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Dynamics of polarization relaxation at solid–liquid interface

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Dynamics of polarization relaxation at the solid–liquid interface is investigated theoretically by using time dependent density functional theory. The time dependence of the building up of solvent polarization 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 initial inhomogeneity of the medium is taken into account and it is calculated by using a weighted density functional theory. Explicit numerical results are obtained for the relaxation of solvent polarization at varying distances from the solid surface and the dynamics of interfacial relaxation is compared with that of the bulk. A slowing down of the rate of relaxation is found for interfacial molecules. However, the relaxation rate changes nonmonotonically with distance from the surface which can be attributed to the layering of solvent molecules in the interfacial region. © 1998 American Institute of Physics. [S0021-9606(98)51746-1]

I. INTRODUCTION

The behavior of fluid molecules in an inhomogeneous medium is a subject of considerable interest in a wide variety of contexts such as electrochemistry, colloid chemistry and transport in biological pores and membranes. A particularly important problem is the dynamics of dipolar molecules at the solid–liquid interface because of its role in understanding the dynamics of chemical reactions occurring at such an interface. For example, the molecular relaxation of solvent near a charged electrode or a membrane can influence the rates of electron transfer and other chemical processes occurring in the interfacial region. During the past few years, there have been many experimental,^{1–4} theoretical^{5–11} and simulation^{12–22} studies on the equilibrium aspects of interfacial dipolar liquids near both uncharged and charged surfaces. Simulation studies have also been carried out to study the dynamics of dipolar solvents near various kinds of solid surfaces.^{12–24} These studies have revealed a slowing down of molecular relaxation at the solid–liquid interface compared to the dynamics of the bulk phase. However, similar studies of dynamical aspects of an interface have not been carried out by using analytical theories.

The interface between a dipolar hard sphere liquid and a neutral hard wall is probably the simplest example of an inhomogeneous dipolar solvent. Theoretical and computer simulation studies of this system have shown layering of fluid molecules in the interfacial region.^{8,14} Since each solvent molecule has a permanent dipole moment, in the presence of an external field they may preferentially align in a particular direction giving rise to an inhomogeneous polarization in the system. Such an external field can be provided by suddenly charging the walls at a certain time instant and a study of the subsequent development of solvent polarization in the interfacial region seems to be a good starting point for the theoretical investigation of dynamics of interfacial solvent molecules.

In this work, we derive equations for the time depen-

dence of inhomogeneous solvent density and polarization next to a charged surface by employing equations of time dependent density functional theory (TDFT).^{25,26} The density functional theory has been recognized as a versatile tool for the studies of inhomogeneous systems and its dynamical extension is employed here for the first time to explore interfacial relaxation. The theory properly includes the initial inhomogeneity of the system, the correlation between solvent molecules and also the effects of inertial motion and time dependent rotational friction of solvent molecules (the non-Markovian effects). The initial inhomogeneity is calculated by using the weighted density functional approach of Tarazona²⁷ which has been shown to be very accurate in describing the structure of dense liquids near neutral hard walls. We have obtained numerical results for solvent polarization at various times and at various distances from the charged surface. The rate of polarization relaxation is found to be much slower in the interfacial regions of high solvent density. The relaxation rate, however, changes nonmonotonically with distance from the surface which can be attributed 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 much slower than that in the bulk, although the rate as such increases when inertial and non-Markovian effects are included.

The outline 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 solvent confined between two solid surfaces. The solvent molecules are characterized by the so-called dipolar hard sphere potential where the dipolar

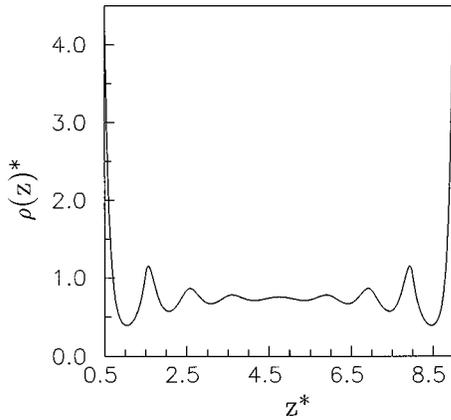


FIG. 1. The variation of solvent density with the distance from the uncharged surfaces.

molecules interact through a short range hard sphere interaction and a long range dipole–dipole interaction potential. The diameter and the dipole moment of a solvent molecule are denoted by σ and μ , 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 molecules 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 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 solvent will get gradually polarized along the direction of the field. Our objective is to calculate the time dependence of this building up of solvent polarization at different distances from the surfaces.

Before the surfaces were charged, there was no polarization in the system but the solvent density distribution was highly inhomogeneous because of the presence of the uncharged solid surfaces. We have calculated this initial structure of the solvent by using a weighted density functional approach²⁷ and the results are shown in Fig. 1. Clearly, the solvent density is highly inhomogeneous near the surfaces and it is fairly homogeneous in the middle portion of the system. Thus, the present system contains both interfacial and bulk regions.

Since the inhomogeneity of the system is along the z direction only, the density distribution of the solvent becomes a function of z and Ω (orientation) and time t (in the nonequilibrium case) and we denote it by $\rho(z, \Omega, t)$. Clearly, $\rho(z, \Omega, t=0) = \rho(z)/4\pi$. We note that the time dependent polarization $P(z, t)$ is related to density by the following equation:

$$P(z, t) = \int d\Omega (\mu \cdot \hat{z}) \rho(z, \Omega, t), \quad (1)$$

where \hat{z} is a unit vector along the z direction. Thus, once we

know the nonequilibrium density distribution, the time dependence of polarization can be found from Eq. (1).

In the present situation, the external field is constant which exerts a torque but no force on dipolar molecules and, therefore, the primary mechanism of density relaxation involves orientational motion of solvent molecules. 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 in an inhomogeneous liquid:

$$\frac{\partial \rho(z, \Omega, t)}{\partial t} = -\nabla_{\Omega} \cdot J_R(z, \Omega, t), \quad (2)$$

$$\begin{aligned} \frac{\partial J_R(z, \Omega, t)}{\partial t} = & -\frac{k_B T}{I} \nabla_{\Omega} \left\{ \rho(z, \Omega, t) - \frac{\rho(z)}{4\pi} \right. \\ & \times \int dz' d\Omega' c(z, z', \Omega, \Omega') \\ & \times \left. \left(\rho(z', \Omega, t) - \frac{\rho(z')}{4\pi} \right) \right\} \\ & - \int_0^t dt' \zeta_R(t-t') \\ & \times J_R(z, \Omega, t') + \rho(z, \Omega, t) \nabla_{\Omega} (\mu \cdot E), \quad (3) \end{aligned}$$

where $J_R(z, \Omega, t)$ is the rotational flux, T is the temperature, I is moment of inertia and $\zeta_R(t)$ is the time dependent rotational friction and

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

where $c(\mathbf{r}, \mathbf{r}', \Omega, \Omega')$ is the two particle direct correlation function between the solvent molecules in the initial state. The last term of Eq. (3) includes the effects of interaction of solvent molecules 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 in the presence of an external field. In the so-called diffusion limit, the friction $\zeta_R(t)$ is approximated by a delta function $\zeta_R(t) = \zeta_R \delta(t)$ and the angular momentum relaxation is considered to be much faster than density relaxation²⁵ and in such a limiting situation the relaxation equation for the density can be described by the following diffusion equation:

$$\begin{aligned} \frac{\partial \rho(z, \Omega, t)}{\partial t} = & D_R \nabla_{\Omega}^2 \rho(z, \Omega, t) - D_R \nabla_{\Omega}^2 \frac{\rho(z)}{4\pi} \\ & \times \int dz' d\Omega' c(z, z', \Omega, \Omega') \\ & \times \left\{ \rho(z', \Omega', t) - \frac{\rho(z')}{4\pi} \right\} \\ & - \beta D_R \nabla_{\Omega} \rho(z, \Omega, t) \nabla_{\Omega} \mu E \cos \theta, \quad (5) \end{aligned}$$

where D_R is the rotational diffusion coefficient equal to $k_B T / I \zeta_R$ 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

be a constant for simplicity. Also, recent MD simulations of simple dipolar liquids near neutral solid surfaces have shown that the rotational diffusion coefficient of interfacial molecules is not very different from that of bulk molecules.^{22,23}

The quantity $c(z, z', \Omega, \Omega')$ in Eq. (5) can be calculated once we know the two particle direct correlation function $c(\mathbf{r}, \mathbf{r}', \Omega, \Omega')$. 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. An analytical solution of the direct correlation function for a uniform liquid of dipolar hard spheres is available within the mean spherical approximation (MSA)²⁸ and is given by

$$c(\mathbf{r}, \mathbf{r}', \Omega, \Omega') = c^{000}(|\mathbf{r} - \mathbf{r}'|) + c^{110}(|\mathbf{r} - \mathbf{r}'|) \phi^{110}(\Omega, \Omega') + c^{112}(|\mathbf{r} - \mathbf{r}'|) \phi^{112}(\Omega, \Omega', \hat{r}), \quad (6)$$

where the angular functions $\phi^{110}(\Omega, \Omega')$ and $\phi^{112}(\Omega, \Omega', \hat{r})$ are defined as: $\phi^{110}(\Omega, \Omega') = (\hat{\mu} \cdot \hat{\mu}')$ and $\phi^{112}(\Omega, \Omega', \hat{r}) = 3(\hat{\mu} \cdot \hat{r})(\hat{\mu}' \cdot \hat{r}) - (\hat{\mu} \cdot \hat{\mu}')$ where $\hat{\mu}$ and $\hat{\mu}'$ 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), $c^{000}(|\mathbf{r} - \mathbf{r}'|)$ represents the isotropic or hard sphere part and the second and third terms represent the anisotropic or dipolar part of the direct correlation function. In MSA, $c^{000}(|\mathbf{r} - \mathbf{r}'|)$ is given by the Percus–Yevick (PY) hard sphere (HS) correlation function^{29,30} and is given by

$$c^{000}(|\mathbf{r} - \mathbf{r}'|) = c_{PY}^{(2)}(|\mathbf{r} - \mathbf{r}'|) = a + b|\mathbf{r} - \mathbf{r}'| + c|\mathbf{r} - \mathbf{r}'|^3, \quad (7)$$

for $|\mathbf{r} - \mathbf{r}'| < \sigma$ and zero otherwise. The coefficients a , b and c are given by

$$a = -\frac{(1+2\eta)^2}{(1-\eta)^4}, \quad (8)$$

$$b = 6\eta \frac{(1+\eta/2)^2}{(1-\eta)^4}, \quad (9)$$

$$c = \frac{1}{2}\eta a, \quad (10)$$

where the packing fraction η is equal to $(\pi/6)\rho_0\sigma^3$ where ρ_0 is the density of the homogeneous (bulk) liquid. The anisotropic parts $c^{110}(|\mathbf{r} - \mathbf{r}'|)$ and $c^{112}(|\mathbf{r} - \mathbf{r}'|)$ are also given in terms of the Percus–Yevick hard sphere correlation functions by the following equations:

$$c^{110}(r, \rho_0) = 2\kappa [c_{PY}^{(2)}(r, 2\kappa\rho_0) - c_{PY}^{(2)}(r, -\kappa\rho_0)], \quad (11)$$

$$c^{112}(r, \rho_0) = c^{(0)112}(r) - \frac{3}{r^3} \int_0^r dr' r'^2 c^{(0)112}(r'), \quad (12)$$

where

$$c^{(0)112}(r, \rho_0) = \kappa [2c_{PY}^{(2)}(r, 2\kappa\rho_0) + c_{PY}^{(2)}(r, -\kappa\rho_0)], \quad (13)$$

and vanishes at $r > \sigma$ where $r = |\mathbf{r} - \mathbf{r}'|$. The quantity κ is determined by the equation

$$\frac{(1+4\kappa\eta)^2}{(1-2\kappa\eta)^4} - \frac{(1-2\kappa\eta)^2}{(1+\kappa\eta)^4} = 3y, \quad (14)$$

where $3y = 4\pi\beta\rho_0\mu^2/3$.

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

$$\begin{aligned} \frac{\partial P(z, t)}{\partial t} = & -2D_R P(z, t) + \frac{2}{3}D_R \rho(z) \\ & \times \left[\int dz' \left\{ c^{110}(z, z') P(z', t) \right. \right. \\ & + \left. \int dx dy d\mathbf{r}' c^{112}(\mathbf{r}, \mathbf{r}') \left(\frac{3|z-z'|^2}{|\mathbf{r}-\mathbf{r}'|^2} - 1 \right) \right. \\ & \left. \left. \times P(z', t) \right\} \right] + \frac{2}{3}\beta D_R \rho(z) \mu E, \quad (15) \end{aligned}$$

where analytical expressions of $c^{110}(z, z')$ and $\int dx dy dx' dy' c^{112}(\mathbf{r}, \mathbf{r}') (3|z-z'|^2/|\mathbf{r}-\mathbf{r}'|^2 - 1)$ can be derived from Eqs. (7)–(13)^{10,28} and they are given by

$$c^{110}(z, z') = 2\pi\kappa \left[\frac{1}{2}a_1(1-|z-z'|^2) + \frac{1}{3}b_1(1-|z-z'|^3) + \frac{1}{5}c_1(1-|z-z'|^5) \right] \quad (16)$$

$$\begin{aligned} \int dx dy dx' dy' c^{112}(\mathbf{r}, \mathbf{r}') \left(\frac{3|z-z'|^2}{|\mathbf{r}-\mathbf{r}'|^2} - 1 \right) \\ = 2\pi\kappa \left[\frac{3}{4}b_2|z-z'|^2(1-|z-z'|) + \left(\frac{1}{2}c_2|z-z'|^2 \right. \right. \\ \left. \left. - \frac{1}{12}b_2 \right) (1-|z-z'|^3) - \frac{1}{10}c_2(1-|z-z'|^5) \right] \\ + 2\pi\beta\mu^2(|z-z'|^2 - 1), \quad (17) \end{aligned}$$

for $|z-z'| < \sigma$ and zero otherwise in both cases. The symbols a_1 , b_1 , c_1 , b_2 and c_2 are defined as

$$\begin{aligned} a_1 &= 2[a(2\kappa\rho_0) - a(-\kappa\rho_0)], \\ b_1 &= 2[b(2\kappa\rho_0) - b(-\kappa\rho_0)], \\ c_1 &= 2[c(2\kappa\rho_0) - c(-\kappa\rho_0)], \\ b_2 &= 2b(2\kappa\rho_0) + b(-\kappa\rho_0), \\ c_2 &= 2c(2\kappa\rho_0) + c(-\kappa\rho_0). \end{aligned} \quad (18)$$

We have solved Eq. (15) numerically by using finite difference methods by discretizing the time derivative and the spatial integrals. The time step used was $0.005D_R^{-1}$ and the spatial grid width was 0.01σ . The initial density was calculated by using weighted density functional 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.

Equation (5) for the density relaxation or Eq. (15) for the polarization relaxation is valid 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

$$\begin{aligned} \frac{\partial P(z,t)}{\partial t} = & -2 \int_0^t dt' D_R(t-t') P(z,t') \\ & + \frac{2}{3} \int_0^t dt' D_R(t-t') \left[\rho(z) \int dz' \left\{ c^{110}(z,z') \right. \right. \\ & \times P(z',t') + \int dx dy d\mathbf{r}' c^{112}(\mathbf{r},\mathbf{r}') \\ & \left. \left. \times \left(\frac{3|z-z'|^2}{|\mathbf{r}-\mathbf{r}'|^2} - 1 \right) P(z',t') \right\} \right] + \frac{2}{3} \beta \\ & \times \int_0^t dt' D_R(t-t') \rho(z) \mu E, \end{aligned} \quad (19)$$

where $D(t)$ can be treated as a time dependent diffusion coefficient. Its Laplace transform is given by $D(s)$ where s is the frequency. The frequency dependent diffusion coefficient $D(s)$ is related to the frequency dependent friction $\zeta_R(s)$ by the following relation:

$$D_R(s) = \frac{k_B T}{I(s + \zeta_R(s))}. \quad (20)$$

There are several approximate forms of $D(s)$ available in the literature. In the present work, we have used the following simple approximation for the frequency dependent diffusion coefficient:^{31,32}

$$D_R(s) = \frac{D_R}{1 + s D_R I / k_B T}. \quad (21)$$

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.³¹ We have obtained the values of $D_R(t)$ by carrying out the numerical Laplace Inversion of Eq. (21) and then we have solved Eq. (19) numerically by discretizing both the time and spatial integrals.

III. NUMERICAL RESULTS

The systems studied here are specified by specifying the values of the reduced parameters: reduced dipole moment $\mu^* = \sqrt{\mu^2 / k_B T \sigma^3}$, reduced electric field $E^* = E \sqrt{\sigma^3 / k_B T}$ and the reduced bulk density $\rho^* = \rho \sigma^3$. The solvent in the present calculations is characterized by $\mu^* = 1.29$ and $\rho^* = 0.74$ and the electric field used is $E^* = 2.0$. The separation between the two walls is 9.5σ . While discussing the results, the polarization (P), time (t) and the distance from the surface (z) are expressed in terms of the corresponding reduced quantities: $P^* = P \sqrt{\sigma^3 / k_B T}$, $t^* = t D_R$ and $z^* = z / \sigma$.

We first discuss the results of the Markovian theory as given by Eq. (15). In Fig. 2, we have shown how the interfacial polarization changes 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

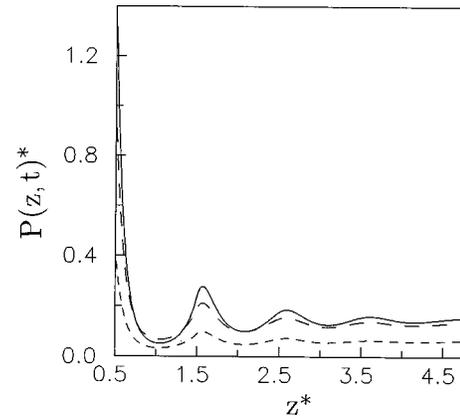


FIG. 2. The variation of solvent polarization with the distance from the charged surface located at $z=0$. The surface is charged at $t=0$. The short dashed, long dashed and the solid curves are for $t^*=0.05, 0.2$ and 3.0 , respectively. The results of this figure and also of Figs. (3)–(5) are obtained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

the time when the polarization relaxation is virtually complete. It can be seen clearly that the final polarization near the surface is much higher than that in the bulk which is because of the enhanced solvent density near the surface. Figure 3(a) shows the variation with time of the polarization at three different distances from the surface. The polarization is cal-

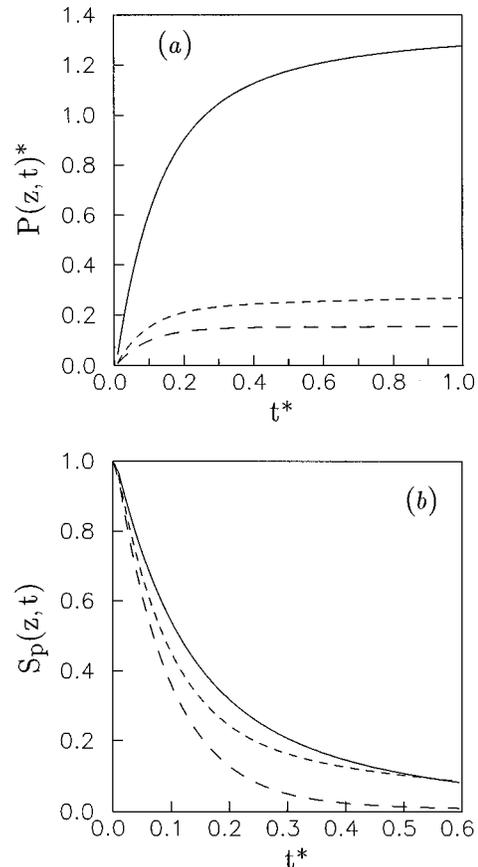


FIG. 3. The time dependence of (a) the polarization and (b) the normalized polarization function at different distances from the charged surface. The solid, short dashed and the long dashed curves are for $z^*=0.5, 1.55$ and 4.75 , respectively.

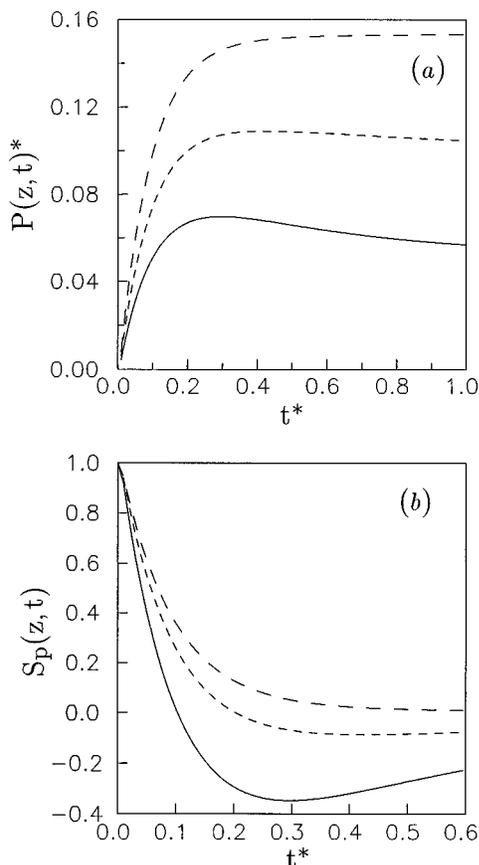


FIG. 4. The time dependence of (a) the polarization and (b) the normalized polarization function at different distances from the charged surface. The solid, short dashed and the long dashed curves are for $z^* = 1.0, 2.05$ and 4.75 , respectively.

culated at $z^* = 0.5, 1.55$ and 4.75 . The first one is the contact distance from the surface, the second one corresponds to the position of the second maximum of density profile from the surface and the third distance belongs to the region of homogeneous bulk density. Again, at a given time the polarization near the surface is found to be larger than that in the bulk. Since a comparison of the relative rates of relaxation is not obvious from a figure like this, we have calculated the normalized polarization function defined by

$$S_p(z, t) = \frac{P(z, t) - P(z, t = \infty)}{P(z = 0) - P(z, t = \infty)}, \quad (22)$$

where $P(z, t = \infty)$ is the the final equilibrium polarization of the medium at distance z from the solid surface. The results of $S_p(z, t)$ 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. The results of interfacial relaxation shown in Fig. 3 are for $z^* = 0.5$ and 1.55 where the solvent density is 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 polarization and normalized polarization function at $z^* = 1.0$ and 2.05 . The interfacial po-

larization at 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. In fact, $S_p(z = \sigma, t)$ becomes negative at about $t^* = 0.1$ and then it approaches zero from the negative side. For bulk systems, such negative values of the normalized polarization function (and also solvation function) usually occur because of the inertial and non-Markovian effects.³³⁻³⁷ The present calculations show that even in a diffusion-level theory where inertial and non-Markovian effects are not included, the normalized polarization function can become negative at certain regions of a highly inhomogeneous system.

We also note that the interfacial polarizations of Fig. 4 are smaller in magnitude compared to the ones at $z^* = 0.5$ and 1.55 . Thus, the contribution of the fast relaxing polarization in the regions of minimum density to the total interfacial polarization may not be significant. To verify this point, we have divided the entire system 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 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 a particular region as follows:

$$\langle P(t) \rangle = \frac{\int_{z_1}^{z_2} dz P(z, t)}{z_2 - z_1}, \quad (23)$$

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 $\langle S_p(t) \rangle$ is defined in terms of $\langle P(t) \rangle$ by a relation similar to Eq. (22). The results of $\langle P(t) \rangle$ and $\langle S_p(t) \rangle$ for the contact interfacial region and bulk region are shown in Fig. 5. A noticeable slowing down of the relaxation of average polarization in the contact interfacial region as compared to the dynamics of the bulk phase is evident from the figure. The results of average polarization for the diffuse interfacial region are very similar to the bulk polarization and, therefore, are not shown in the figure.

The results presented so far are based on Markovian theory [Eq. (15)] which is accurate at long times only as discussed previously. In the next figure (Fig. 6), we have shown the non-Markovian results for the polarization relaxation at the surface and in the bulk. We have also included the Markovian results for comparison. Figure 7 shows the variation of the normalized polarization with time for the non-Markovian case. The results are for $z^* = 0.5, 1.55$ and 4.75 . The dynamics at the interface is again found to be slower than that in the bulk, although the rate as such has increased. Finally, in Fig. 8, we have shown the non-Markovian results of the relaxation of $\langle S_p(t) \rangle$ for the contact interface and bulk regions. The slowing down of the relaxation near the surface is found to be a rather general feature of interfacial relaxation. We note that a similar slowing down of the orientational relaxation of interfacial molecules

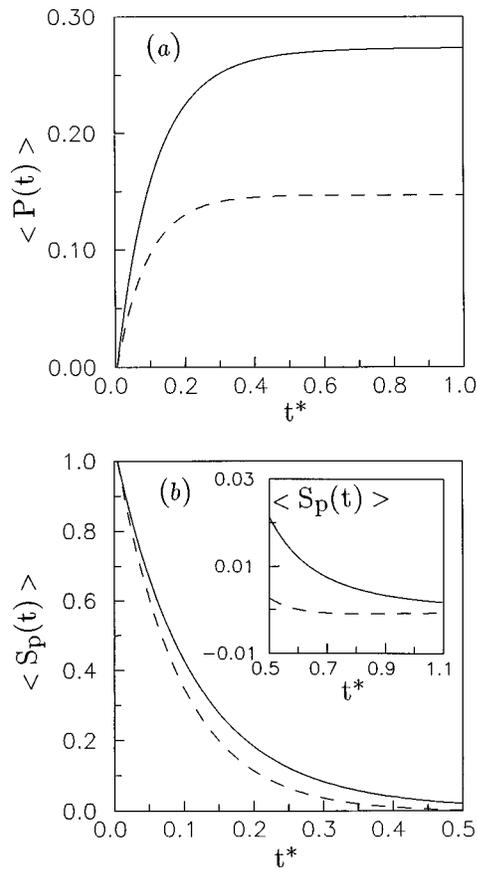


FIG. 5. The time dependence of (a) the average polarization and (b) the average normalized polarization function. The solid and dashed curves are for regions I (contact interface) and III (bulk), respectively.

has also been observed in recent molecular dynamics simulations of interfacial dipolar liquids.^{22,23}

IV. SUMMARY AND CONCLUSIONS

We summarize the main results of the present paper. We have investigated the dynamics of polarization relaxation at the solid-liquid interface by using equations of time depen-

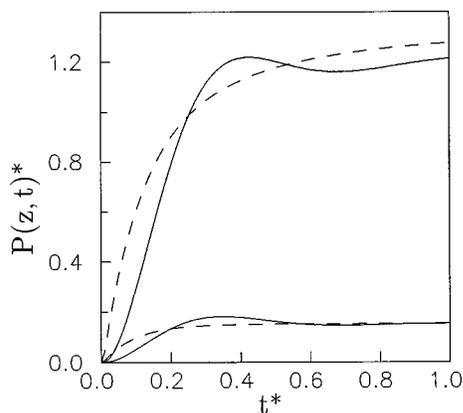


FIG. 6. The time dependence of the polarization at two different distances from the charged surface. The solid curves show the results of the non-Markovian theory [Eq. (19)]. The results of the Markovian theory [Eq. (15)] are shown by dashed curves for comparison. The upper curves are for $z^* = 0.5$ and the lower curves are for $z^* = 4.75$.

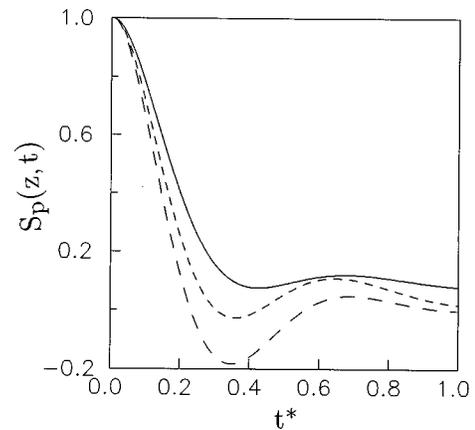


FIG. 7. The time dependence of the normalized polarization function at different distances from the charged surface. The results are from the non-Markovian theory. The solid, short dashed and the long dashed curves are for $z^* = 0.5, 1.55$ and 4.75 , respectively.

dent density functional theory. The main purpose was to explore the effects of inhomogeneity of the medium on the orientational relaxation of interfacial dipolar molecules. Both Markovian and non-Markovian equations of motion are considered for the relaxation of solvent polarization near a newly charged solid surface. The initial inhomogeneity of the medium is properly taken into account in the dynamical theory and it is calculated by using an accurate weighted density functional theory. The final dynamical equations are solved numerically in real space and explicit numerical results are obtained for the relaxation of solvent polarization 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 is found for interfacial molecules. The rate of relaxation, however, changes nonmonotonically with the distance from the surface which can be attributed to the layering of solvent molecules in the interfacial region. We note that the effects of inhomogeneity of the medium on orientational relaxation of dipolar molecules are investigated here for the first time by using an analytical theory.

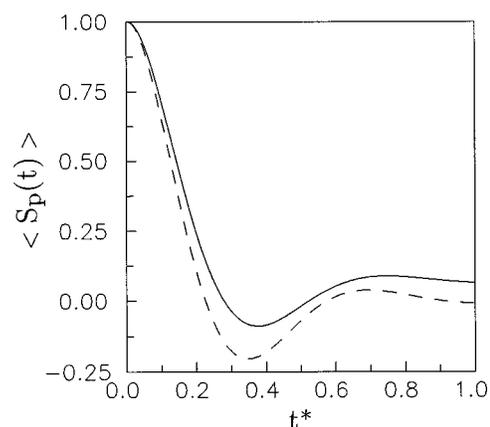


FIG. 8. The non-Markovian results for the time dependence of the average normalized polarization function. The solid and dashed curves are for regions I (contact interface) and III (bulk), respectively.

The present theory can be extended to study a number of other related problems. For example, Eqs. (15) and (19) can be modified to study the polarization relaxation in an inhomogeneous system in the presence of a position dependent external field such as the one produced by an ion or a charged colloidal particle. The relaxation dynamics can also be studied in the presence of a metal surface which would be useful in the studies of interfacial dynamical effects on electrochemical charge transfer processes. Also, in the present work, we have employed linearized equations of motion for the polarization relaxation. It would be interesting to explore the possible nonlinear effects by retaining the nonlinear terms in the dynamical equation of the polarization relaxation. We hope to address these issues in future publications.

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