

## Dielectric friction and solvation dynamics: Novel results on relaxation in dipolar liquids

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**Abstract.** In this article we present a new, general but simple, microscopic expression for time-dependent solvation energy of an ion. This expression is surprisingly similar to the expression for the time-dependent dielectric friction on a moving ion. We show that both the Chandra–Bagchi and the Fried–Mukamel formulations of solvation dynamics can be easily derived from this expression. This expression leads to an almost perfect agreement of the theory with all the available computer simulation results. Second, we show here for the first time that the mobility of a light solute ion can significantly accelerate its own solvation, specially in the underdamped limit. The latter result is also in excellent agreement with the computer simulations.

**Keywords.** Ionic mobility; solvation dynamics; dense dipolar liquids.

### 1. Introduction

Solvation dynamics has been the focus of intense research activities for the past few years (Bagchi 1989; Barbara and Jarzaba 1990; Fleming and Wolynes 1990; Bagchi and Chandra 1991). Recent computer simulations (Maroncelli 1991; Papazyan and Maroncelli 1991; Neria and Nitzan 1992; Perera and Berkowitz 1992), experimental (Rosenthal *et al* 1991) and theoretical studies (Bagchi and Chandra 1992; Cho *et al* 1992; Zhou *et al* 1992) have revealed several unusual results which have given rise to a renewed interest in this field. The solvation of ions in important dipolar liquids like water and acetonitrile was found to be complete in less than 100 fs with a biphasic decay (Rosenthal *et al* 1991; Neria and Nitzan 1992). On the other hand, in liquids like methyl alcohol and propylene carbonate, a much longer time, of the order of a few picoseconds, is required. Therefore, one needs to understand microscopically the behaviour of the time-dependent solvation energy in very short time as well as in longer time scales. In this communication we present a new, fully microscopic but simple expression of the solvation energy valid both in the underdamped and overdamped limits of momentum relaxation. This general expression for the solvation energy provides excellent agreement with computer simulation results in both the limits of momentum relaxation mentioned above. A general expression for the dissipative kernel is also presented. The latter is used to recover the two popular theories of solvation dynamics, namely, the molecular hydrodynamic theory (MHT) (Chandra and Bagchi 1989, 1991) and the memory function theory (MFT) (Fried and Mukamel 1990) from the general microscopic expression.

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We present a generalization of the hydrodynamic theory to include, for the first time, the motion of the solute in the case of the solvation of a light ion in a dipolar solvent. Here also, the theoretical results agree very well with the computer simulation.

## 2. Theory and results

### 2.1 Immobile solute ion

Solvation of an ion in a dipolar liquid requires the creation of a space- and time-dependent polarization  $\mathbf{P}(\mathbf{r}, t)$  of the solvent. The time-dependent solvation energy is expressed by the following equation

$$E_{\text{sol}}(t) = -\frac{1}{2} \int d\mathbf{r} \mathbf{E}_0(\mathbf{r}) \cdot \mathbf{P}(\mathbf{r}, t). \quad (1)$$

Here,  $\mathbf{E}_0(\mathbf{r})$  is the bare ionic electric field produced at the position  $\mathbf{r}$ . The ion is assumed to be immobile and located at the origin of the coordinate axes.

The polarization of the solvent molecules is given by the angular integration of the position ( $\mathbf{r}$ ) and orientation ( $\boldsymbol{\Omega}$ ) dependent number density,  $\rho(\mathbf{r}, \boldsymbol{\Omega}, t)$ , multiplied by the dipole moment vector  $\boldsymbol{\mu}$  (Bagchi and Chandra 1991). The latter can be obtained from the molecular hydrodynamic theory (MHT), by solving the coupled conservation equations of number and momentum densities. In this description, the relaxations of the rotational and the translational momentum densities depend critically on the interaction part of the free energy that explicitly depends on the intermolecular correlations. It also depends on the position and time-dependent rotational and translational dissipative kernels. It is convenient to solve the equations of motion of these hydrodynamic variables by using the Fourier and Laplace transformations in space and time, respectively. For the calculation of the solvation energy, we need the longitudinal part of the wavevector and frequency dependent polarization, which is given by (Bagchi and Chandra 1992)

$$\mathbf{P}_L(\mathbf{k}, z) = \frac{\mathbf{P}_L(\mathbf{k}, t=0)}{z + \Sigma(\mathbf{k}, z)}, \quad (2)$$

where

$$\Sigma(\mathbf{k}, z) = \frac{2k_B T f_L(k)}{I\Gamma_R(k, z)} + \frac{pk^2 f_L(k)}{I\Gamma_T(k, z)} \quad (3)$$

Here, the wavevector  $\mathbf{k}$  is the Fourier variable conjugate to  $\mathbf{r}$ .  $f_L(k) = 1 - (\rho_0/4\pi)c_{110}(k)$ ,  $c_{110}$  is the (110) coefficient of the spherical harmonic expansion of the two-particle direct correlation function (Gray and Gubbins 1984) and  $\rho_0$  is the average number density of the solvent.  $I$  is the moment of inertia of a solvent molecule.  $\Gamma_R(k, z)$  and  $\Gamma_T(k, z)$  are the rotational and the translational dissipative kernels respectively. For a molecule of mass  $m$  and diameter  $\sigma$ , the translational parameter  $p = I/m\sigma^2$  determines the relative importance of the rotational and translational modes of the solvent molecules. Equation (2) can be used to obtain the frequency-dependent solvation energy  $E_{\text{sol}}(z)$  by using it in the Laplace transformed form of (1).  $E_{\text{sol}}(t)$  can be easily obtained by numerically Laplace-inverting  $E_{\text{sol}}(z)$ .

Next the dissipative kernels in (2) and (3) are replaced by more useful quantities.

From the linear response theory, the polarization  $\mathbf{P}(\mathbf{k}, z)$  can be expressed in terms of the wavevector and frequency dependent dielectric function  $\varepsilon(k, z)$  as

$$1 - \varepsilon^{-1}(k, z) = \frac{4\pi\beta}{V} [C_{ML}(k, t = 0) - zC_{ML}(k, z)], \quad (4)$$

where the longitudinal part of the collective dipole moment correlation function,  $C_{ML}$  is  $\langle \mathbf{P}_L(-\mathbf{k}, t = 0) \mathbf{P}_L(\mathbf{k}, z) \rangle \cdot \beta = (k_B T)^{-1}$  and  $V$  is the volume of the system. Next, we use (2) to express  $\Gamma(k, z)$  in terms of  $\varepsilon(k, z)$ . This leads to the following exact relation

$$\Sigma(k, z) = \frac{z\varepsilon(k)[\varepsilon(k, z) - 1]}{\varepsilon(k) - \varepsilon(k, z)}. \quad (5)$$

Use of this dissipative kernel in (2) along with (5) provides the following general expression for the solvation energy of an ion in a dipolar liquid,

$$E_{\text{solv}}(z) = -\frac{Q^2}{\pi} \int_0^\infty dk \left( \frac{\sin k}{k} \right)^2 \frac{1}{z} \left[ \frac{1}{\varepsilon(k, z)} - \frac{1}{\varepsilon(k)} \right]. \quad (6)$$

Equation (6) is the main result of this communication. Equations (5) and (6) are particularly interesting because both of them are exact and general. This general expression for the solvation energy closely resembles the recently derived equation for the translational dielectric friction on a moving ion (Bagchi 1991) which is given by

$$\zeta_{\text{DF}}^{\text{ion}}(z) = \frac{2Q^2}{3\pi r_c^3} \int_0^\infty dk \sin^2 k \frac{1}{z} \left[ \frac{1}{\varepsilon(k)} - \frac{1}{\varepsilon(k, z)} \right]. \quad (7)$$

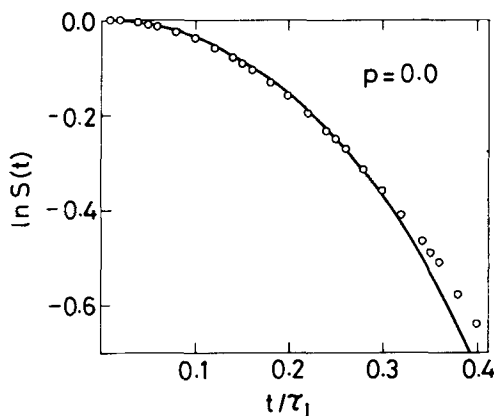
We now discuss how (5) and (6) can be used to recover two currently popular theories of solvation dynamics, namely, the molecular hydrodynamic theory (MHT) (Chandra and Bagchi 1989, 1991) and the memory function theory (MFT) (Fried and Mukamel 1990). It is evident from (5) and (6) that the knowledge of the dissipative kernel  $\Gamma(k, z)$  is a necessary prerequisite for the calculation of solvation energy. Unfortunately, an accurate determination of this kernel is not possible except at the two limiting conditions of long wavelength and large wavenumber. If the dissipative kernel is replaced by its 'collective' or the long wavelength (i.e.  $k \rightarrow 0$ ) limiting value, the resultant expression for the solvation energy reduces exactly to that of the memory function theory of Fried and Mukamel (1990). Note that this can be obtained directly from (5) by setting  $k = 0$ , that is one assumes that  $\Gamma(k, z) = \Gamma(k = 0, z)$ . Originally, it was derived by using the language of memory function formalism. On the other hand, if this kernel is approximated by its 'local' or the large wavenumber limit, it is then equal to the friction  $\zeta(z)$  on a single solvent molecule. This is the approximation necessary to obtain the Chandra–Bagchi formulation (Bagchi and Chandra 1991).

The results of a fully microscopic calculation of the molecular hydrodynamic theory in the underdamped and the overdamped limits of momentum relaxation are presented below. As usual, the results are discussed in terms of the solvation time correlation function,  $S(t)$ , defined as

$$S(t) = \frac{E_{\text{solv}}(t) - E_{\text{solv}}(\infty)}{E_{\text{solv}}(0) - E_{\text{solv}}(\infty)}. \quad (8)$$

2.1a *The underdamped limit:* Here the working system is the model Stockmayer fluid, where the molecules interact via Lennard–Jones and dipolar interactions. This system is interesting because computer simulation results exist for this system (Neria and Nitzan 1992; Perera and Berkowitz 1992). We first calculate the single particle friction. Here, dielectric friction is the only source of rotational friction. Consequently, in the extremely short time scale of underdamped momentum relaxation, the rotational single-particle friction can be very well approximated from the angular velocity autocorrelation function in terms of the orientational Einstein frequency (Bagchi and Chandra 1992). The collective approximation of the dissipative kernel is easily calculable in this limit in terms of the frequency dependent dielectric function which can again be accurately calculated in the high frequency limit. Both the single particle and the collective limits of the kernel were used to obtain an interpolating form of  $\Gamma(\mathbf{k}, z)$  (Roy and Bagchi 1992) that enabled us to find the solvation energy accurately from (3). Note that no adjustable parameter has been used in this calculation. The static orientational correlations are obtained from the mean spherical approximation (MSA) (Gray and Gubbins 1984) for a dipolar hard sphere by mapping the Lennard–Jones system into the hard sphere fluid (Bagchi and Chandra 1992).

The resultant solvation energy has a Gaussian decay in time which is significantly faster than a free inertial decay. This is shown in figure 1 where the prediction of MHT in the absence of solvent translational modes is compared with the simulation results of Neria and Nitzan (1992) for the same system of Stockmayer fluids. The theory is in almost perfect agreement with the simulation. Here, the translational motion of the solute is frozen by taking solvent molecules of infinite mass. We have also found that in the presence of the translational modes of the solvent, the solvation becomes accelerated as expected (Roy and Bagchi 1992).

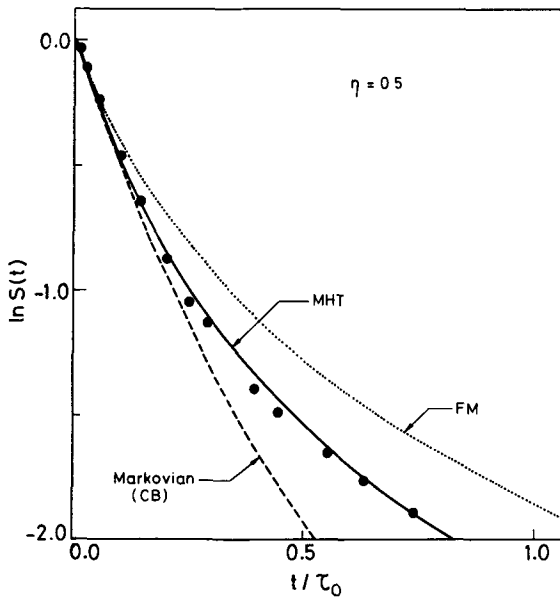


**Figure 1.** The comparison between the present theory and the computer simulation results on ionic solvation in an underdamped Stockmayer liquid. Here we plot the normalized solvation energy time correlation function  $S(t)$  for the case when both the solute ion and the solvent molecules are translationally frozen, that is  $p = 0.0$  for the solvent. The solid line represents the molecular hydrodynamic theory (MHT) while the simulation results (Neria and Nitzan 1992) are shown by open circles. The latter compare extremely well with the theoretical predictions. The details of the parameters used are as follows. Reduced density,  $\rho^*(= \rho\sigma^3) = 0.81$ , reduced dipole moment  $\mu^{*2}(= \mu^2/k_B T\sigma^3) = 1.32$ , reduced temperature  $T^* = (k_B T/\epsilon) = 1.23$ . Here  $\sigma$  is solvent molecular diameter,  $\mu$  is the dipole moment,  $\epsilon$  is the usual Lennard–Jones energy parameter and  $k_B$  is the Boltzmann constant. For details see Roy and Bagchi (1992).

2.1b *The overdamped limit:* The Brownian dipolar lattice (Zwanzig 1963) provides a particularly useful system to study the overdamped limit, where the momentum relaxation can be neglected. In this case, the single-particle friction is the sum of the bare friction and the dielectric friction (DF). The bare part is related to the bare rotational diffusion coefficient  $D_0$  by the Einstein relation. It has a significant non-zero value and is supplied from outside (Zwanzig 1963). The polarity of this system is characterized by the dimensionless quantity  $\eta$ , defined as  $\eta = \beta\mu^2/3a^3$ , where  $\mu$  is the value of the dipole moment and  $a$  is the cell length. The dielectric friction is obtained from the microscopic expression provided by Vijayadamodar *et al* (1989). The predicted decay of the solvation energy for the polarity parameter  $\eta = 0.50$  is compared with the computer simulation results in figure 2. We have also shown the results from the Fried–Mukamel theory and the Markovian version of the hydrodynamic theory in the same figure. The last one neglects the dielectric friction completely. Evidently, inclusion of  $\zeta_{DF}$  provides excellent agreement with the simulation data. The details of this calculation are available elsewhere (Komath and Bagchi 1992).

## 2.2 Mobile solute

Although most of the experimental studies are concerned with situations where the solute ion is immobile, solvation of lighter particles like protons or lithium cation may derive important contributions from the motion of the solute itself. We now discuss an ‘effective’ hydrodynamic description which takes into account, for the first time, the coupled solute–solvent dynamics when the solute to solvent mass ratio is



**Figure 2.** The calculated solvation energy time correlation function,  $S(t)$ , for solvation of an ion in a Brownian dipolar lattice is compared with the simulation results. The solid circles are the simulation results for the polarity parameter  $\eta = 1/2$ . The solid line is the result of the full hydrodynamic calculation with the frequency dependent dielectric friction. The dotted line is the Fried–Mukamel (1990) theory and the dashed line represents the predictions of the Markovian theory. For details, see Komath and Bagchi (1992).

not too small. Here, the origin is fixed on the moving ion so that the solvent molecules move with an effective mass and a relative velocity with respect to the solute ion. Correspondingly, there is a change in the velocity autocorrelation function and hence in the friction retarding the motion of the solvent molecules.

A composite velocity autocorrelation function  $c_v^{\text{comp}}(z)$  which is related to the complete dielectric friction  $\zeta_{\text{comp}}(z)$  is defined by the following equation

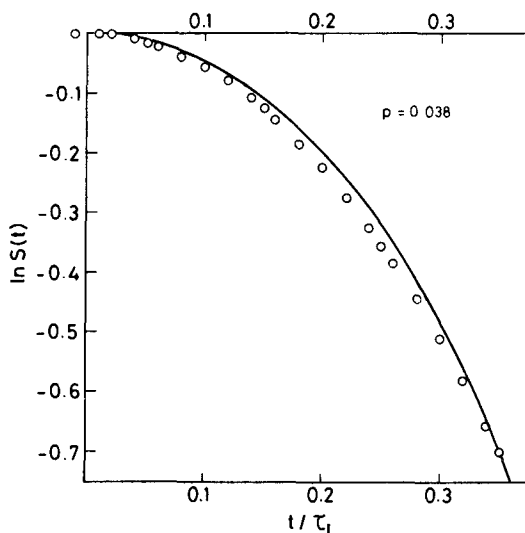
$$c_v^{\text{comp}}(z) = [c_v^{\text{comp}}(t=0)]/[z + \zeta_{\text{comp}}(z)]. \quad (9)$$

$\zeta_{\text{comp}}(z)$  derives significant contribution from both the solute and the solvent. For a solute mass  $M$  and solvent mass  $m$ ,  $c_v^{\text{comp}}(t)$  is given by the following linear response expression at very short times (Roy and Bagchi 1992)

$$c_v^{\text{comp}}(t) = \frac{k_B T}{m} \exp(-\frac{1}{2}\Omega_0^2 t^2) + \frac{k_B T}{M} \exp(-\frac{1}{2}\Omega_M^2 t^2). \quad (10)$$

Here,  $\Omega_0$  and  $\Omega_M$  are the Einstein frequencies of the solvent molecule and the solute ion respectively. The rest of the treatment remains the same as that of the immobile solute mentioned earlier in this section.

This generalization of the molecular hydrodynamic theory to include solute motion leads to very good agreement between theory and simulation in the underdamped limit, as shown in figure 3. As expected, the time constant of the Gaussian decay is much smaller than that observed when the solute motion is absent.



**Figure 3.** The solvation energy time correlation function,  $S(t)$ , is plotted for the case where both the solute ion and the solvent molecules are translationally mobile. Here comparison is made between the predictions of the MHT (the solid line) and the computer simulation results (the open circles). The parameters used:  $p = 0.038$ , the solute-solvent mass ratio = 0.5 and the solute-solvent size ratio = 0.875, as in the simulation of Neria and Nitzan (1992).

### 3. Conclusion

In this communication, we have presented a general microscopic expression for the solvation energy which is equally applicable to both the underdamped and the overdamped limits of momentum relaxation. It was also shown that the translational motion of a light solute ion makes important contributions to its own solvation. The predictions of this microscopic theory are in excellent agreement with simulation results not only for the underdamped Stockmayer liquid but also for the Brownian dipolar lattice. It is important to realize that our calculations in both the cases are fully microscopic. Moreover, we have shown that both the Chandra–Bagchi and the Fried–Mukamel formulations of solvation dynamics are just the two extreme limits of the general microscopic expression.

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