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# Dynamics of polarization relaxation in a dipolar mixture at a solid–liquid interface

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Dynamics of polarization relaxation in a dipolar mixture at solid–liquid interface is investigated theoretically by using time dependent density functional theory. The time dependence of the building up of polarization of different dipolar species next to a newly charged solid surface is calculated by solving both Markovian and non-Markovian equations of motion for density and momentum variables. The inhomogeneity of the interface is taken into account in the dynamical theory. The theory also includes the various intra- and interspecies molecular correlations and the surface–molecule interactions. Both the molecular size and the dipole moment of various species in the dipolar mixture can be unequal. The initial inhomogeneity of the interface is calculated by using a weighted density functional theory. Explicit numerical results are obtained for the polarization relaxation in a binary dipolar liquid at varying distances from the solid surface and the dynamics of interfacial relaxation of the two species are compared with that in the bulk phase. A slowing down of the rate of relaxation is found for interfacial molecules of both the species. However, the extent of slowing down is found to be different for different species. Also, the rate of relaxation is found to change nonmonotonically with distance from the surface due to the layering of solvent molecules at the interface. © 2000 American Institute of Physics. [S0021-9606(00)51425-1]

## I. INTRODUCTION

An understanding of the dynamical behavior of dipolar molecules in the vicinity of solid surfaces is extremely important for investigations of many electrochemical and surface processes. For example, the solvent relaxation near a charged electrode or a membrane can influence the rates of electron transfer and other chemical processes occurring at these interfaces. Many recent studies have investigated the dynamical properties of pure dipolar liquids near uncharged and charged solid surfaces by means of computer simulations<sup>1–14</sup> and analytical theories.<sup>15</sup> These studies have provided significant information about the dynamical behavior of a pure dipolar liquid at solid–liquid interfaces. In contrast, relatively scant attention has been focused on the dynamics of mixed dipolar liquids near solid surfaces, despite great importance of such interfaces in electrochemistry and surface science. In fact, we are aware of only one simulation study on this problem which considered a binary dipolar liquid in contact with an uncharged surface<sup>16</sup> and, to the best of our knowledge, no analytical theory has yet been developed to investigate the molecular relaxation in a dipolar mixture near a solid surface. Consequently, the dynamical behavior of solid–liquid interfaces involving mixed dipolar liquids is poorly understood. The dynamics of such an interface is expected to be much more complex than that of a pure solvent–solid interface because of different degree of inhomogeneity and different time scales of relaxation of different species at the interface. These differences can arise from unequal molecular size, dipole moment and also from unequal density of the different components forming the dipolar mixture. The

goal of the present work is to develop an analytical theory to investigate this molecular relaxation in a mixed dipolar liquid in the vicinity of a solid surface.

In the present work, we employ time dependent density functional theory<sup>17,18</sup> to derive equations for the time dependence of inhomogeneous polarization in a multicomponent dipolar mixture next to a charged surface. The time dependent density functional theory has been proved to be a very useful and versatile tool for the studies of dynamics of both homogeneous and inhomogeneous systems and it is employed here for the first time to explore interfacial relaxation in a mixed dipolar liquid. The theory properly includes the initial inhomogeneity of the interfacial mixture, the intra- and interspecies molecular correlations, the surface–solvent interactions and also the effects of inertial motion and time dependent rotational friction of solvent molecules of various species. The initial inhomogeneity is calculated by using the weighted density functional approach which has been shown to be very accurate in describing the structure of both pure and mixed liquids near hard walls.<sup>19–24</sup> We have obtained numerical results for polarization relaxation in a binary dipolar mixture at various times and at various distances from the charged surface. Both the molecular sizes and the dipole moments of the two species are unequal. The rate of polarization relaxation is found to be slower in the interfacial region of high solvent density. However, the extent of slowing down is found to be different for different species. Also, the relaxation rate changes nonmonotonically with distance from the surface for both the species due to the presence of molecular layering in the interfacial region. The effects of memory and inertial motion of solvent molecules on the interfacial relaxation are also calculated and the results are compared with those obtained by ignoring these effects. The relaxation at the surface is always found to be slower than

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that in the bulk, although the rate as such increases to some extent when inertial and non-Markovian effects are included. Thus, the slowing down of the relaxation near the surface is found to be a rather general feature of interfacial relaxation.

The organization of the rest of the paper is as follows. In Sec. II, we describe the theory and in Sec. III, we present the numerical results. Our conclusions are summarized in Sec. IV.

## II. THEORY

We consider a dipolar mixture consisting of dipolar molecules of  $n$  different species. The molecules are confined between two solid surfaces. The solvent molecules are modeled as dipolar hard spheres where both the molecular diameter and the dipole moment of various species can be different. The diameter and the dipole moment of a solvent molecule of species  $\alpha$  are denoted by  $\sigma_\alpha$  and  $\mu_\alpha$ , respectively. The solvent molecules also interact with the two solid surfaces which are considered to be infinite hard walls located at positions  $z=0$  and  $z=L$  along the  $z$  axis and  $x$  and  $y$  axes are parallel to the surfaces. The separation between the surfaces is taken to be large enough so that the interfacial structure at one surface is not affected by that at the other surface and there exists a homogeneous region of bulk mixture in the system. The surfaces were uncharged to begin with and suddenly they are uniformly charged to generate an electric field  $E$  along the  $z$  direction at time  $t=0$ . Because of the interaction of dipolar molecules of various species with the charge density of the surfaces, reorientation of solvent molecules in response to the external field occurs at time  $t > 0$  and as a result the dipolar mixture will get gradually polarized along the direction of the field. However, the dynamics of this polarization buildup would be different for different species because of unequal molecular diameter, polarity, and also the density of different species in the mixture. Besides, the initial inhomogeneity at the interface may also play an important role in determining the dynamics of polarization relaxation of various components near the solid surface. Our objective is to calculate the time dependence of this building up of solvent polarization of different species at different distances from the surfaces.

Theoretical and simulation studies have shown that the dipolar molecules would tend to lie parallel to the surface near an uncharged hard wall without creating any net polarization in the system.<sup>23-25</sup> Thus, initially the polarization was zero in the system but the density distributions of various species were highly inhomogeneous near the surfaces. We have calculated this initial inhomogeneity for a binary dipolar solvent of unequal molecular diameter, dipole moment, and density by using the weighted density functional approach of Denton and Ashcroft<sup>20</sup> and the results are shown in Fig. 1. The values of the various parameters used in the calculation are specified later in Sec. III. The densities of both the species are found to be highly inhomogeneous near the surfaces and they are fairly homogeneous in the middle portion of the system. Thus, both interfacial and bulk regions are contained in the present system. Since the inhomogeneity of the system is along  $z$  direction only, the density distribution becomes a function of  $z$  and  $\Omega$  (orientation) and time  $t$

(in nonequilibrium case). We denote the density of species  $\alpha$  by  $\rho_\alpha(z, \Omega, t)$ , so that  $\rho_\alpha(z, \Omega, t=0) = \rho_\alpha(z)/4\pi$ . We note that the time dependent polarization of species  $\alpha$ ,  $P_\alpha(z, t)$ , is related to density by the following equation:

$$P_\alpha(z, t) = \int d\Omega (\mu_\alpha \cdot \hat{z}) \rho_\alpha(z, \Omega, t), \quad (1)$$

where  $\hat{z}$  is a unit vector along the  $z$  direction.

The external field generated by the uniformly charged surfaces is constant which exerts a torque but no force on the dipolar molecules and, therefore, the primary mechanism of density relaxation involves orientational motion of solvent molecules of various species. The relaxation of the density can be described by the rotational continuity equation which is an exact equation involving the time dependent angular flux. The relaxation equation for the angular flux can be derived from time dependent density functional theory. We start with the following basic equations for the relaxation of density and angular flux of species  $\alpha$  in an inhomogeneous liquid mixture

$$\frac{\partial \rho_\alpha(z, \Omega, t)}{\partial t} = -\nabla_\Omega \cdot J_\alpha(z, \Omega, t), \quad (2)$$

$$\begin{aligned} \frac{\partial J_\alpha(z, \Omega, t)}{\partial t} &= -\frac{k_B T}{I_\alpha} \nabla_\Omega \left\{ \rho_\alpha(z, \Omega, t) - \frac{\rho_\alpha(z)}{4\pi} \right. \\ &\quad \times \sum_{\beta=1}^n \int dz' d\Omega' c_{\alpha\beta}(z, z', \Omega, \Omega') \\ &\quad \times \left. \left( \rho_\beta(z', \Omega, t) - \frac{\rho_\beta(z')}{4\pi} \right) \right\} \\ &\quad - \int_0^t dt' \zeta_\alpha(t-t') J_\alpha(z, \Omega, t') + \rho_\alpha(z, \Omega, t) \nabla_\Omega (\mu_\alpha \cdot E), \end{aligned} \quad (3)$$

where  $J_\alpha(z, \Omega, t)$  is the rotational flux of species  $\alpha$ ,  $T$  is the temperature,  $I_\alpha$  is moment of inertia, and  $\zeta_\alpha(t)$  is the time dependent rotational friction acting on a molecule of species  $\alpha$  and

$$c_{\alpha\beta}(z, z', \Omega, \Omega') = \int dx dy dx' dy' c_{\alpha\beta}(\mathbf{r}, \mathbf{r}', \Omega, \Omega'), \quad (4)$$

where  $c_{\alpha\beta}(\mathbf{r}, \mathbf{r}', \Omega, \Omega')$  is the two particle direct correlation function of species  $\alpha$  and  $\beta$  in the initial state. The last term of Eq. (3) includes the effects of interaction of solvent molecules of species  $\alpha$  with the external field produced by charge density of the surfaces. We note that Eq. (3) is a linear generalized Langevin equation for the relaxation of angular flux of a particular species in a mixture in presence of an external field. In the so-called diffusion limit, the friction  $\zeta_\alpha(t)$  is approximated by a delta function  $\zeta_\alpha(t) = \zeta_\alpha \delta(t)$  and the angular momentum relaxation is considered to be much faster than density relaxation<sup>17</sup> and in such

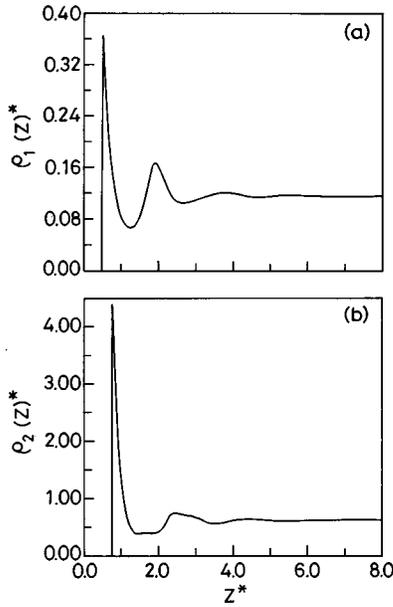


FIG. 1. The variation of solvent density of (a) species 1 and (b) species 2 with distance from the uncharged surfaces.

limiting situation the relaxation equation for the density of species  $\alpha$  can be described by the following diffusion equation:

$$\begin{aligned} \frac{\partial \rho_\alpha(z, \Omega, t)}{\partial t} &= D_{R;\alpha} \nabla_\Omega^2 \rho_\alpha(z, \Omega, t) - D_{R;\alpha} \nabla_\Omega^2 \frac{\rho_\alpha(z)}{4\pi} \\ &\times \sum_{\beta=1}^n \int dz' d\Omega' c_{\alpha\beta}(z, z', \Omega, \Omega') \\ &\times \left\{ \rho_\beta(z', \Omega', t) - \frac{\rho_\beta(z')}{4\pi} \right\} \\ &- \beta^* D_{R;\alpha} \nabla_\Omega \rho_\alpha(z, \Omega, t) \nabla_\Omega \mu_\alpha E \cos \theta, \end{aligned} \quad (5)$$

where  $D_{R;\alpha}$  is the rotational diffusion coefficient of species  $\alpha$  which is equal to  $k_B T / I_\alpha \zeta_\alpha$  and  $\beta^* = 1/k_B T$ . We note that although for an inhomogeneous system, the rotational diffusion coefficient should depend on position, in the present work it is taken to be a constant for simplicity.

In the present work, the direct correlation function for the initial state of the solvent is taken to be the same as the one of uniform liquid at the same average density. For convenience, we expand the direct correlation function in terms of angular functions as follows:

$$\begin{aligned} c_{\alpha\beta}(\mathbf{r}, \mathbf{r}', \Omega, \Omega') &= c_{\alpha\beta}^{000}(|\mathbf{r}-\mathbf{r}'|) + c_{\alpha\beta}^{110}(|\mathbf{r}-\mathbf{r}'|) \phi^{110}(\Omega, \Omega') \\ &+ c_{\alpha\beta}^{112}(|\mathbf{r}-\mathbf{r}'|) \phi^{112}(\Omega, \Omega', \hat{r}), \end{aligned} \quad (6)$$

where the angular functions  $\phi^{110}(\Omega, \Omega')$  and  $\phi^{112}(\Omega, \Omega', \hat{r})$  are defined as:  $\phi^{110}(\Omega, \Omega') = (\widehat{\mu}_\alpha \cdot \widehat{\mu}_\beta)$  and  $\phi^{112}(\Omega, \Omega', \hat{r}) = 3(\widehat{\mu}_\alpha \cdot \hat{r})(\widehat{\mu}_\beta \cdot \hat{r}) - (\widehat{\mu}_\alpha \cdot \widehat{\mu}_\beta)$  where  $\widehat{\mu}_\alpha$  and  $\widehat{\mu}_\beta$  are the unit vectors along dipole moments of particles located at  $\mathbf{r}$  and  $\mathbf{r}'$  and  $\hat{r} = (\mathbf{r}-\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$ . In Eq. (6),  $c_{\alpha\beta}^{000}(|\mathbf{r}-\mathbf{r}'|)$  represents the isotropic or hard sphere part and the second and third terms represent the anisotropic or dipolar part of the intra and inter-species direct correlation function. We substitute Eq.

(6) into Eq. (5) and carry out the angular integrations to obtain the following linearized diffusion equation for the relaxation of polarization:

$$\begin{aligned} \frac{\partial P_\alpha(z, t)}{\partial t} &= -2D_{R;\alpha} P_\alpha(z, t) + \frac{2}{3} D_{R;\alpha} \rho_\alpha(z) \\ &\times \sum_{\beta=1}^n \left[ \int dz' \left\{ c_{\alpha\beta}^{110}(z, z') P_\beta(z', t) \right. \right. \\ &+ \int dx dy d\mathbf{r}' c_{\alpha\beta}^{112}(\mathbf{r}, \mathbf{r}') \\ &\times \left. \left. \left( \frac{3|z-z'|^2}{|\mathbf{r}-\mathbf{r}'|^2} - 1 \right) P_\beta(z', t) \right\} \right] \\ &+ \frac{2}{3} \beta^* D_{R;\alpha} \rho_\alpha(z) \mu_\alpha E. \end{aligned} \quad (7)$$

Analytical solutions of the direct correlation functions are available within mean spherical approximation (MSA) for a binary mixture of unequal sized dipolar hard spheres.<sup>26</sup> In MSA,  $c_{\alpha\beta}^{000}(|\mathbf{r}-\mathbf{r}'|)$  is given by the Percus-Yevic (PY) hard sphere (HS) correlation function.<sup>26-28</sup> For a binary mixture of unequal sized hard spheres, the solutions are given by

$$\begin{aligned} c_{\alpha\alpha;hs}^{000}(|\mathbf{r}-\mathbf{r}'|) &= c_{\alpha\alpha}^{PY}(|\mathbf{r}-\mathbf{r}'|), \\ &= a_\alpha + b_\alpha |\mathbf{r}-\mathbf{r}'| + d' |\mathbf{r}-\mathbf{r}'|^3, \quad \alpha = 1, 2, \end{aligned} \quad (8)$$

for  $|\mathbf{r}-\mathbf{r}'| < \sigma_\alpha$  and zero otherwise, while

$$\begin{aligned} c_{\alpha\beta;hs}^{000}(|\mathbf{r}-\mathbf{r}'|) &= c_{\alpha\beta}^{PY}(|\mathbf{r}-\mathbf{r}'|), \\ &= a_\gamma + \Theta(R) [bR^2 + 4\lambda d'R^3 + d'R^4] / |\mathbf{r}-\mathbf{r}'|, \end{aligned} \quad (9)$$

for  $|\mathbf{r}-\mathbf{r}'| < \sigma_{\alpha\beta}$  and zero otherwise. Here  $\Theta$  is the Heaviside step function,  $\lambda = |\sigma_\alpha - \sigma_\beta|/2$ ,  $R = |\mathbf{r}-\mathbf{r}'| - \lambda$ ,  $\sigma_{\alpha\beta} = (\sigma_\alpha + \sigma_\beta)/2$  and the  $\gamma$  component refers to the species of smaller molecular diameter. The coefficients  $a_\alpha$ ,  $b_\alpha$ ,  $b$ , and  $d'$  depend on the bulk densities of the two components and on the diameter ratio. The analytical expressions of these coefficients are given in the work of Ashcroft and Langreth.<sup>28</sup> The anisotropic terms can be expressed in terms of the Percus-Yevick hard sphere correlation function by the following equations:<sup>26</sup>

$$c_{\alpha\beta}^{110}(r) = 2\kappa_{\alpha\beta} [c_{\alpha\beta}^{PY}(r, \rho_1^{+\alpha\beta}, \rho_2^{+\alpha\beta}) - c_{\alpha\beta}^{PY}(r, \rho_1^{-\alpha\beta}, \rho_2^{-\alpha\beta})], \quad (10)$$

$$c_{\alpha\beta}^{112}(r) = c_{\alpha\beta}^{(0)112}(r) - \frac{3}{r^3} \int_0^r dr' r'^2 c_{\alpha\beta}^{(0)112}(r'), \quad (11)$$

where

$$\begin{aligned} c_{\alpha\beta}^{(0)112}(r) &= \kappa_{\alpha\beta} [2c_{\alpha\beta}^{PY}(r, \rho_1^{+\alpha\beta}, \rho_2^{+\alpha\beta}) \\ &+ c_{\alpha\beta}^{PY}(r, \rho_1^{-\alpha\beta}, \rho_2^{-\alpha\beta})], \end{aligned} \quad (12)$$

and vanishes at  $r > (\sigma_\alpha + \sigma_\beta)/2$  where  $r = |\mathbf{r}-\mathbf{r}'|$ . The modified densities  $\rho_m^{+\alpha\beta}$  and  $\rho_m^{-\alpha\beta}$  are defined as

$$\rho_m^{+\alpha\beta} = 2 \frac{\kappa_{\alpha m} \kappa_{m\beta}}{\kappa_{\alpha\beta}} \rho_m, \quad (13a)$$

$$\rho_m^{-\alpha\beta} = -\frac{\kappa_{\alpha m}\kappa_{m\beta}}{\kappa_{\alpha\beta}}\rho_m, \quad (13b)$$

where the index  $m$  labels the  $m$ th species. The quantities  $\kappa_{11}$ ,  $\kappa_{12}$ , and  $\kappa_{22}$  are obtained from the solutions of the following three coupled equations:<sup>26</sup>

$$\begin{aligned} \frac{4\pi}{3}\beta^*\rho_1\mu_1^2 &= \Phi_{11}(2\kappa_{11}\rho_1, 2\kappa_{12}^2\rho_2/\kappa_{11}) \\ &- \Phi_{11}(-\kappa_{11}\rho_1, -\kappa_{12}^2\rho_2/\kappa_{11}), \end{aligned} \quad (14a)$$

$$\begin{aligned} \frac{4\pi}{3}\beta^*\rho_1\mu_1\mu_2 &= \Phi_{12}(2\kappa_{11}\rho_1, 2\kappa_{22}\rho_2) \\ &- \Phi_{12}(-\kappa_{11}\rho_1, -\kappa_{22}\rho_2), \end{aligned} \quad (14b)$$

$$\begin{aligned} \frac{4\pi}{3}\beta^*\rho_2\mu_2^2 &= \Phi_{22}(2\kappa_{12}^2\rho_1/\kappa_{22}, 2\kappa_{22}\rho_2) \\ &- \Phi_{22}(-\kappa_{12}^2\rho_1/\kappa_{22}, -\kappa_{22}\rho_2), \end{aligned} \quad (14c)$$

where

$$\Phi_{\alpha\beta}(\rho_1, \rho_2) = \rho_\alpha \frac{\partial \beta^* \mu_\alpha(\rho_1, \rho_2)}{\partial \rho_\beta}, \quad (15)$$

where  $\beta^* = 1/k_B T$  and  $\mu_\alpha(\rho_1, \rho_2)$  is the chemical potential of the  $\alpha$ th species in the binary hard sphere mixture whose analytical expression is given in Ref. 26. With the help of above solutions, one can derive analytical expressions of  $c_{\alpha\beta}^{110}(z, z')$  for  $\alpha, \beta = 1, 2$  and these are given by

$$\begin{aligned} c_{\alpha\alpha}^{110}(z, z') &= 2\pi\kappa_{\alpha\alpha}[\frac{1}{2}A_\alpha(\sigma_\alpha^2 - |z - z'|^2) \\ &+ \frac{1}{3}B_\alpha(\sigma_\alpha^3 - |z - z'|^3) + \frac{1}{5}D'(\sigma_\alpha^5 - |z - z'|^5)], \\ &z < \sigma_\alpha, \\ &= 0, \quad \text{otherwise,} \end{aligned} \quad (16a)$$

$$\begin{aligned} c_{12}^{110}(z, z') &= 2\pi\kappa_{12}[A_1(\sigma_{12}^2 - |z - z'|^2) \\ &+ \frac{1}{3}B\sigma_1^3 + D'\lambda\sigma_1^4 + \frac{1}{5}D'\sigma_1^5], \quad z < \sigma_{12}, \\ &= 0, \quad \text{otherwise,} \end{aligned} \quad (16b)$$

where

$$A_\alpha = 2[a_\alpha(\rho_1^{+\alpha\alpha}, \rho_2^{+\alpha\alpha}) - a_\alpha(\rho_1^{-\alpha\alpha}, \rho_2^{-\alpha\alpha})], \quad \alpha = 1, 2, \quad (17)$$

$$B_\alpha = 2[b_\alpha(\rho_1^{+\alpha\alpha}, \rho_2^{+\alpha\alpha}) - b_\alpha(\rho_1^{-\alpha\alpha}, \rho_2^{-\alpha\alpha})], \quad \alpha = 1, 2, \quad (18)$$

$$B = 2[b(\rho_1^{+12}, \rho_2^{+12}) - b(\rho_1^{-12}, \rho_2^{-12})], \quad (19)$$

$$D' = 2[d'(\rho_1^{+12}, \rho_2^{+12}) - d'(\rho_1^{-12}, \rho_2^{-12})]. \quad (20)$$

The value of the integral  $\int dx dy dx' dy' c_{\alpha\beta}^{112}(\mathbf{r}, \mathbf{r}') \times (3|z - z'|^2/|\mathbf{r} - \mathbf{r}'|^2 - 1)$  for  $\alpha, \beta = 1, 2$  is evaluated numerically by using the solutions of  $c_{\alpha\beta}^{112}(\mathbf{r} - \mathbf{r}')$  as given by Eqs. (11) and (12).

Equation (7) describes the dynamics of polarization relaxation in the diffusion limit where inertial and non-Markovian effects are not important. The results of the diffusion equation approach are expected to be valid at long times where memory effects can be ignored. At short times, the time dependence of friction may play an important role and the inertial and non-Markovian effects are to be taken into account. In a non-Markovian theory including inertial effects, the dynamical equation for the polarization relaxation becomes

$$\begin{aligned} \frac{\partial P_\alpha(z, t)}{\partial t} &= -2 \int_0^t dt' D_{R;\alpha}(t - t') P_\alpha(z, t') + \frac{2}{3} \sum_{\beta=1}^n \int_0^t dt' D_{R;\alpha}(t - t') \left[ \rho_\alpha(z) \int dz' \left\{ c_{\alpha\beta}^{110}(z, z') P_\beta(z', t') \right. \right. \\ &+ \left. \left. \int dx dy d\mathbf{r}' c_{\alpha\beta}^{112}(\mathbf{r}, \mathbf{r}') \left( \frac{3|z - z'|^2}{|\mathbf{r} - \mathbf{r}'|^2} - 1 \right) P_\beta(z', t') \right\} \right] + \frac{2}{3} \beta^* \int_0^t dt' D_{R;\alpha}(t - t') \rho_\alpha(z) \mu_\alpha E, \end{aligned} \quad (21)$$

where  $D_{R;\alpha}(t)$  can be treated as a time dependent rotational diffusion coefficient of species  $\alpha$ . Its Laplace transform is given by  $D_{R;\alpha}(s)$  where  $s$  is the frequency. The frequency dependent diffusion coefficient  $D_{R;\alpha}(s)$  is related to the frequency dependent friction  $\zeta_\alpha(s)$  by the following relation:

$$D_{R;\alpha}(s) = \frac{k_B T}{I_\alpha(s + \zeta_\alpha(s))}. \quad (22)$$

There are several approximate forms of  $D_{R;\alpha}(s)$  available in the literature. In the present work, we have used the following simple approximation for the frequency dependent diffusion coefficient.<sup>29,30</sup>

$$D_{R;\alpha}(s) = \frac{D_{R;\alpha}}{1 + s D_{R;\alpha} I_\alpha / k_B T}. \quad (23)$$

The above expression was derived from an approximate form of the time dependent friction which ensures that the short time and the long time dynamics are described correctly.<sup>29</sup> The values of  $D_{R;\alpha}(t)$  are obtained by numerical Laplace Inversion of Eq. (23).

We have solved Eqs. (7) and (21) numerically by using finite difference methods by discretizing the time derivative and the spatial integrals. The time integral is also discretized when Eq. (21) is solved numerically. The time step used was  $0.005 D_{R;1}^{-1}$  and the spatial grid width was  $0.02 \sigma_1$ . The initial density was calculated by using weighted density functional

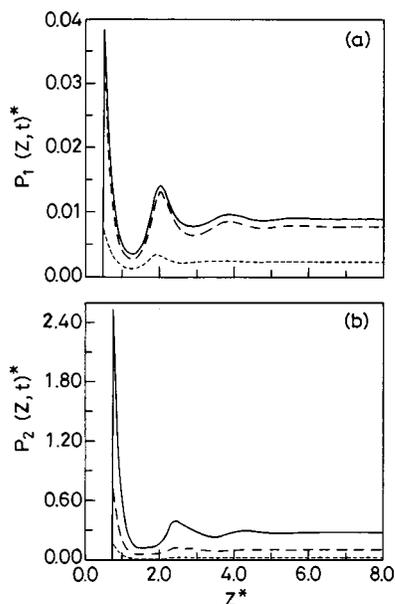


FIG. 2. The variation of solvent polarization of (a) species 1 and (b) species 2 with distance from the charged surface located at  $z=0$ . The surface is charged at  $t=0$ . The short dashed, long dashed, and the solid curves are for  $t^*=0.05, 0.2$ , and  $3.0$ , respectively. The results of this figure and also of Figs. 3–5 are obtained by using the Markovian theory [Eq. (7)].

theory as has been mentioned earlier. The results of the time dependence of polarization at various distances from the surfaces are discussed in the next Section.

### III. NUMERICAL RESULTS

The systems studied in this work are specified by the values of the following reduced parameters: The bulk density of species  $\alpha$ :  $\rho_\alpha^* = \rho_\alpha \sigma_\alpha^3$ , the dipole moment of a molecule of species  $\alpha$ :  $\mu_\alpha^* = \sqrt{\mu_\alpha^2/k_B T \sigma_\alpha^3}$ , the molecular size ratio:  $\Gamma = \sigma_2/\sigma_1$ , the ratio of rotational diffusion coefficients:  $Q = D_{R;2}/D_{R;1}$ , and the electric field produced by the two charged surfaces:  $E^* = E \sqrt{\sigma_1^3/k_B T}$ . In the numerical calculations, we have taken  $E^*=2$ . The values of the other parameters characterizing the two solvent species:  $\rho_1^* = 0.11$ ,  $\rho_2^* = 0.63$ ,  $\mu_1^* = 0.65$ ,  $\mu_2^* = 1.29$ ,  $\Gamma = 1.5$ , and  $Q = 0.25$ . While discussing the results, the polarization ( $P_\alpha$ ), time ( $t$ ) and the distance from the surface ( $z$ ) are expressed in terms of the corresponding reduced quantities:  $P_\alpha^*(z) = P_\alpha(z) \sqrt{\sigma_\alpha^3/k_B T}$ ,  $t^* = t D_{R;1}$ , and  $z^* = z/\sigma_1$ .

We first discuss the results of the Markovian theory as given by Eq. (7). In Fig. 2, we have shown how the interfacial polarization profiles of the two species change with time, when the electric field is applied at  $t^*=0.0$ . The polarization profiles at various times are shown starting from  $t^*=0.05$  to  $t^*=3.0$ , which is the time when the polarization relaxation is virtually complete. It can be seen clearly that the final polarizations near the surface are highly inhomogeneous. Figure 3(a) shows the variation of polarization with time at two different distances from the surface. The polarizations are calculated at  $z^*=0.5$  for component 1 and  $z^*=0.75$  for component 2 which are the contact distances of the two species from the surface, and also at  $z^*=8.0$  which corresponds

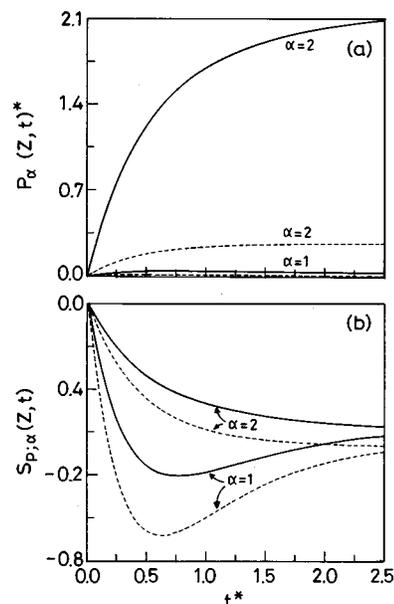


FIG. 3. The time dependence of (a) the polarization and (b) the normalized polarization function of species 1 and 2 at different distances from the charged surface. The solid and the dashed curves show the relaxation at contact distance from the surface and in the bulk region, respectively.

to the homogeneous bulk region. Again, at a given time the polarization at the surface is found to be larger than those in the bulk for both the species.

Since a comparison of the relative rates of relaxation is not obvious from Fig. 3(a), we have calculated the normalized polarization function defined by

$$S_{p;\alpha}(z, t) = \frac{P_\alpha(z, t) - P_\alpha(z, t=\infty)}{P_\alpha(z=0) - P_\alpha(z, t=\infty)}, \quad (24)$$

where  $P_\alpha(z, t=\infty)$  is the final equilibrium polarization of species  $\alpha$  at distance  $z$  from the solid surface. The results of  $S_{p;\alpha}(z, t)$  are shown in Fig. 3(b). It is clearly seen that the rate of polarization relaxation near the surface is much slower than the rate of relaxation in the bulk phase for both the species. In fact,  $S_{p;1}(z^*=0.5, t)$  becomes negative at about  $t^*=0.4$  and then it approaches zero from negative side. For one-component bulk systems, such negative values of the normalized polarization function (and also solvation function) usually occur because of the inertial and non-Markovian effects.<sup>31–35</sup> The present calculations show that, for a dipolar mixture, even in a diffusion-level theory where inertial and non-markovian effects are not included, the normalized polarization function of a particular species can become negative at certain times. The results of interfacial relaxation shown in Fig. 3 are for  $z^*=0.5$  (species 1) and  $z^*=0.75$  (species 2) where the solvent densities are maximum and higher than the bulk. The entire interface consists of regions of higher and lower density and thus it would be interesting to study the relaxation at a distance where the density is minimum and smaller than the bulk density. Results of such a calculation are shown in Fig. 4. In this figure, we have shown the time dependence of the polarization and normalized polarization functions at  $z^*=1.20$  (species 1) and  $z^*=1.60$  (species 2). The interfacial polarization at

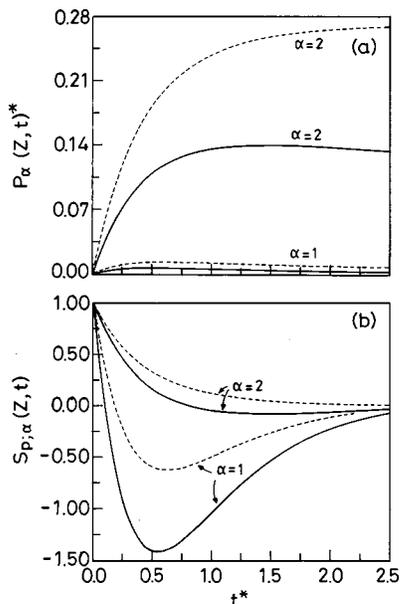


FIG. 4. The time dependence of (a) the polarization and (b) the normalized polarization function of species 1 and 2 at different distances from the charged surface. The solid and the dashed curves show the dynamics at the distance of first minimum in the density profiles ( $z^*=1.2$  for species 1 and  $z^*=1.6$  for species 2) and in the bulk region, respectively.

these distances is found to be smaller than the bulk polarization at a given time and, more importantly, the relaxation at these distances is found to occur at a faster rate than the bulk relaxation.

It may be noted that the interfacial polarization profiles of Fig. 4 are smaller in magnitude compared to the ones at contact distances ( $z^*=0.5$  for species 1 and  $z^*=0.75$  for species 2). Thus, the contribution of the fast relaxing polarization in the regions of minimum density to the total interfacial polarization is unlikely to be significant. To verify this point, we have divided the entire polarization profile of a particular species into three regions: Region I or the contact interfacial region consists of molecules which are within the distance of first minimum of the solvent density of that particular species from the surface. Region II or the diffuse interfacial region contains molecules within the distance of the first minimum and the third minimum of solvent density from the surface and the rest of the system belongs to the bulk region. We define the average polarization of species  $\alpha$  in a particular region as follows

$$\langle P_\alpha(t) \rangle = \frac{\int_{z_1}^{z_2} dz P_\alpha(z, t)}{z_2 - z_1}, \quad (25)$$

where  $z_1$  and  $z_2$  are the lower and upper limits of  $z$  for the region under consideration. The corresponding average normalized polarization function  $\langle S_{p,\alpha}(t) \rangle$  is defined in terms of  $\langle P_\alpha(t) \rangle$  by a relation similar to Eq. (24). The results of  $\langle P_\alpha(t) \rangle$  and  $\langle S_{p,\alpha}(t) \rangle$  for the contact interfacial region and bulk region are shown in Fig. 5 for both the species. A slowing down of the relaxation of average polarization in the contact interfacial region is observed for both the species. This slowing down is more evident in the inset of Fig. 5. The

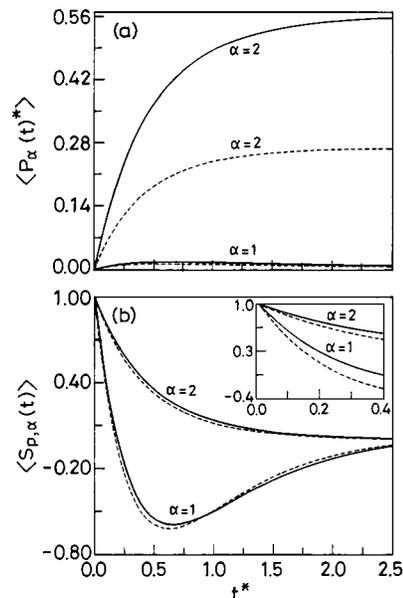


FIG. 5. The time dependence of (a) the average polarization and (b) the average normalized polarization function of species 1 and 2. The solid and dashed curves are for contact interfacial region and the bulk, respectively. The inset shows the dynamics at short times.

results of average polarization for the diffuse interfacial region are very similar to the bulk polarization and, therefore, are not shown in the figure.

Till now, we have presented results of the Markovian theory [Eq. (7)] which is accurate at long times as discussed previously. In the next figure (Fig. 6), we have shown the non-Markovian results for the polarization relaxation of the two species at the surface and in the bulk. We also have

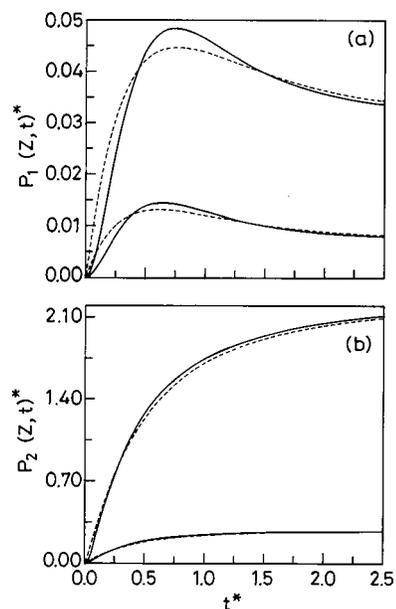


FIG. 6. The time dependence of the polarization of (a) species 1 and (b) species 2 at two different distances from the charged surface. The solid curves show the results of the non-Markovian theory [Eq. (21)]. The results of the Markovian theory [Eq. (7)] are shown by dashed curves for comparison. The upper curves are for contact distance ( $z^*=0.5$  for species 1 and  $z^*=0.75$  for species 2) and the lower curves are for the bulk region.

included the Markovian results for comparison. In these calculations we have assumed that the moment of inertia of molecules of both species are the same. The normalized polarization functions are shown in Fig. 7. The dynamics at the interface is again found to be slower than that in the bulk. Thus, the slowing down of the relaxation near the surface is found to be a rather general feature of interfacial relaxation.

We note that a slowing down of the orientational relaxation of interfacial molecules has also been observed in recent molecular dynamics simulations of mixed dipolar liquids at solid-liquid interfaces<sup>16</sup>. On the experimental side, no study has yet been carried out to measure the solvent relaxation at solid-liquid interfaces. Over past two decades, the solvent relaxation in bulk phases has been investigated by measuring the time dependent fluorescence Stokes shift (TDFSS) of a newly excited chromophore which undergoes a charge transfer in the excited state.<sup>36</sup> Similar techniques have also been used to study solvent relaxation in confined systems such as water in reverse micelles.<sup>37</sup> The experimental measurement of solvent dynamics at solid-liquid interfaces can be made by studying the TDFSS of a newly excited chromophore probe which is selectively adsorbed at the surface. Such selective adsorption of the chromophore at the surface can be achieved by attaching a surface active group to the chromophore. Of course, practical implementation of this experiment at interface may have other technical difficulties, but, if successful, it can provide direct information on the dynamics of molecular relaxation at solid-liquid interfaces. Direct experimental study of the perturbation of solvent dynamics by a solid surface remains an important goal for future *in situ* studies of solid-liquid interfaces.

#### IV. SUMMARY AND CONCLUSIONS

We have investigated the dynamics of polarization relaxation in a mixed dipolar liquid at solid-liquid interface by using equations of time dependent density functional theory. The main goal was to explore the effects of inhomogeneity of the medium on the orientational relaxation of interfacial dipolar molecules. The initial inhomogeneity of the medium is calculated by using an accurate weighted density functional theory. We have considered both Markovian and non-Markovian equations of motion for the relaxation of polarizations of various species near a newly charged solid surface. The theory properly takes into account the intra and interspecies interactions, the surface-molecule interactions and also the inhomogeneity of the medium. The final dynamical equations are solved numerically in real space and explicit numerical results are obtained for the relaxation of solvent polarizations in a binary dipolar liquid at varying distances from the solid surface. The dynamics of interfacial relaxation is compared with that of the bulk. A slowing down of the relaxation dynamics for both the species is found for interfacial molecules. However, the extent of slowing down is found to be different for different species. Also, the rate of relaxation is found to change nonmonotonically with distance from the surface due to the layering of solvent molecules in the interfacial region. It may be noted that the ef-

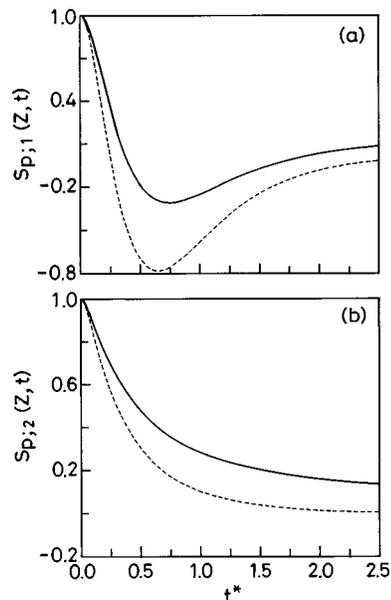


FIG. 7. The time dependence of the normalized polarization function of (a) species 1 and (b) species 2 at different distances from the charged surface. The results are from the non-Markovian theory. The solid and the dashed curves show the relaxation at contact distance from the surface and in the bulk region, respectively.

fects of inhomogeneity of the medium on orientational relaxation in a mixed dipolar liquid are investigated here for the first time by using an analytical theory.

The results of the present work would be useful in understanding the dynamics of many interfacial chemical processes such as charge transfer reactions at solid-liquid interfaces.<sup>38-40</sup> In order to fully understand interfacial charge transfer processes, one needs information on the electronic coupling between two resonant electronic states undergoing electron exchange, the nuclear activation barrier to attaining this condition of electronic resonance and also the nuclear relaxation dynamics in reactant and product wells. In the adiabatic limit, where the electronic coordinate equilibrates faster than the nuclear motion at the reaction saddle point, the electron transfer time scale becomes equivalent to the nuclear relaxation dynamics. Both intramolecular and solvent reorganization contribute to the nuclear relaxation, although the solvent coordinate is usually the dominant factor. Thus, the solvent dynamics at the solid surface can play a crucial role in determining the rates of charge transfer processes at solid-liquid interfaces and the theory presented in this work can be used to understand this interfacial solvent dynamics.

The present study can be extended to study a number of other related problems. For example, Eqs. (7) and (21) can be extended to study the polarization relaxation in an inhomogeneous ionic solution near a charged surface. Such studies would be useful in investigating the dynamics of electrochemical processes at surfaces. An extension of the present theory to study the dynamics of electrical double layer formation next to a charged surface would also be very useful. It would also be interesting to study the solvent relaxation near a charged metal surface. In such cases, even for the uncharged surface there would be a finite polarization at the

interface because of the inhomogeneous electron density of the metal surface and one would need to solve the dynamical equations with a finite polarization to begin with. Work in this direction is in progress.

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- <sup>1</sup>S. H. Lee, J. C. Rasaiah, and J. B. Hubbard, *J. Chem. Phys.* **85**, 5232 (1986); **86**, 2383 (1987).
- <sup>2</sup>E. Sphor, *J. Phys. Chem.* **93**, 6171 (1989).
- <sup>3</sup>S.-B. Zhu and G. W. Robinson, *J. Chem. Phys.* **94**, 1403 (1991).
- <sup>4</sup>K. Raghavan, K. Foster, K. Motakabbir, and M. Berkowitz, *J. Chem. Phys.* **94**, 2110 (1991).
- <sup>5</sup>X. Xia and M. Berkowitz, *Phys. Rev. Lett.* **74**, 3193 (1995).
- <sup>6</sup>S. H. Lee and P. J. Rossky, *J. Chem. Phys.* **100**, 3334 (1994).
- <sup>7</sup>D. A. Rose and I. Benjamin, *J. Chem. Phys.* **95**, 6856 (1991); **98**, 2283 (1993).
- <sup>8</sup>J. N. Glosli and M. R. Philpott, *J. Chem. Phys.* **96**, 6962 (1992).
- <sup>9</sup>G. Nagy, K. Heinzinger, and E. Spohr, *Faraday Discuss.* **94**, 307 (1992).
- <sup>10</sup>L. Zhang, H. T. Davis, D. M. Kroll, and H. S. White, *J. Phys. Chem.* **99**, 2878 (1995).
- <sup>11</sup>R. M. Lynden-Bell and J. C. Rasaiah, *J. Chem. Phys.* **105**, 9266 (1996).
- <sup>12</sup>S. Senapati and A. Chandra, *Chem. Phys.* **231**, 65 (1998); *J. Mol. Struct.: THEOCHEM* **455**, 1 (1998).
- <sup>13</sup>A. Chandra and S. Senapati, *J. Mol. Liq.* **77**, 77 (1998).
- <sup>14</sup>S. Senapati and A. Chandra, *J. Chem. Phys.* **111**, 1223 (1999).
- <sup>15</sup>A. Chandra, S. Senapati, and D. Sudha, *J. Chem. Phys.* **109**, 10439 (1998).
- <sup>16</sup>S. Senapati and A. Chandra, *Chem. Phys.* **242**, 353 (1999).
- <sup>17</sup>B. Bagchi and A. Chandra, *Adv. Chem. Phys.* **80**, 1 (1991).
- <sup>18</sup>T. Munakata, *J. Chem. Phys.* **43**, 1725 (1977); **58**, 2434 (1989); **59**, 1299 (1990).
- <sup>19</sup>A. R. Denton and N. W. Ashcroft, *Phys. Rev. A* **39**, 426 (1989).
- <sup>20</sup>A. R. Denton and N. W. Ashcroft, *Phys. Rev. A* **44**, 8242 (1991).
- <sup>21</sup>P. Tarazona, *Phys. Rev. A* **31**, 2672 (1985); **32**, 3148 (1985).
- <sup>22</sup>C. N. Patra and S. K. Ghosh, *J. Chem. Phys.* **106**, 2752 (1997); *Phys. Rev. E* **49**, 2826 (1994).
- <sup>23</sup>D. Das, S. Senapati, and A. Chandra, *J. Chem. Phys.* **110**, 8129 (1999).
- <sup>24</sup>S. Senapati and A. Chandra, *J. Chem. Phys.* (in press).
- <sup>25</sup>D. Berard and G. N. Patey, *J. Chem. Phys.* **95**, 5281 (1991).
- <sup>26</sup>D. Isbister and R. J. Bearman, *Mol. Phys.* **28**, 1297 (1974).
- <sup>27</sup>J. L. Lebowitz, *Phys. Rev. A* **133**, A895 (1964).
- <sup>28</sup>N. M. Ashcroft and D. C. Langreth, *Phys. Rev.* **156**, 685 (1967).
- <sup>29</sup>A. Chandra, D. Wei, and G. N. Patey, *J. Chem. Phys.* **99**, 2083 (1993).
- <sup>30</sup>K. Mahajan and A. Chandra, *J. Chem. Phys.* **106**, 2360 (1997).
- <sup>31</sup>M. Maroncelli, *J. Chem. Phys.* **94**, 2084 (1991).
- <sup>32</sup>A. Chandra and B. Bagchi, *J. Chem. Phys.* **94**, 3177 (1991).
- <sup>33</sup>S. Roy and B. Bagchi, *J. Chem. Phys.* **99**, 1310 (1993); **99**, 9938 (1993).
- <sup>34</sup>A. Chandra, D. Wei, and G. N. Patey, *J. Chem. Phys.* **99**, 4926 (1993).
- <sup>35</sup>A. Chandra, *Chem. Phys. Lett.* **235**, 133 (1995).
- <sup>36</sup>See, for example, P. F. Barbara and W. Jarzeba, *Adv. Photochem.* **15**, 1 (1990); B. Bagchi, *Annu. Rev. Phys. Chem.* **40**, 115 (1989); G. R. Fleming and P. G. Wolynes, *Phys. Today* **43**, 36 (1990); M. Maroncelli, *J. Mol. Liq.* **57**, 1 (1993); R. Jimenez, G. R. Fleming, P. V. Kumar, and M. Maroncelli, *Nature (London)* **369**, 471 (1994).
- <sup>37</sup>See, for example, N. Sarkar, K. Das, A. Dutta, S. Das, and K. Bhattacharya, *J. Phys. Chem.* **100**, 10523 (1996); A. Dutta, D. Mandal, S. K. Pal, and K. Bhattacharya, *J. Phys. Chem. B* **101**, 10221 (1997); R. E. Riter, J. R. Kimmel, E. P. Undiks, and N. E. Levinger, *ibid.* **101**, 8292 (1997); R. E. Riter, D. M. Willard, and N. E. Levinger, *ibid.* **102**, 2705 (1998).
- <sup>38</sup>J. M. Lanzafame, S. Palese, D. Wang, R. J. D. Miller, and A. A. Muentner, *J. Phys. Chem.* **98**, 11020 (1994).
- <sup>39</sup>R. R. Nazmutdinov, G. A. Tsirlina, Y. I. Kharkats, O. A. Petrii, and M. Probst, *J. Phys. Chem. B* **102**, 677 (1998).
- <sup>40</sup>B. Burfeindt, T. Hannappel, W. Storck, and F. Willig, *J. Phys. Chem.* **100**, 16463 (1996).