time t, and $\delta\rho(\mathbf{r},\Omega,t)$ is the fluctuation in the position ($\mathbf{r}$), orientation (Ω) and time ($\mathbf{t}$)-dependent number density of the dipolar solvent. $c_{b-d}(\mathbf{r},\mathbf{r}',\Omega')$ is the bubble–dipole direct correlation function (DCF) (Chan *et al* 1979) and $k_B T$ is Boltzmann constant (k_B) times the absolute temperature (T). Note that in this expression, the coupling between the ionic solute and the dipolar solvent enters through $c_{b-d}(k)$. At large distances from the solute this term gives the usual coupling between the electric field of the ion and the dipole moment density. At small distances it includes the molecular aspects and the equilibrium distortion of the solvent due to the polar solute. Note that (3) leads to an expression of solvation energy that *includes the effects of self-motion of the charge bubble.*

At this point one should justify the use of (3) to obtain the time-dependent solvation energy of the charge bubble which arises mainly due to the coupling of the electric field on the charge bubble with the solvent polarization mode. We have assumed that the main interaction of the bubble with the surrounding water dipoles is electrical in origin. However, it is also assumed that the bubble *on the average* retains its spherical shape. The latter is possible because of a short range soft-sphere type repulsive interaction between the bubble and the water molecules.

In the calculations presented here, we assume that the bubble–water molecule correlation function is given by the mean spherical approximation (MSA) model which is equivalent to assuming a hard core repulsive short range potential. The nature of the effective potential operative between the charge bubble–water dipole pair is given as follows

$$g_{b-d}(r) = 0, \quad r < (\sigma_b + \sigma_{H_2O})/2, \tag{4}$$

and

$$c_{b-d}(r) = -\beta(q\hat{\mu}\cdot\mathbf{r}/r^3), \quad r \geqslant (\sigma_b + \sigma_{H_2O})/2, \tag{5}$$

where $g_{b-d}(r)$ describes the space (r)-dependent radial distribution function between the charge bubble and the water dipoles and $c_{b-d}(r)$ is the bubble–dipole direct correlation function in real space. q is the charge on the bubble and μ is the dipole moment of a solvent molecule positioned at $\mathbf{r}$ from the centre. The use of the above MSA-type closure is reasonable because of the uniform charge distribution. We calculate the c_{b-d} using the mean spherical approximation (MSA).

We use (3) as a starting point to calculate the solvation-time correlation function, $S(t)$. The steps necessary for arriving at the final expression of $S(t)$ have been discussed in detail in many of our earlier studies (Nandi *et al* 1995) and thus we give here only the final expressions. The solvation energy–energy time correlation function (EETCF) is given as follows.

$$\langle E(0)E(t)\rangle = \frac{(4\pi k_B T)^2}{V}\int_0^\infty \mathrm{d}k\, k^2 |c^{10}_{b-d}(k)|^2\, S_b(k,t)\, S_{\text{solvent}}(k,t), \tag{6}$$

where V is the total volume of the system. $S_b(k,t)$ is the self-dynamic structure factor of the bubble and $S_{\text{solvent}}(k,t)$ is the dynamic structure factor of the solvent. The analytical expressions for these two functions have been given elsewhere (Nandi *et al* 1995). The final expression of the solvation time correlation function is obtained by following the steps outlined elsewhere (Biswas and Bagchi 1996) and is given by

$$C_{\text{EE}}(t) = \frac{\int_0^\infty \mathrm{d}k\, k^2 |c^{10}_{b-d}(k)|^2 [1 - 1/\varepsilon_L(k)] S_b(k,t)\, \mathscr{L}^{-1}[z + \Sigma(k,z)]^{-1}}{\int_0^\infty \mathrm{d}k\, k^2 |c^{10}_{b-d}|^2 [1 - 1/\varepsilon_L(k)]}. \tag{7}$$

The important ingredients to calculate $C_{\text{EE}}(t)$ from (7) are the bubble–dipole direct correlation function (c_{b-d}), the self-dynamic structure factor ($S_b(k,t)$), the static orientational correlation function ($\varepsilon_L(k)$) and the generalized rate $\Sigma(k,z)$ of polarization relaxation. This rate is given by, (Nandi *et al* 1995; Biswas and Bagchi 1996),

$$\Sigma(k,z) = \frac{2k_B T f_L(k)}{I[z + \Gamma_R(k,z)]} + \frac{k_B T k^2 f_L(k)}{m\sigma^2[z + \Gamma_T(k,z)]}, \tag{8}$$

where I is the average moment of inertia of a solvent molecule of diameter σ and mass m. $\Gamma_R(k,z)$ and $\Gamma_T(k,z)$ are the rotational and the translational dissipative kernels, respectively. The longitudinal components of the static structural correlations of the pure solvent are expressed by (Bagchi and Chandra 1991)

$$f_L(k) = 1 - (\rho_0/4\pi)c(110;k), \tag{9}$$

where $c(110;k)$ denotes the (110) th component of the direct correlation function in the intermolecular frame with $\mathbf{k}$ parallel to z axis. $f_L(k)$ is also related to the longitudinal

part of the wave-number dependent dielectric function, $\varepsilon_L(k)$, by the following exact relation (Bagchi and Chandra 1991),

$$1-\frac{1}{\varepsilon_L(k)}=\frac{3Y}{f_L(k)}, \tag{10}$$

$3Y$ is the polarity parameter of the pure solvent which can be calculated from the number density (ρ) and dipole moment (μ) of the solvent as follows, $3Y=4\pi/3\times(k_BT)^{-1}\mu^2\rho$. For the self-dynamic structure factor, we assume here that $S_b(k,t)=\exp(-D_T^b k^2 t)$, where D_T^b is the translational self-diffusion coefficient of the bubble. This has been calculated self-consistently as described below.

3. Calculational procedure

The accurate calculation of the frequency kernels is a non-trivial exercise. These quantities are crucial in determining the time scale of the time-dependent solvation of a solute–be it ionic or dipolar. We have calculated the $\Gamma_R(k,z)$ directly from the experimentally available dielectric relaxation data and far-infrared (FIR) lineshape measurements of water. In order to do so we approximate $\Gamma_R(k,z)$ by its $k=0$ limiting value (Biswas and Bagchi 1996). The connecting relation between the $\Gamma_R(k,z)$ and the frequency-dependent dielectric function, $\varepsilon(z)$, is as follows (Biswas and Bagchi 1996),

$$\frac{k_BT}{I[z+\Gamma_R(k=0,z)]}=\frac{(\varepsilon_0-1)}{3Yn^2}\,\frac{z[\varepsilon(z)-n^2]}{\varepsilon_0-\varepsilon(z)}, \tag{11}$$

where ε_0 and n^2 are static and optical dielectric constants of water, respectively. In the present calculations, $\Gamma_R(k,z)$ for water has been obtained using the above relation in the following way. The frequency-dependent dielectric function, $\varepsilon(z)$ in the low frequency regime is described by two Debye relaxations with time constants equal to 8·3 and 1·3 ps, while at high frequency $\varepsilon(z)$ derives major contributions from the librational and intermolecular vibrational motions of the hydrogen-bonded network. These high frequency motions appear as three peaks around 700, 200 and 50 cm^{-1} as found in FIR line-shape studies. $\Gamma_T(k,z)$ has been obtained using the known value of the respective translational diffusion coefficient, D_T. For water, additional contributions from the intermolecular vibrations have also been taken into account; details of this have been discussed elsewhere (Biswas and Bagchi 1996).

The static bubble–dipole direct correlation function, $c_{b-d}^{10}(k)$ is obtained using the mean spherical approximation (MSA) given by Chan *et al* (1979) in the limit of zero ionic concentration. The other important input is $c(110;k)$ which has again been obtained from MSA corrected for the limits of both $k\to 0$ and $k\to\infty$ by using the XRISM results of Raineri *et al* (1992). The details are available elsewhere (Nandi *et al* 1995; Biswas and Bagchi 1996). We have used $T=298$ K in all the calculations.

In order to include the self-motion of the bubble, we need to find the friction on it. This is calculated by using the following mode-coupling theory expression (Sjogren and Sjolander 1979) $\zeta(z)=\zeta_{\text{bare}}+\zeta_{DF}(z)$, where ζ_{bare} is the bare friction on the ion acting from collisons. The expression for the frequency dependent dielectric friction, $\zeta_{DF}(z)$ is given as follows (Biswas *et al* 1995; Biswas and Bagchi 1997)

$$\zeta_{DF}(z)=\frac{2k_BT\rho_0}{3(2\pi)^2}\int_0^\infty dt e^{-zt}\int_0^\infty dk\, k^4|c_{b-d}^{10}(k)|^2 S_b(k,t)S_{\text{solvent}}^{10}(k,t). \tag{12}$$

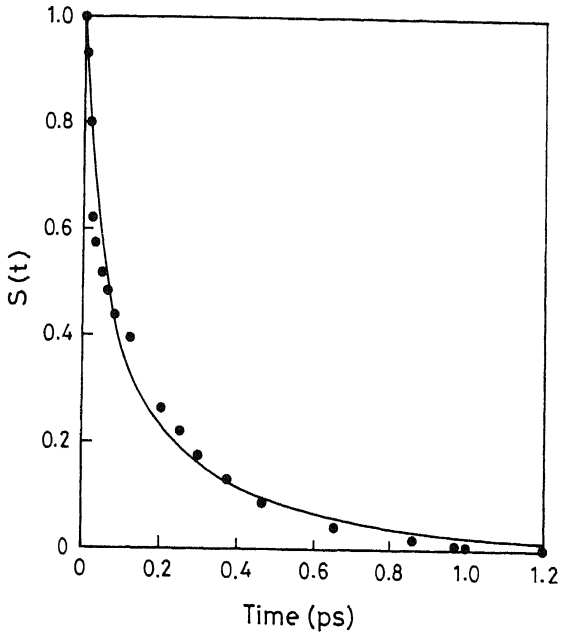

Figure 1. Calculated equilibrium solvation-time correlation function of a light, mobile charge bubble is compared with that of a solvated electron – the latter was obtained by Schwartz and Rossky (1994) via quantum simulation. The solid line represents the decay of the calculated function with $D_T^b = 2{\cdot}2 \times 10^{-4}\text{cm}^2\text{s}^{-1}$; filled circles represent the simulated results (non-equilibrium) of Schwartz and Rossky (1994).

For the light bubble considered here $\zeta_{\text{bare}} \simeq 0$. The friction, therefore, originates fully from the interaction with solvent polarization and has been calculated by a self-consistent calculation. We find that

$$D_T^b = \frac{k_B T}{\zeta} = 2{\cdot}2 \times 10^{-4}\text{cm}^2\text{s}^{-1},$$

which is approximately four times larger than that of the solvated electron in water. Clearly the bare term is important, neglect of which has led to such high values.

4. Results and discussion

In figure 1 we plot the calculated equilibrium solvation time correlation function ($S(t)$) of the mobile charge–bubble in water. The diameter of the charge–bubble is taken as that of a bromide (Br^-) ion. Thus the solute–solvent size ratio is 1·3. The calculated $S(t)$ shows a pronounced biphasic character. For comparison, we also plot the computer simulation results on electron solvation in water. There are several points to note. First, as the short time part of the calculated $S(t)$ is governed by the small wave-number (that is, $k \to 0$) processes, the initial part of $S(t)$ is *insensitive* to the size of the probe. Second, the short time decay is also rather insensitive to the value of D_T^b, although the long time part is sensitive to it.

There could be several reasons for the observed numerical agreement with electron solvation dynamics. The short time part of both may derive contribution from the long

wave-length modes. In the long time, quantum effects such as non-adiabatic transitions may play a role in electron solvation. For classical charge bubble, this is compensated by the enhanced translational self-diffusion.

The present theory neglects any change in the size and shape of the cavity. It is also possible that an extra relaxation channel of the equilibrium correlation function is made available through the fluctuation of the cavity size and the shape. Some of these effects were included in the hydrodynamic model of Rips (1995).

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