

## Microscopic expression for time-dependent solvation energy of ions and dipoles in dense polar liquids<sup>†</sup>

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**Abstract.** Microscopic expressions for the time dependence of solvation energies of newly created ions and dipoles in a dense dipolar liquid are presented. It is shown that: (i) the dynamics of solvation of an ion differ considerably from that of a dipole, especially that the long wavelength ( $k = 0$ ) component of solvent response is totally absent for dipoles, and (ii) the translational modes of the solvent molecules lead to a breakdown of Onsager's conjecture on the distance dependence of solvent polarization relaxation.

Recent theoretical (Wolynes 1987; Loring and Mukamel 1987; Bagchi and Chandra 1988, 1989; Castner *et al* 1988; Chandra and Bagchi 1988, 1989b; Rips *et al* 1988) and experimental (Castner *et al* 1987, 1988; Kahlow *et al* 1987, 1988, 1989; Maroncelli and Fleming 1987; Simon and Su 1987; Maroncelli *et al* 1988; Simon 1988; Barbara and Jarzaba 1988) studies on solvation dynamics have led to a considerably improved understanding of the mechanism of solvation. Clearly, an understanding of this phenomena is fundamental to our understanding of liquid phase chemistry.

In this communication we present microscopic expressions for the time dependence of solvation energies of ions and dipoles in a dense dipolar liquid. Our expressions include, for the first time, the contributions of the solvent translational modes in the polarization relaxation subsequent to the creation of the ion or the dipole. We find that the solvation dynamics of an ion and that of a dipole differ considerably from each other. In particular, the long wavelength ( $k = 0$ ) mode of solvent response is absent in dipolar solvation while it makes a significant contribution in ionic solvation. We further show that the well-known Onsager (1977) conjecture, which states that the polarization relaxation of solvent molecules closer to the solute ion takes place at a slower rate than of those which are away in the **bulk**, breaks down in the presence of a sizeable translational contribution.

The time-dependent solvation energy is given by the following expression

$$E_{\text{solv}}(t) = -\frac{1}{2} \int d\mathbf{r} \mathbf{D}(\mathbf{r}) \cdot \delta \mathbf{P}(\mathbf{r}, t), \quad (1)$$

where  $\mathbf{D}(\mathbf{r})$  is the displacement vector of the solute ion or the dipole and  $\delta \mathbf{P}(\mathbf{r}, t)$  is the polarization fluctuation of the solvent because of the creation of the polar solute

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molecule. It is convenient to work in the Fourier space with  $k$  as the Fourier variable. In Fourier space, the expression for solvation energy is given by

$$E_{\text{solv}}(t) = -\frac{1}{2}(2\pi)^{-3} \int d\mathbf{k} \mathbf{D}(\mathbf{k}) \cdot \delta\mathbf{P}(\mathbf{k}, t), \quad (2)$$

where  $\mathbf{D}(\mathbf{k})$  and  $\delta\mathbf{P}(\mathbf{k}, t)$  are, respectively, the Fourier transforms of  $\mathbf{D}(\mathbf{r})$  and  $\delta\mathbf{P}(\mathbf{r}, t)$ . The polarization fluctuation of a dipolar solvent is related to the fluctuation in the position and orientation dependent density by the following relation

$$\delta\mathbf{P}(\mathbf{r}, t) = \int d\boldsymbol{\omega} \hat{\boldsymbol{\alpha}}(\boldsymbol{\omega}) \delta\rho(\mathbf{r}, \boldsymbol{\omega}, t), \quad (3)$$

where  $\delta\rho(\mathbf{r}, \boldsymbol{\omega}, t) = \rho(\mathbf{r}, \boldsymbol{\omega}, t) - \rho_{\text{eq}}(\mathbf{r}, \boldsymbol{\omega})$  and  $\hat{\boldsymbol{\alpha}}(\boldsymbol{\omega})$  is a unit vector given by angles  $\boldsymbol{\omega}$ . For a homogeneous solvent,  $\rho_{\text{eq}}(\mathbf{r}, \boldsymbol{\omega}) = \rho_0/4\pi$ ,  $\rho_0$  is the average number density of the pure solvent. Thus; an equation of motion of the polarization vector can be obtained from an equation of motion of the density field. We assume that the decay of the density fluctuation is given by a generalized Smoluchowski equation, described earlier (Chandra and Bagchi 1988, 1989a; Calef and Wolynes 1983). It is straightforward to derive and solve the equation of motion for wavevector-dependent polarization fluctuation. The longitudinal component of the wavevector-dependent polarization fluctuation vector is then given by (Chandra and Bagchi 1988, 1989a)

$$P_L(k, t) = P_L(k) \exp[-t/\tau_L(k)], \quad (4)$$

with

$$\tau_L(k) = (2D_R)^{-1} \{ [1 + p'(k\sigma)^2] [1 - (\rho_0/3)(C_\Delta + 2C_D)] \}^{-1}, \quad (5)$$

where  $p'$  is equal to  $D_T/(2D_R\sigma^2)$ ,  $\sigma$  is the solvent molecular diameter, and  $D_R$  and  $D_T$  are, respectively, the rotational and translational diffusion coefficients of the solvent molecules. Thus,  $p'$  is a convenient measure of the relative importance of the translational diffusion mechanism in polarization relaxation.  $P_L(k)$  is the value of  $P_L(k, t)$  at  $t=0$ .  $C_\Delta$  and  $C_D$  are the anisotropic parts of the two-particle direct correlation function and are defined by the following equations

$$c(\mathbf{k}, \boldsymbol{\omega}, \boldsymbol{\omega}') = c_{\text{iso}}(\mathbf{k}) + \hat{\boldsymbol{\alpha}}(\boldsymbol{\omega}) \cdot \mathbf{C}(\mathbf{k}) \cdot \hat{\boldsymbol{\alpha}}(\boldsymbol{\omega}') + \dots, \quad (6)$$

$$\mathbf{C}(\mathbf{k}) = C_\Delta \mathbf{I} + C_D \mathbf{D}, \quad (7)$$

$$\mathbf{D} = 3\hat{k}\hat{k} - \mathbf{I}, \quad (8)$$

where  $c(\mathbf{k}, \boldsymbol{\omega}, \boldsymbol{\omega}')$  is the Fourier transform of the two particle direct correlation function,  $c_{\text{iso}}(\mathbf{k})$  is the Fourier transform of the isotropic part of the two particle direct correlation function and  $\hat{k}$  is a unit vector parallel to  $\mathbf{k}$ . The decomposition of the tensor  $\mathbf{C}(\mathbf{k})$ , as given by (7), is valid in the linearized theories of dipolar liquids (such as MSA, LHNC) (Gray and Gubbins 1984). In order to evaluate the solvation energy, we need the value of the function  $P_L(k)$  which is the initial value of the polarization. We assume that  $P_L(k)$  is given by the following expression

$$P_L(k) = -(1/4\pi) [1 - (1/\varepsilon(k))] \mathbf{D}(k), \quad (9)$$

where  $\varepsilon(k)$  is the wavevector-dependent static dielectric constant of the dipolar liquid. Recently, we have presented a microscopic calculation of  $\varepsilon(k)$  for a dipolar liquid

(Chandra and Bagchi 1989a) and have shown that  $\epsilon(k)$  has a rich structure as a function of  $k$ .

Since the displacement vector of ionic and dipolar field is known, we can combine the above equations to obtain microscopic expressions of time-dependent solvation energy for both ions and dipoles which we present below.

### Ionic solvation

The time dependence of solvation energy subsequent to a newly created ion of charge  $Ze$  at time  $t=0$  is given by

$$E_{\text{solv}}(t) = \frac{(Ze)^2}{\pi} \int_0^\infty dk \left[ 1 - \frac{1}{\epsilon(k)} \right] \exp[-t/\tau_L(k)] \cdot \left[ \int_{k \cdot f(a,R)}^\infty dx \frac{\sin x}{x} \right]^2, \quad (10)$$

where  $R$  is the solute-solvent size ratio, equal to  $2a/\sigma$ , where  $a$  is the radius of the solute ion (assumed to be spherical) and  $f(a, R)$  is a cut-off value greater than or equal to  $a$ . This cut-off arises because of the finite size of the solute and solvent molecules and enters through the Fourier transformation of the polarization vector. The results are not critically dependent on this cut-off if an accurate  $\epsilon(k)$  is used. However, our earlier calculation (Chandra and Bagchi 1989a) has shown that we do not have a reliable expression for  $\epsilon(k)$  for large values of  $k$ . This is unfortunate because this is the range which controls the cut-off. A reasonable approximation is to set  $f(a, R) = r_c = a + \sigma/2$ . Note that in the continuum model calculations (such as the one performed by Born many years ago),  $f(a, R) = a$ , that is, the molecular nature of the solvent molecules is ignored. The cut-off  $r_c$  is more realistic.

### Dipolar solvation

In this case the polarisation vector consists of both longitudinal and transverse components, so the solvation energy is a sum of two terms. The time-dependence of solvation energy of a newly created dipole  $\mu (= \mu \hat{\mu})$  at time  $t=0$  is given by the following expression

$$E_{\text{solv}}(t) = \frac{\mu^2}{\pi a^3} \left\{ 2 \int_0^\infty dq' \left( 1 - \frac{1}{\epsilon(q')} \right) j_1^2[k \cdot f(a, R)] \exp[-t/\tau_L(q')] \times \right. \\ \times \left[ \frac{a^2}{f^2(a, R)} \right] + \int_0^\infty dq' q'^2 \left[ 1 - \frac{1}{\epsilon(q')} \right] \exp[-t/\tau_L(q')] \times \\ \left. \times \left[ \frac{\sin[k \cdot f(a, R)]}{k \cdot f(a, R)} + \int_{k \cdot f(a, R)}^\infty dx \frac{\cos x}{x} \right]^2 \right\}, \quad (11)$$

where  $j_1(z)$  is the spherical Bessel function of order unity and argument  $z$  and  $q' = \mathbf{k}a$ . We have evaluated the integrations involved in (10) and (11); the detailed results will be presented elsewhere (Chandra and Bagchi 1989b). In the following we summarize the main results of this communication.

(i) As evident from (10) and (11),  $E_{\text{solv}}(t)$  depends on the value of the static dielectric constant, on density of the host solvent, on the parameter  $p'$  and also on the solute-

solvent size ratio,  $R$ . The decay is, in general, non-exponential for both ions and dipoles.

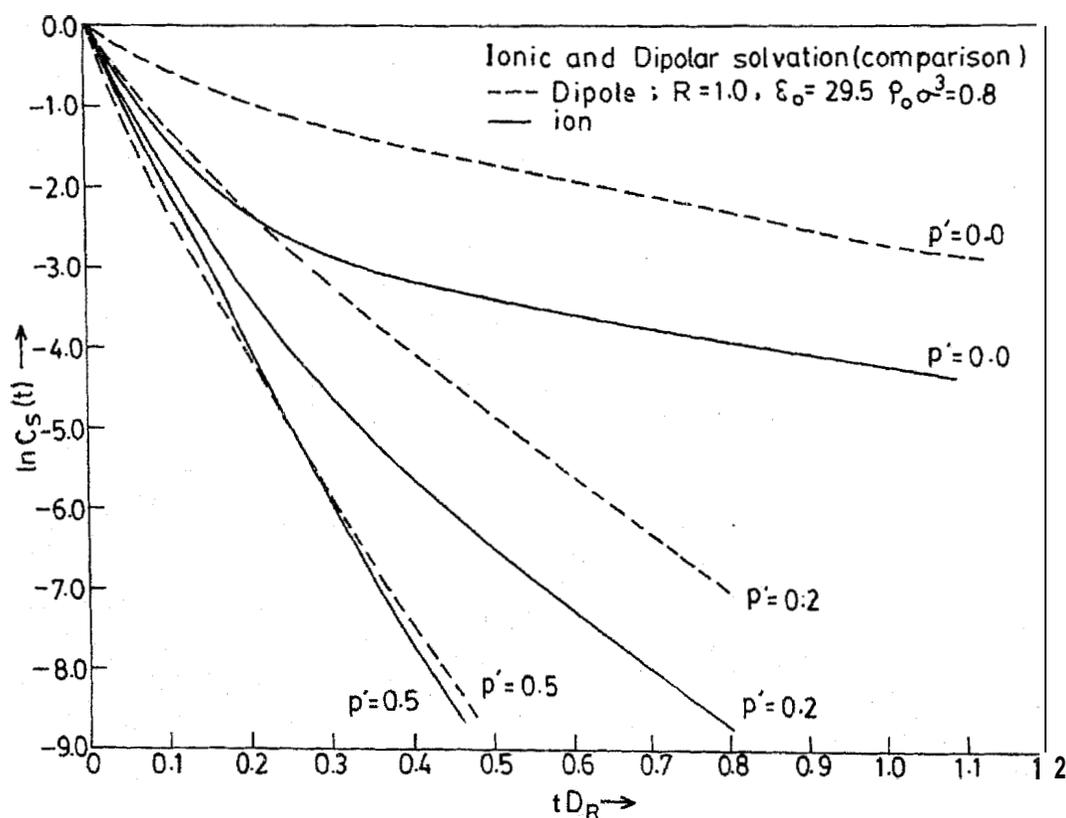
(ii) In the case of ionic solvation, the relaxation of  $E_{\text{solv}}(t)$  becomes faster as  $p'$  increases and in fact for sufficiently large  $p'$  ( $p' \geq 0.5$ ) the long time decay approaches the continuum limit of relaxation given by the longitudinal relaxation time constant  $\tau_L (= \tau_L(k=0))$ . The continuum limit is also recovered for large  $R$ .

(iii) We can calculate position and time-dependent polarization by Fourier inverting (4) and testing the well-known conjecture of Onsager (1977). We find that although Onsager's conjecture is accurate for  $p' = 0$  (or for very small  $p'$ ), it breaks down when  $p'$  is significant ( $p' \geq 0.5$ ). In the latter limit, the nearest-neighbour solvent molecules relax fastest.

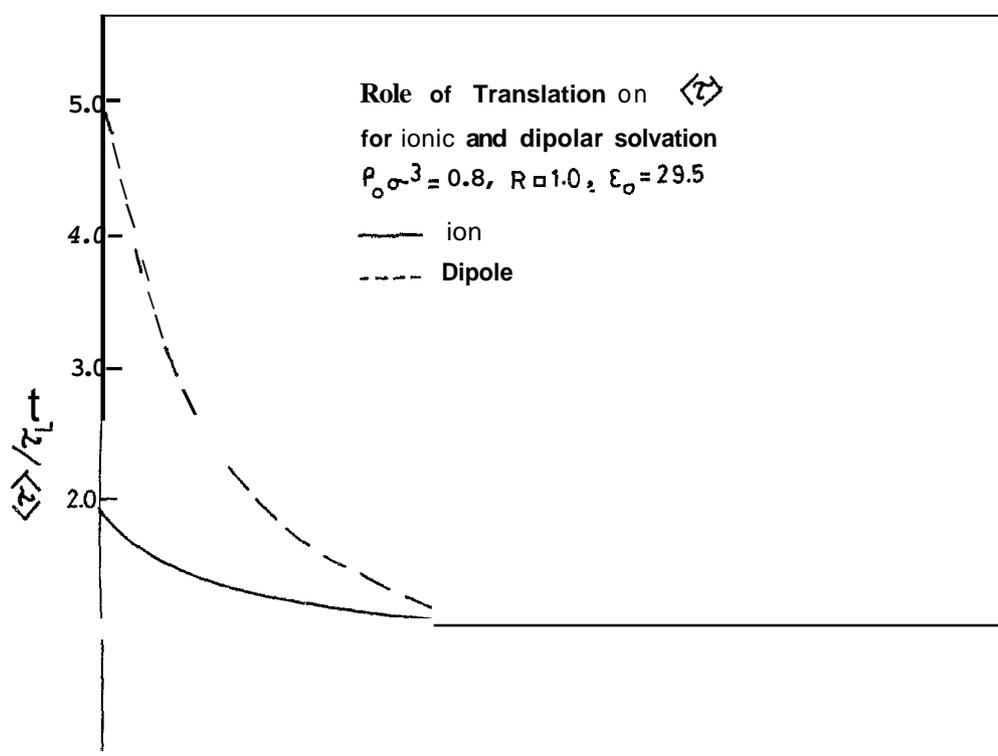
(iv) Equation (11) gives the rather surprising result that the *long wavelength,  $k = 0$ , component of solvent response is totally absent for dipolar solvation*. Thus, the continuum model may be grossly inaccurate in this case because the model includes only the long wavelength limit of solvent polarization relaxation.

We have shown that the dynamics of ionic and dipolar solvation are quite different from each other, especially that the role of solvent translational modes are different in the two cases. This is shown in figure 1 where we have plotted the solvation energy time correlation function, defined by

$$C_s(t) = E_{\text{solv}}(t)/E_{\text{solv}}(t=0), \quad (12)$$



**Figure 1.** The dependence of the solvation energy time correlation function  $C_s(t)$  for ionic and dipolar solvation on translational diffusion. The calculated values of  $C_s(t)$  are plotted against time for several different values of the parameter  $p'$ . The values of the static dielectric constant ( $\epsilon_0$ ), the reduced density ( $\rho_0 \sigma^3$ ) and the solute-solvent size ratio ( $R$ ) are indicated in the figure. The calculations shown here were carried out by setting  $\epsilon(k) = \epsilon_0$  and  $f(a, R) = a$ .



**Figure 2** The dependence of the average relaxation time,  $\langle \tau \rangle$ , for ionic and dipolar solvation on translational diffusion. The calculated values of  $\langle \tau \rangle$  are plotted against  $p'$  for both ionic and dipolar solvation. The values of the other parameters remain the same as in figure 1.

versus time for several values of  $p'$ . It can be seen from figure 1, that for  $p' = 0$ , that is, when the translational contribution is absent, the dipolar solvation is slower than the ionic. This is because the relaxation of the  $k = 0$  mode is the fastest in the absence of translational diffusion (Chandra and Bagchi 1988). The situation, however, changes drastically when a sizeable translational component is present. For  $p' = 0.5$ , the dipolar and the ionic solvation rates are comparable, as shown in figure 1. For larger  $p'$ , the dipolar solvation becomes faster than the ionic. This is illustrated in figure 2 where the average solvation energy time,  $\langle \tau \rangle$ , defined by

$$\langle \tau \rangle = \int_0^{\infty} C_s(t) dt, \quad (13)$$

is plotted against  $p'$  for both dipolar and ionic solvation. It is clear that for large  $p'$ , dipolar solvation proceeds at a faster rate. This is because translational modes are more important in the dipolar solvation than in the ionic case.

The results presented in this paper may have important consequences in many charge transfer reactions. Especially, the role of short range correlations and of translational diffusion mechanism should not be neglected as was usually done in the past.

**References**

- Bagchi B and Chandra A 1988 *Proc. Indian Acad. Sci. (Chem. Sci.)* **100** 353  
Bagchi B and Chandra A 1989a *Chem. Phys. Lett.* (submitted)  
Bagchi B and Chandra A 1989b *J. Chem. Phys.* (in press)  
Barbara P F and Jarzeba W 1988 *Acc. Chem. Res.* **21** 195  
Calef D F and Wolynes P G 1983 *J. Chem. Phys.* 78 4145  
Castner E W Jr, Fleming G R and Bagchi B 1988a *Chem. Phys. Lett.* **143** 270  
Castner E W Jr, Fleming G R, Bagchi B and Maroncelli M 1988b *J. Chem. Phys.* **89** 3519  
Chandra A and Bagchi B 1988 *Chem. Phys. Lett.* **151** 47  
Chandra A and Bagchi B 1989a *J. Chem. Phys.* **90** (in press)  
Chandra A and Bagchi B 1989b *J. Phys. Chem.* (submitted)  
Gray C G and Gubbins K E 1984 *Theory of molecular fluids* (Oxford: Clarendon) vol. 1  
Kahlow M A, Kang T-J and Barbara P F 1987 *J. Phys. Chem.* **91** 6452  
Kahlow M A, Rang T-J and Barbara P F 1988 *J. Chem. Phys.* **88** 2372  
Kahlow M A, Jarzeba W, Kang T-J and Barbara P F 1989 *J. Chem. Phys.* (in press)  
Loring R F and Mukamel S 1987 *J. Chem. Phys.* **87** 1272  
Maroncelli M and Fleming G R 1987 *J. Chem. Phys.* **86** 6221  
Maroncelli M, Castner E W Jr, Bagchi B and Fleming G R 1988 *Farad. Discuss. Chem. Soc. (Solvation)* **85** 1  
Onsager L 1977 *Can. J. Chem.* **55** 1819  
Rips I, Klafter J and Joriner J 1988 *J. Chem. Phys.* **88** 6425  
Simon J D 1988 *Acc. Chem. Phys.* **21** 128  
Simon J D and Su S -G 1987a *J. Chem. Phys.* **87** 7016  
Simon J D and Su S -G 1987b *J. Phys. Chem.* **91** 2693  
Wolynes P G 1987 *J. Chem. Phys.* **86** 5133