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Journal of Photochemistry and Photobiology A: Chemistry 102 (1996) 29–33

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

Dynamics of molecules near interfaces

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Abstract

The nature of the pair interaction and of relaxation of dipoles embedded in a liquid in the vicinity of a non-metallic interface is investigated in the continuum limit. It is shown that dipole–dipole interaction as well as the rotational behaviour of a dipole can be significantly modified in the presence of a boundary in liquids characterized by a non-local dielectric function, or in liquids whose dielectric properties change as a result of geometrical restrictions. Structural changes may develop in the interfacial region which affect processes such as translational diffusion, rotations and charge transfer. Different limits are studied and relationships to experimental observables are discussed.

Keywords: Dynamics; Pair interaction; Relaxation; Dipole

1. Introduction

A large number of molecular processes in chemical and in biological related systems occur at solid–liquid or liquid–liquid interfaces. Examples include translational and rotational diffusion in porous silicas [1–4] and micelles [5,6], solvation dynamics under confinement conditions [7,8], proton diffusion at water-membrane interfaces [9] etc. The presence of an interface has been shown to modify the dynamical behaviours of molecules relative to their bulk properties [10,11]. These modifications influence reaction kinetics and photochemical processes in reduced dimensions. While the confining geometry itself may play a major role in slowing down translational diffusion and conformational changes, it is by no means the only aspect which affects the dynamics. For instance, at the interface between a liquid and a solid, or between two liquids, the structure and dielectric properties of the liquid may change, which in turn also influences the dynamics of embedded molecules [1,12–15].

Here we discuss changes in the dipole–dipole interaction and in the relaxation of point dipoles embedded in a liquid near a non-metallic interface when compared with the bulk liquid. We follow Refs. [16,17] where we represented the liquid in the *continuum approximation* in terms of a non-local dielectric function $\epsilon(\boldsymbol{k}, \omega)$. In analogy to this previous work the effect of the interface is introduced through the concept of additional boundary conditions [18]. We analyse the dependence of the dipole–dipole interaction and of the rotational behaviour on the distance between the dipoles and between the dipoles and the boundary, as well as on the dielectric parameters that characterize the interface region. The approach used here is suitable for both static and dynamic limits. Although the continuum framework does not explicitly include molecular level details, it enables closed expressions that relate microscopic quantities to measurable observables such as dielectric functions to be derived [12,19,20]. Continuum approximations and their modifications have been shown to be powerful in unravelling leading physical processes in complex systems.

The non-local nature of the liquid defines a length scale Λ, which is a measure of spatial correlations in the liquid. This parameter can be estimated on the basis of diffraction experiments [21] and on molecular dynamic simulations of liquids [22,23]. For instance, in aqueous solutions the correlation length Λ is of the order of the extension of local hydrogen-bonded clusters, $\Lambda \approx 4$ Å; in solutions of dipolar polymers the correlation length may be much larger [24]. The introduction of this new length scale is of particular importance in the case of a liquid under geometrical restriction. When properties of the system are measured within distances comparable with the correlation length, Λ, fundamental differences between the response of the liquid under geometrical restriction and its bulk response are observed. Only beyond the distance Λ are the limits of the bulk description reached.

The non-local description introduces short-range order within the liquid, at least phenomenologically, and leads to dipole–dipole and dipole–boundary distance and pore size dependences which do not appear in the case of a local dielectric function. The possibility that the liquid itself changes its dielectric behaviour as a result of interaction with the boundary [1,13,14] can be modelled by a region of modified liquid near the boundary. The influence of a modified surface

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PII S1010-6030(96)04363-8

layer of a liquid on ion–ion and dipole–dipole interactions at a metal-electrolyte solution interface was previously considered and shown to provide interpretations of experimental observations of ionic adsorption in electrochemical systems which could not be understood in the framework of the traditional description [25].

2. The model

We now consider the model for the description of electromagnetic interaction of time-dependent point dipoles embedded in a liquid near a substrate. As in Refs. [16,17] we assume that the substrate is characterized by a local dielectric function $\epsilon_{\mathrm{sub}}(\omega)$ and the liquid is described by the non-local dielectric function

$$\frac{1}{\epsilon(k,\omega)}=\frac{1}{\epsilon^*(\omega)}-\left[\frac{1}{\epsilon^*(\omega)}-\frac{1}{\epsilon_b(\omega)}\right]\frac{1}{1+k^2\Lambda^2} \tag{1}$$

Here $\epsilon_*(\omega)$ is the short-wavelength dielectric constant of a bulk liquid, $\epsilon_b(\omega)=\epsilon_b(\boldsymbol{k}=0,\omega)$ and $\boldsymbol{k}$ is a wavevector. The quantity ϵ_* is close to unity and in the low frequency range which we consider in this paper the relationship $|\epsilon_*(\omega)| \ll |\epsilon_b(\omega)|$ is satisfied. Generalizations to a more complex non-local dielectric function are possible.

As already mentioned in Section 1, the continuum approximation is valuable in obtaining analytical relationships between the dielectric properties of the participating media and the details of the dipole–dipole interaction. The non-local nature of the liquid, as introduced in Eq. (1), accounts phenomenologically for some structural aspects of the liquid through the length Λ.

Let us denote the coordinates of the centers of dipoles with dipole moments μ_d and μ_a by $\boldsymbol{r}_d=(0,0,z_d)$ and $\boldsymbol{r}_a=(\boldsymbol{R},z_a)$ respectively, where z_d and z_a are the distances of dipoles from the substrate and R is the distance between dipoles along the surface (Fig. 1). The substrate surface plane coincides with the plane $z=0$.

The energy of the electromagnetic interaction between dipoles with moments μ_d and μ_a in a general orientation with respect to the interface can be written in the following form:

$$U=-\mu_d\cdot\frac{\partial^2\Phi(r_d,r_a)}{\partial r_d\partial r_a}\cdot\mu_a=U^{(dip)}+U^{(ind)} \tag{2}$$

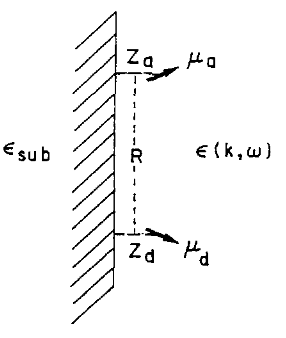

Fig. 1. Dipoles at the substrate–liquid interface.

where $\Phi(\boldsymbol{r}_d,\boldsymbol{r}_a)$ is the potential at a point $\boldsymbol{r}=\boldsymbol{r}_a$ created by a point charge located at $\boldsymbol{r}=\boldsymbol{r}_d$ near the interface and the terms $U^{(\mathrm{dip})}$ and $U^{(\mathrm{ind})}$ describe direct interaction between dipoles and interaction induced by the presence of an interface correspondingly.

The energy $U^{(\mathrm{ind})}$ of indirect interaction which arises from the polarization at the interfacial region has been previously calculated in Ref. [17]. Using the results obtained in Ref. [17], we analyse here the dependence of the interaction energy on the distance between the dipoles and on the substrate and liquid parameters. Here we focus on the consideration of the interaction between molecules with dipole moments μ_d and μ_a *perpendicular* to the surface. The energy of interaction between dipoles has the following asymptotic behaviour: (**1**) *at large distances between dipoles*, $R \gg z_d$, z_a, $g\Lambda$,

$$U\approx\frac{2}{R^3}\frac{|\mu_a\mu_b|\ \epsilon_{sub}}{\epsilon_b\epsilon^{2*}(\epsilon_{sub}+\epsilon_b)}\mathrm{f}(z_a/\Lambda,\ z_d/\Lambda;\ \ \epsilon^*,\ \epsilon_b) \tag{3}$$

(**2**) *in the intermediate region*, z_d, z_a, $\Lambda \ll R \ll g\Lambda$,

$$U\approx\frac{2}{R\Lambda^2}\frac{\epsilon_{sub}+\epsilon_b}{\epsilon_b\epsilon_{sub}(\epsilon_b-\epsilon^*)^2}f(z_a/\Lambda,\ z_d/\Lambda;\ \ \epsilon^*,\ \epsilon_b) \tag{4}$$

Here

$$\begin{aligned}&f(z_a/\Lambda,\ z_d/\Lambda;\ \ \epsilon^*,\ \epsilon_b)=\\&\quad\epsilon^{2*}+(\epsilon_b-\epsilon^*)^2\exp[-(z_d+z_a)/\Lambda]+\epsilon^*(\epsilon_b-\epsilon^*)\\&\quad\times[\exp(-z_d/\Lambda)+\exp(-z_a/\Lambda)]\end{aligned} \tag{5}$$

ϵ_{sub} is the dielectric constant of the substrate and $g=\epsilon_b\epsilon_{\mathrm{sub}}/\epsilon_*(\epsilon_{\mathrm{sub}}+\epsilon_b)$. As an example, at the interface between silica and water $\epsilon_{\mathrm{sub}}=11.6$, $\epsilon_b=80$ and $\epsilon_*=1$ and for low frequencies the parameter $g\approx 10$.

The region of intermediate asymptotics, Eq. (4), with anomalously slow (Coulomb like) decrease in dipole–dipole interaction with distance R exists only in systems with high values of the dielectric constants ϵ_{sub} and ϵ_b of the substrate and of the liquid, when $\epsilon_{\mathrm{sub}}/\epsilon_* \gg 1$ and $\epsilon_b/\epsilon_* \gg 1$, and therefore correspondingly the coefficient $g \gg 1$. For instance, at the silica–water interface, as discussed in case (1), and for $\Lambda\approx 4$ Å [12] the limiting Eq. (4) can apply for a wide range of distances 3 Å$\langle R \langle$20 Å. Also, at an interface between two immiscible liquids (for instance the water–nitrobenzene system; for nitrobenzene $\epsilon_b=34.8$), the slow R dependence of Eq. (5) can play an important role.

When both dipoles are placed at small distances from the surface, z_d, $z_a\langle\Lambda$, equations for the energy of interaction are simplified to

$$U\approx\frac{2|\mu_a\mu_b|}{R^3}\frac{\epsilon_{\mathrm{sub}}\epsilon_b}{\epsilon^{2*}(\epsilon_{\mathrm{sub}}+\epsilon_b)}\ \ R\gg g\Lambda \tag{6}$$

$$U\approx\frac{2|\mu_a\mu_b|}{R\Lambda^2}\frac{(\epsilon_{\mathrm{sub}}+\epsilon_b)\epsilon_b}{\epsilon_{\mathrm{sub}}(\epsilon_b-\epsilon^*)^2}\ \ z_d,z_a,\Lambda\ll R\ll g\Lambda \tag{7}$$

These equations are appropriate for the description of the interaction between dipoles located in the first few layers closest to the substrate, as well as the interaction between adsorbed molecules, i.e. $z_a = z_d \approx r_m$, where r_m is the molecular size. It should be noted that in this case the expression for the dipole–dipole interaction energy at large R is directly proportional to the bulk dielectric constant ϵ_b of a liquid, in contrast to the traditional description obtained for a local representation of the liquid in contact with a substrate, in which the energy U^0 is inversely proportional to ϵ_b:

$$U^0 \approx \frac{2|\mu_a\mu_b|}{R^3}\frac{\epsilon_{sub}}{\epsilon_b(\epsilon_{sub}+\epsilon_b)}, \quad R \gg z_a, z_d \tag{8}$$

When the bulk dielectric constant ϵ_b of a liquid is larger than both ϵ_{sub} and ϵ_* Eqs. (6) and (7) can be written as

$$U \approx \frac{2|\mu_a\mu_b|}{R^3}\frac{\epsilon_{sub}}{\epsilon_*^2} \text{ at } R \gg g\Lambda, z_d, z_a \tag{9}$$

$$U \approx \frac{2|\mu_a\mu_b|}{R\Lambda^2}\frac{1}{\epsilon_{sub}}, \text{ at } z_d, z_a, \Lambda < g\Lambda \tag{10}$$

The different behaviours in Eqs. (3) and (4), Eqs. (6) and (7) and Eqs. (9) and (10) originate solely from our non-local description of the liquid and is essentially insensitive to the details of the imposed boundary conditions [16,26]. At large distances between dipoles (and $\epsilon_b \rangle \epsilon_{sub}$) the interaction energy, Eq. (9), has the same form as the traditional expression, U but with a reduced effective dielectric constant ϵ_*.

Our results demonstrate that the non-local description of liquids leads to a non-uniform distribution of polarization fluctuations in the interfacial region reflected in the dependence of the dielectric response of the liquid on the distance from the substrate. A new characteristic length, the correlation length Λ in a liquid, appears in the problem. Comparison of Eqs. (3)–(10) with the results obtained in a model of the modified liquid layer at the substrate surface [16,25] shows that this effect corresponds to the formation of the interface layer with reduced dielectric constant, ϵ_*. The presence of such a layer reflects the structuring effect of a substrate [12,13]. The thickness of the layer is of the order of the characteristic liquid structure distance Λ. Only when the dipoles are placed far beyond the interfacial layer does the traditional description of Eq. (8) apply. The structuring effect (interfacial hydration) gives rise also to hydration forces which are of crucial importance in the interaction and fusion of biological membranes and macromolecules [13,27].

We see that *for all distances* between dipoles our results differ from the corresponding local behaviour, Eq. (8). The effect of non-locality may lead to an enhancement in the interaction between dipoles. At large distances, $R \gg g\Lambda$, the ratio U/U^0 of interaction energies is about $(\epsilon_b/\epsilon_*)^2$ which for water is of the order of 10^2–10^3. Similar non-local enhancement of dipole–dipole interaction at large distances R was predicted in Ref. [28]. The interaction at the substrate–liquid interface can be larger than the interaction near a free substrate, as described by the ratio

$$(U/U^0)(\epsilon_b = 1) = (\epsilon_{sub}+1)/\epsilon_*^2(\epsilon_{sub}+\epsilon_b)$$

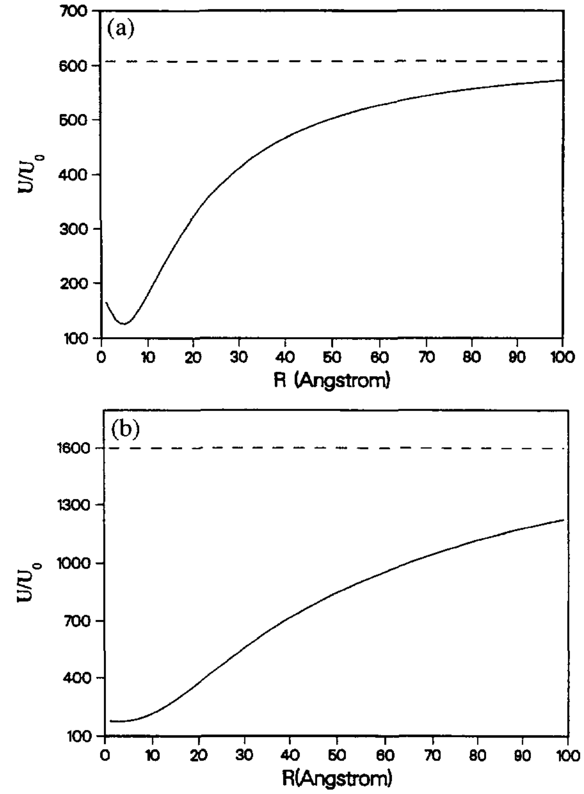

Fig. 2. Dependence of the energy U of interaction between dipoles perpendicular to the interface, on the distance between them. The energy is normalized by the function U^0 representing the traditional expression for the energy of dipole–dipole interaction (in perpendicular orientation) inside a local medium near a substrate. Solid lines are results of exact calculations; dashed lines are long-range asymptotes (3). The calculations were carried out for the following values of parameters: $\epsilon_{sub} = 10$, $\epsilon_* = 2$, $\epsilon_b = 80$, $z_d = z_a = 1$ Å, (a) $\Lambda = 2$ Å and (b) $\Lambda = 5$ Å.

We see that the presence of a dielectric medium by no means weakens the dipole–dipole interaction. This is due to the pulling of electrostatic lines into the interfacial layer with the reduced dielectric constant ϵ_*. It should also be mentioned that in a non-local medium instead of Eq. (8) for $R \gg z_d, z_a$, we have a more complicated behaviour of the dipole–dipole interaction. This behaviour reveals a significant change in the form of $U(R)$ at a new characteristic length $g\Lambda$. The dependences of the interaction on the distance R between dipoles, calculated over the whole range of distances R using the exact equation for U, are shown in Fig. 2.

The interaction between dipoles with other orientations of the dipole moments μ_d and μ_a can be found similarly. Our calculations show that, for large values of dielectric constants ϵ_b or ϵ_{sub} of the liquid or of a substrate, the interaction between dipoles with moments parallel to the surface is weaker than the interaction between dipoles perpendicular to the surface. Again, the inclusion of non-local dielectric properties leads to an enhancement of dipole–dipole interaction. However, in this case the effect of enhancement is not so pronounced. In contrast to the case of perpendicular dipoles where for all values of parameters (ϵ_b, ϵ_{sub}, ϵ_*, Λ, R, z_d and z_a) we had a repulsion between dipoles now the type of interaction (repulsive or attractive) depends on these parameters. For given parameters characterizing the liquid and substrate (ϵ_b, ϵ_{sub}, ϵ_*, Λ) the interaction energy may change sign as a function of the distance between dipoles.

3. Dipole relaxation near boundaries

The formalism described in this paper has also been applied [16] to the study of the rotational relaxation of a time-dependent point dipole in a liquid near a substrate. The relaxation properties of a dipole at the interface can be expressed through its effective polarizability and dielectric friction $\xi_D(\omega)$. In order to calculate these quantities one has to find the field $\boldsymbol{E}'(\boldsymbol{r}_0,\omega)$ induced by an oscillating dipole at the point of its location.

The dielectric friction relates [19,29] the frictional torque $\boldsymbol{T}$ to the angular velocity Ω of a dipole:

$$T(\omega) = -\xi_D(\omega)\Omega(\omega) \tag{11}$$

A frequency-dependent rotational time $\tau_R(\omega)$ can be defined through the dielectric friction:

$$\tau_R(\omega) = \xi_D(\omega)/2kT \tag{12}$$

The net dielectric friction $\xi_D(\omega)$ is the sum of the bulk, $\xi_D^{(b)}(\omega)$, and the surface, $\xi_D^{(s)}(\omega)$, terms. The influence of boundary on the rotational relaxation can be obtained by studying the change in the friction due to an interface which is also derived from the induced field.

For a dipole perpendicular to the interface and located at a distance z_0 from the substrate we found [16] the following limiting behaviours of the surface component of the dielectric friction $\xi_D^{(s)}(\omega)$.

(1) $z_0 \gg \Lambda$

$$\xi_D^{(s)}(\omega) = \frac{\mu^2}{4Iz_0^3} Im\left[\frac{1}{\epsilon_b(\omega)}\frac{\epsilon_b(\omega)-\epsilon_{sub}}{\epsilon_b(\omega)+\epsilon_{sub}}\right] \tag{13}$$

where I is the moment of inertia of the dipole. Eq. (13) is the classical result obtained [30] for a local representation of the liquid in contact with a substrate and is due to the effect of image charges.

(2) For $z_0 \ll \Lambda$,

$$\xi_D^{(s)}(\omega) = \frac{\mu^2}{4Iz_0^3} Im\left[\frac{1}{\epsilon^*(\omega)}\frac{\epsilon^*(\omega)-\epsilon_{sub}}{\epsilon^*(\omega)+\epsilon_{sub}}\right] \tag{14}$$

This result originates from the non-local description of the liquid and is again insensitive to the details of the boundary. We see that at small distances from the substrate the dielectric friction has the same "image force" form as for large distances, Eq. (13), but with a reduced effective dielectric constant ϵ_*.

Comparing Eqs. (13) and (14) with the expression for the dielectric friction in the liquid bulk [16] we conclude that in the two limiting cases, $z_0 \langle \Lambda$ and $z_0 \rangle \Lambda$, the boundary corrections to $\xi_D^{(b)}(\omega)$ are small, being of the relative order of R_c^3/z_0^3, where R_c is the radius of the cavity around a dipole molecule. The radius of the cavity is estimated to be of the order of few molecular radii which limits the contribution of the boundary to the dielectric friction and consequently to the rotational time. Larger contributions can arise, as discussed in the previous section, when the properties of the liquid itself are changed by the presence of the interface [16]. One also expects the surface contribution to be significant for macromolecules near an interface where R_c is larger than the radius of the liquid molecules. For such cases a more realistic approach is required in order to account of the detailed charge distribution in molecules.

4. Conclusions

We have investigated the influence of a non-metallic interface on the interaction between point dipoles located near the interface in the liquid side and on dipole relaxation. Both the liquid and the boundary are described in terms of the continuum approach by their dielectric properties. We assumed that the substrate is given by a local dielectric function and the liquid by a non-local dielectric function which introduces a typical length Λ into the problem. The results reveal some new limits of the dipole–dipole interaction and of dipole relaxation which originate from the non-local nature of the liquid. The results strongly depend on the embedding and neighbouring dielectric functions and display a rich range of behaviours which may be amenable to experimental tests.

Our studies demonstrate that in order to provide a correct description of the interaction between dipoles in a liquid near an interface it is necessary to take into account the influence of the bulk liquid and not only the first few layers. There is a difference between dipoles interacting inside one monolayer of liquid molecules on a substrate–vacuum interface and those in the first layer at a substrate–liquid interface. The polarization of the region in the liquid with thickness of the order of the distance R between dipoles may contribute significantly to the interaction between two dipoles at a surface. This fact should be taken into account in numerical simulations of the interfacial properties of liquid.

The approach introduced in the paper can be used also in describing liquid–liquid interfaces where one takes into account the non-local properties of both liquids in terms of their structure parameter Λ. In such cases the functional form of the interaction energy, Eqs. (3) and (4), is retained. The parameter Λ should, however, be replaced by an effective length characterizing the thickness of the surface layer of both liquids.

In general, the importance of liquid structuring near an interface has been reported in a number of studies on confining geometries. Direct measurements of the dielectric function, solvation in pores and proton transfer in membranes demonstrate the heterogeneous nature of a confined liquid. It is worth mentioning the effect of the modified dipole–dipole interaction on adsorption isotherms which enters through the contribution to the chemical potential of the surface layer. For low concentrations one expects therefore that the slope of the isotherm (surface coverage vs. concentration) will depend on the nature of the liquid through Λ and the dielectric functions in the interface region. For dipoles perpendicular to the surface the slope should decrease as a result of the non-local nature of the liquid.

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