

## 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 Jarzeba 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

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

where  $\delta\rho(\mathbf{r}, \omega, t) = \rho(\mathbf{r}, \omega, t) - \rho_{\text{eq}}(\mathbf{r}, \omega)$  and  $\hat{\alpha}(\omega)$  is a unit vector given by angles  $\omega$ . For a homogeneous solvent,  $\rho_{\text{eq}}(\mathbf{r}, \omega) = \rho_0/4\pi$ ,  $\rho_0$  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

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

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  $t=0$ .  $C_A$  and  $C_D$  are the anisotropic parts of the two-particle direct correlation function and are defined by the following equations

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

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

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

where  $c(\mathbf{k}, \omega, \omega')$  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

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

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







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