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**QC173.4.R44 D58 1994**



**Disorder effects on relaxational processes**

Vol: Issue:

Date: 1994 Pages: 279-305

Title: , Chapter title: Boundary Effects on Dipole-Dipole  
Interactions and Molecular Relaxation

## 9 Boundary Effects on Dipole–Dipole Interactions and Molecular Relaxation

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### List of Symbols and Abbreviations

#### *English Symbols*

<b>D</b>	electric displacement
<b>E</b>	electric field
<b>E'</b>	induced electric field
$H_0^{(1)}(z)$	Hankel function of zero order
<b>I</b>	moment of inertia of a dipole
$J_0(z)$	Bessel function of zero order
$K_0(z)$	modified Bessel function of third kind
<b>k</b>	wave vector
<b>k<sub>1</sub></b>	projection of the wave vector on the surface
<b>P</b>	polarization
$R_c$	radius of cavity
$T_{ij}$	tensor of dipole–dipole interaction
<b>U</b>	energy of interaction between dipoles

#### *Greek Symbols*

$\alpha_0(\omega)$	polarizability of a dipole molecule
$\epsilon_b(\omega)$	local dielectric constant of a medium

$\epsilon_{\text{sub}}$	dielectric constant of a substrate
$\epsilon_*(\omega)$	short wave-length dielectric constant of a medium
$\epsilon_{ij}(\mathbf{r}, \mathbf{r}'; \omega)$	nonlocal dielectric tensor
$\epsilon(\mathbf{k}, \omega)$	Fourier component of longitudinal component of nonlocal dielectric tensor
$\omega$	frequency
$\lambda$	correlation length
$\mu$	dipole moment
$\zeta_{\text{D}}$	dielectric friction coefficient
$\zeta_{\text{D}}^{(\text{s})}$	surface component of dielectric friction
$\zeta_{\text{D}}^{(\text{b})}$	bulk component of dielectric friction
$\tau$	relaxation time
$\tau_{\text{R}}$	rotational time
$\Phi$	electric potential
$\chi_{ij}(\mathbf{r}, \mathbf{r}'; \omega)$	nonlocal dielectric permeability tensor

## 9.1 Introduction

Recent experimental and theoretical studies [1–5] have demonstrated that spatial restrictions can strongly affect the dynamic and thermodynamic properties of embedded liquids and molecules. The effects observed and predicted include the influence of interfaces on the pair-interaction energy between charged or uncharged particles [6–7], translational and rotational diffusion of probe molecules [4, 8] as well as chemical reactions and energy transfer properties [1, 8]. It is by now well established that liquids in small confinements differ significantly from bulk liquids [5].

The behavior of molecular systems under geometrical restrictions is of importance in a wide range of problems related to catalysis, microemulsions, lubrication, polymer solutions, biological membranes and more [1–5]. The influence of boundaries on the properties of molecules in their vicinity is of course related to the nature of the intermolecular forces and to how they are modified near an interface. These modifications can directly influence processes such as adsorption, electron or energy transfer and diffusional properties at interfaces.

In this paper we discuss changes in the rotational relaxation of a dipole and in the interaction between dipoles embedded in a liquid near a nonmetallic interface when compared to the bulk liquid. We follow [9, 10] where we represented the liquid in the *continuum approximation*, in terms of a nonlocal dielectric function  $\epsilon(\mathbf{k}, \omega)$ . In analogy to these previous works the effect of the interface is introduced through the concept of additional boundary conditions [11]. We analyze the dependence of the dipole–dipole interaction and the rotational relaxation time 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 one to derive closed expressions that relate microscopic quantities to measurable observables such as dielectric functions [12–14]. Continuum approximations and their modifications have been shown to be powerful in unravelling leading physical processes in complex systems.

The nonlocal nature of the liquid defines, in our case, a length scale,  $\lambda$ , which is a measure of spatial correlations in the liquid. This parameter can be estimated on the base of diffraction experiments [15] and on molecular dynamic simulations of liquids [16, 17]. For instance, in aqueous solutions the correlation length,  $\lambda$ , is of the order of the extension of local hydrogen-bonded clusters. The introduction of this new length scale is of particular importance in the consideration of a liquid under geometrical restriction. When the characteristic size of the system is comparable with the structure distance,  $\lambda$ , the spatial correlations cause a fundamental difference between the response of the liquid under geometrical restriction and its macroscopic response. Only beyond this distance are the limits of the macroscopic description reached.

The nonlocal description introduces a short range order within the continuum model of the liquid, at least phenomenologically, and leads to dipole-dipole and dipole-boundary distance and pore size dependencies which do not appear in the case of a local dielectric function. In particular, the effect of nonlocality leads to the essential enhancement of the interaction between dipoles in the interfacial layer. Corrections to the bulk polarizability of a dipole and to the dielectric friction due to the boundary are also considered, but are shown to be small for most of the relevant parameters. In order to mimic the possibility that the liquid itself changes its dielectric behavior due to interaction with the boundary [4, 18, 19] we assume a region of modified liquid near the boundary. This allows for more significant changes in the dipole relaxation and concurs with experimental observations [4]. The influence of a modified surface 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 to experimental observations of ionic adsorption in electrochemical systems which could not be understood in the framework of the traditional description [7, 20].

## 9.2 Basic Concepts of Nonlocal Screening Theory

Classical macroscopic electrodynamics is based on the local constitutive relation between the displacement  $\mathbf{D}$  and the macroscopically averaged electric field  $\mathbf{E}$  in a medium

$$\mathbf{D} = \varepsilon_b(\omega)\mathbf{E} , \quad (9.1)$$

where  $\varepsilon_b(\omega)$  is the macroscopic dielectric function which depends on the frequency  $\omega$ . The dielectric function  $\varepsilon_b(\omega)$  is a global characteristic of the medium response which does not reveal the subtle features of the short range structure of

the medium. A step towards the incorporation of some structural aspects of the medium within the continuum model can be made by invoking a nonlocal relationship

$$D_i(\mathbf{r}; \omega) = \sum_j \int d\mathbf{r}' \varepsilon_{ij}(\mathbf{r}, \mathbf{r}'; \omega) E_j(\mathbf{r}'; \omega), \quad i, j = x, y, z \quad (9.2)$$

instead of Eq. (9.1). Here  $\varepsilon_{ij}(\mathbf{r}, \mathbf{r}'; \omega)$  is a nonlocal dielectric tensor which characterizes short range order of the medium. In contrast to the classical local approach the nonlocal description does not assume any additional space averaging of fields apart from quantum-mechanical and statistical. In a homogeneous isotropic medium this dielectric function depends on difference  $\mathbf{r} - \mathbf{r}'$  rather than on  $\mathbf{r}$  and  $\mathbf{r}'$  separately.

The meaning of Eq. (9.2) becomes more obvious when it is written in terms of the vector of local polarization,

$$P_i(\mathbf{r}; \omega) = \sum_j \int d\mathbf{r}' \chi_{ij}(\mathbf{r}, \mathbf{r}'; \omega) E_j(\mathbf{r}'; \omega), \quad (9.3)$$

where

$$\chi_{ij}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{4\pi} \{ \varepsilon_{ij}(\mathbf{r}, \mathbf{r}'; \omega) - \delta_{ij} \delta(\mathbf{r} - \mathbf{r}') \} \quad (9.4)$$

is the nonlocal dielectric permeability tensor. Equation (9.4) states that the value of the polarization at point  $\mathbf{r}$  is determined not only by the field  $\mathbf{E}(\mathbf{r})$ , at the same point, but also by the field at other points  $\mathbf{r}'$  in some vicinity of  $\mathbf{r}$ . The origin of the nonlocality is the correlation of polarization fluctuations in space, and only the range of points  $\mathbf{r}'$  around  $\mathbf{r}$  where the correlation function  $\langle \tilde{\mathbf{P}}(\mathbf{r}) \tilde{\mathbf{P}}(\mathbf{r}') \rangle$  differs from zero contributes to the integral in Eq. (9.3).

The fluctuation-dissipation theorem [21] gives a relationship between the “spectral function” of the polarization fluctuations

$$S_{ij}(\mathbf{k}; \omega) = \int d\mathbf{r} dt \langle \tilde{P}_i(\mathbf{r}, t) \tilde{P}_j(0, 0) \rangle \exp(-i\mathbf{k}\mathbf{r} + i\omega t) \quad (9.5)$$

and the dielectric function. In a homogeneous isotropic medium this relationship has the following form

$$\text{Im} \left\{ \frac{1}{\varepsilon(\mathbf{k}; \omega)} \right\} = \frac{1}{4\pi^2} [\exp(-\hbar\omega/kT) - 1] S(\mathbf{k}; \omega), \quad (9.6)$$

where  $S(\mathbf{k}; \omega)$  and  $\varepsilon(\mathbf{k}; \omega)$  are the longitudinal components of  $S_{ij}$  and  $\varepsilon_{ij}$  respectively. Equation (9.6) provides the tool for the determination of  $\varepsilon(\mathbf{k}; \omega)$  on the basis of microscopic calculations, molecular dynamic simulations or based on some suitable models [12, 16, 17]. The form of the fluctuation-dissipation theorem is much more complicated in the inhomogeneous case.

It is usually natural to assume that the spatial correlations for each frequency decay exponentially with a characteristic correlation length  $\Lambda(\omega)$ . In this case, neglecting for simplicity the difference in the behavior of longitudinal and

transversal components of  $S_{ij}$  with respect  $\mathbf{r}$  we have

$$S_{ij}(\mathbf{r}, \omega) = \delta_{ij} S(\mathbf{k} = 0; \omega) \frac{\exp(-r/\Lambda(\omega))}{4\pi\Lambda^2(\omega)r}. \quad (9.7)$$

When the correlation length is only weakly frequency-dependent (in the frequency region where  $\Lambda$  differs from zero) Eq. (9.7) leads to the following expression for the nonlocal dielectric function

$$\frac{1}{\varepsilon(k, \omega)} = \frac{1}{\varepsilon_*(\omega)} - \left( \frac{1}{\varepsilon_*(\omega)} - \frac{1}{\varepsilon_b(\omega)} \right) \frac{1}{1 + k^2\Lambda^2}. \quad (9.8)$$

Here  $\varepsilon_*(\omega)$  is the short-wavelength dielectric constant of medium and  $\varepsilon_b(\omega) = \varepsilon_b(k = 0, \omega)$ . One usually assumes the Debye form of the local dielectric function,  $\varepsilon_b(\omega)$ ,

$$\varepsilon_b(\omega) = \frac{\varepsilon_b - i\omega\tau}{1 - i\omega\tau}, \quad (9.9)$$

where  $\tau$  is the characteristic relaxation time, although other forms may be chosen. A similar expression is used for  $\varepsilon_*(\omega)$ . The quantity  $\varepsilon_*$  is close to unity and in the low frequency range which we consider in this paper the relationship  $|\varepsilon_*(\omega)| \ll |\varepsilon_b(\omega)|$  is satisfied.

Equation (9.8) can also be considered as the simplest interpolation relation which describes the transition between short and long wavelength asymptotics of nonlocal dielectric function. Generalization to a more complex nonlocal dielectric function is possible, i.e.  $\Lambda$  can be frequency dependent. Here, for simplicity, we assume that  $\Lambda$  is  $\omega$ -independent. It should be stressed that the final conclusions of this work depend only on two important parameters of the medium:  $\varepsilon_b(\omega)/\varepsilon_*(\omega)$  and  $\Lambda$  rather than on the explicit form of nonlocal dielectric function in Eq. (9.8).

In order to demonstrate the physical meaning of the nonlocal screening concept we will consider the electric potential,  $\Phi$ , produced by a static unit point charge located at  $\mathbf{r} = \mathbf{r}_0$  in a nonlocal medium. According to Eq. (9.2) the Poisson equation takes the form

$$\sum_{i,j} \frac{\partial}{\partial r_i} \int d\mathbf{r}' \varepsilon_{ij}(\mathbf{r}, \mathbf{r}') \frac{\partial}{\partial r_j'} \Phi(\mathbf{r}') = -4\pi\delta(\mathbf{r} - \mathbf{r}_0). \quad (9.10)$$

In an infinite isotropic medium,  $\varepsilon_{ij}(\mathbf{r}, \mathbf{r}') = \varepsilon_{ij}(\mathbf{r} - \mathbf{r}')$  and the integro-differential Eq. (9.10) is solved with the help of a Fourier transform. The solution is

$$\Phi(\mathbf{r}) = \Phi(|\mathbf{r} - \mathbf{r}_0|) = \frac{2}{\pi} \int_0^\infty \frac{dk}{\varepsilon_L(k)} \frac{\sin k|\mathbf{r} - \mathbf{r}_0|}{k|\mathbf{r} - \mathbf{r}_0|}, \quad (9.11)$$

where  $\varepsilon_L(k)$  is the longitudinal component of dielectric function

$$\varepsilon_L(k) = \sum_{i,j} \frac{k_i k_j}{k^2} \int d(\mathbf{r} - \mathbf{r}') \varepsilon_{ij}(\mathbf{r} - \mathbf{r}') \exp[i\mathbf{k}(\mathbf{r} - \mathbf{r}')]. \quad (9.12)$$

For media with local screening

$$\varepsilon_{ij}(\mathbf{r}, \mathbf{r}') = \varepsilon_b \delta_{ij} \delta(\mathbf{r} - \mathbf{r}') . \quad (9.13)$$

Equation (9.10) is reduced to the usual Poisson equation and Eq. (9.11) to the Coulomb field form,  $\Phi = 1/\varepsilon_b |\mathbf{r} - \mathbf{r}_0|$ .

Equation (9.11) can be rewritten in the form

$$\Phi(R) = \frac{1}{\varepsilon_{\text{eff}}(R)R} , \quad R = |\mathbf{r} - \mathbf{r}_0| . \quad (9.14)$$

Here

$$\varepsilon_{\text{eff}}(R) = \left\{ \frac{2}{\pi} \int_0^\infty \frac{dk}{\varepsilon_L(k)} \frac{\sin kR}{k} \right\}^{-1} \quad (9.15)$$

is the effective dielectric constant which varies with the distance from the charge.

The physical meaning of Eqs. (9.14) and (9.15) is quite obvious: due to structural effects, at small distances  $r$  (large  $k$ ) from an external charge or other external perturbations, the medium manifests reduced effective dielectric function  $\varepsilon_*(\omega)$  and only at distances larger than  $\Lambda$  (small  $k$ ) are the limits of microscopic description reached. Note that the ratio  $\varepsilon_b(\omega)/\varepsilon_*(\omega)$  is quite large, so that the noticeable deviation of the dielectric response  $\varepsilon(\mathbf{k}; \omega)$  from  $\varepsilon_b(\omega)$  should be observed over spatial scales substantially larger than  $\Lambda$ .

It should be mentioned that the use of the nonlocal dielectric function, Eq. (9.8), is equivalent to the description of the medium by the Landau free energy functional

$$F = \int d\mathbf{r} \{ a\phi(\mathbf{r}) + c[\nabla\phi(\mathbf{r})]^2 \} , \quad (9.16)$$

where  $\phi$  is a scalar fluctuation field of the order parameter. In our model the order parameter is related to the polarization,  $\mathbf{P} \propto \nabla\phi$ , and the characteristic length of decay of the correlation function  $\Lambda = (c/a)^{1/2}$ . This free energy functional has been often used for the description of interactions in liquid [22–24].

In the presence of an interface the dielectric tensor depends on  $\mathbf{r}$  and  $\mathbf{r}'$  separately and to solve Eq. (9.10) the knowledge of the concrete form of  $\varepsilon_{ij}(\mathbf{r}, \mathbf{r}')$  is necessary. The method of additional boundary conditions (ABC) is used here to simplify the problem. Within this method the interface is supposed to be sharp and the solution of the complete spatial non-homogeneous problem is constructed by matching the bulk solutions known for the medium on either side of the interface [11, 25]. These approximations are justified when the thickness of an interfacial layer, where the dielectric function differs essentially from the corresponding bulk values, is much less than the scale of the change of any bulk solutions.

The usual boundary conditions, continuity of the potential,  $\Phi$ , and of the normal component of the displacement  $\mathbf{D}$ , are sufficient for the matching of the bulk solutions of Eq. (9.10) at boundaries of local media. In the nonlocal media new types of bulk waves (longitudinal modes) can arise. Therefore, ABC has to be added to make the problem well-defined. In the framework of linear elec-

rodynamics, the general type of the ABC is quite clear. These conditions should linearly interlink the fields  $\mathbf{E}$  and  $\mathbf{D}$  and their derivatives on the surface [11]; of course, the relationship should be a homogeneous equation (surface sources of fields are absent). Hence, if derivatives are disregarded, the ABC can be written as

$$D_i(z=0, k_1) + \sum_{j=1}^3 \Gamma_{ij} E_j(z=0, k_1) = 0. \quad (9.17)$$

Here  $\Gamma_{ij}$  is a tensor which depends on the properties of the boundary. The ABC method was used previously for the description of the light reflection from the surface of semiconductors and molecular crystals [11, 25] and for the calculation of the effective dipole polarizability near a metal described by the nonlocal dielectric function [26].

In the following sections we use the nonlocal screening theory in the consideration of dipole relaxation and dipole–dipole interactions in a liquid close to a boundary. As in [9, 10] we assume that the substrate is characterized by a local dielectric function,  $\varepsilon_{\text{sub}}(\omega)$ , and the liquid is described by the nonlocal dielectric function Eq. (9.8). In order to calculate the rotational relaxation time and the energy of pair interaction between dipoles one has to find the potential induced by an oscillating unit point charge in a liquid. Let us denote the distance of a dipole from the substrate by  $z_0$ . The substrate surface plane coincides with the plane  $z=0$ .  $z_0$  is assumed to be smaller than the radiation wavelength in liquid, so that retardation can be neglected and the Poisson equation, Eq. (9.10) applies.

In order to solve Eq. (9.10) it is convenient to Fourier transform the potential and the dielectric function from the two-dimensional spatial vector  $\mathbf{R}$  (parallel to the surface) to the corresponding wave vector  $\mathbf{k}_1$ .

The total potential created by a charge in a liquid near an interface is the sum of the bulk (Coulomb like) term,  $\Phi^{(c)}$ , and the term arising due to the interaction with an interface,  $\Phi^{(\text{ind})}$ . The potential of the point charge in the bulk liquid has the form [27]

$$\begin{aligned} \Phi^{(c)}(z, k_1) &= 2 \int_{-\infty}^{\infty} dk_z \frac{\exp(ik_z(z - z_0))}{k^2 \varepsilon(k, \omega)} \\ &= 2\pi \left( C_1 \frac{\exp(-k_1|z - z_0|)}{k_1} + C_2 \frac{\exp(-\Gamma|z - z_0|)}{\Gamma} \right). \end{aligned} \quad (9.18)$$

Here  $\Gamma$  is the solution of the equation

$$\varepsilon(\mathbf{q}, \omega) = 0, \quad \mathbf{q} = (\mathbf{k}_1, \Gamma), \quad \Gamma = \sqrt{k_1^2 + 1/\Lambda^2}, \quad (9.19)$$

and

$$C_1 = 1/\varepsilon_b(\omega), \quad C_2 = 1/\varepsilon_*(\omega) - 1/\varepsilon_b(\omega), \quad \mathbf{k}^2 = \mathbf{k}_1^2 + \mathbf{k}_z^2. \quad (9.20)$$

The point charge induces in the liquid side two waves, transverse and longitudinal, reflected from the substrate. Correspondingly the potential of these



waves can be written in the form

$$\Phi^{(\text{ind})}(z, k_1) = A \exp(-k_1 z) + B \exp(-\Gamma z), \quad z > 0. \quad (9.21)$$

In the substrate the potential has the form

$$\Phi^{(\text{sub})}(z, k_1) = D \exp(k_1 z), \quad z < 0. \quad (9.22)$$

The prefactors  $A$ ,  $B$  and  $D$  are obtained from the boundary conditions at  $z = 0$  discussed above:

(a) Continuity of the potential

$$(\Phi^{(\text{c})} + \Phi^{(\text{ind})})_{z=0} = \Phi^{(\text{sub})}|_{z=0} \quad (9.23)$$

(b) Continuity of the normal component of the displacement  $D_z(z, k_1)$

$$-\epsilon_b \frac{d}{dz} (\Phi^{(\text{c})} + \Phi^{(\text{ind})})_{z=0} = -\epsilon_{\text{sub}} \frac{d}{dz} \Phi^{(\text{sub})}|_{z=0} \quad (9.24)$$

(c) Additional boundary condition due to the nonlocal nature of the liquid.

As in our previous papers [9, 10] we use the particular case of ABC, Eq. (9.18), assuming that on the liquid side the nonlocal part of the polarization (or the polarization current density) must vanish at the boundary

$$P_z(z, k_1) = (D_z(z, k_1) - \epsilon_* E_z(z, k_1))/4\pi|_{z=+0} = 0. \quad (9.25)$$

This assumption is based on the premise that the solvent dipoles which carry the polarization cannot penetrate into the substrate. It can be shown that at low frequencies the results are weakly dependent on the form of the tensor  $\Gamma_{ij}$  characterizing properties of the interface [28]. The solution of Eqs. (9.23)–(9.25) gives the expression for the induced potential in the liquid.

### 9.3 Dipole Relaxation near Boundaries

We now consider a model for the rotational relaxation of a time-dependent point dipole embedded 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 [29]. In order to calculate these quantities one has to find the field induced by an oscillating dipole at the point of its location. This problem can be solved within the nonlocal screening theory described in previous section.

As already mentioned in the introduction, the continuum approximation is valuable in obtaining analytical relationships between the dielectric properties of the participating media and the details of the molecular relaxation and dipole–dipole interaction. The nonlocal nature of the liquid, as introduced in Eq. (9.8), accounts phenomenologically for some structural aspects of the liquid through the length  $\Lambda$ .

Starting with the induced potential  $\Phi^{(\text{ind})}$  for a single charge we find the potential for a dipole in the  $z$  direction by adding potentials for a charge  $q$  at

$\mathbf{r} = (0, 0, z_0)$  and a charge  $-q$  at  $\mathbf{r} = (0, 0, z_0 - \Delta)$ . Expanding the solution of Eqs. (9.23)–(9.25) to first order in  $\Delta$  and introducing dipole moment  $\mu_z = q\Delta$ , we find the following expression for the potential induced by the point dipole in the liquid

$$\begin{aligned} \Phi_{\text{dip}}^{(\text{ind})}(z, k_1) = & -2\pi\mu_z \left( C_1 \exp(-k_1 z_0) - 2\varepsilon_{\text{sub}} \right. \\ & \times \frac{C_1^2 \exp(-k_1 z_0) + C_1 C_2 \exp(-\Gamma z_0)}{1 + C_1 \varepsilon_{\text{sub}} + C_2 \varepsilon_{\text{sub}} k_1 / \Gamma} \Big) \exp(-k_1 z) \\ & - 2\pi\mu_z \left( C_2 \exp(-\Gamma z_0) - 2\varepsilon_{\text{sub}} \frac{k_1}{\Gamma} \right. \\ & \times \frac{C_2^2 \exp(-\Gamma z_0) + C_1 C_2 \exp(-k_1 z_0)}{1 + C_1 \varepsilon_{\text{sub}} + C_2 \varepsilon_{\text{sub}} k_1 / \Gamma} \Big) \exp(-\Gamma z). \end{aligned} \quad (9.26)$$

We take the inverse Fourier transform to find the potential at the arbitrary point  $\mathbf{r} = (\mathbf{R}, z)$ . Differentiating with respect to  $z$  gives the induced electric field

$$E'_z(z, k_1) = - \frac{d\Phi_{\text{dip}}^{(\text{ind})}(z, k_1)}{dz} \quad (9.27)$$

so that

$$E'_z(\mathbf{r}) = \frac{1}{(2\pi)^2} \int d^2\mathbf{k}_1 E'_z(z, k_1) \exp(i\mathbf{k}_1 \mathbf{R}). \quad (9.28)$$

Combining Eqs. (9.26)–(9.28) the induced field at  $\mathbf{r}_0 = (R=0, z=z_0)$  can be expressed as

$$\mathbf{E}'(\mathbf{r}_0) = -F(z_0, \omega) \mu_z \hat{\mathbf{z}}, \quad (9.29)$$

where  $\hat{\mathbf{z}}$  is the unit vector in  $z$ -direction, and

$$\begin{aligned} F(z_0, \omega) = & \int_0^\infty dk_1 k_1 \left\{ C_1 k_1 \exp(-2k_1 z_0) + C_2 \Gamma \exp(-2\Gamma z_0) - 2\varepsilon_{\text{sub}} k_1 \right. \\ & \times \frac{C_1^2 \exp(-2k_1 z_0) + C_2^2 \exp(-2\Gamma z_0) + 2C_1 C_2 \exp[-(\Gamma + k_1)z_0]}{1 + C_1 \varepsilon_{\text{sub}} + C_2 \varepsilon_{\text{sub}} k_1 / \Gamma} \Big\}. \end{aligned} \quad (9.30)$$

Introducing the dimensionless variables,  $u = k_1 z_0$ , and  $\tilde{\Gamma} = \Gamma z_0 = \sqrt{u^2 + z_0^2 / \Lambda^2}$  we obtain

$$\begin{aligned} F(z_0, \omega) = & \frac{1}{z_0^3} \int_0^\infty du u \left\{ C_1 u \exp(-2u) + C_2 \tilde{\Gamma} \exp(-2\tilde{\Gamma}) \right. \\ & \left. - 2\varepsilon_{\text{sub}} u \frac{C_1^2 \exp(-2u) + C_2^2 \exp(-2\tilde{\Gamma}) + 2C_1 C_2 \exp[-(\tilde{\Gamma} + u)]}{1 + C_1 \varepsilon_{\text{sub}} + C_2 \varepsilon_{\text{sub}} u / \tilde{\Gamma}} \right\}. \end{aligned} \quad (9.31)$$

The induced field for a dipole in the  $\hat{x}$  direction is found similarly and the result differs from Eq. (9.29) only by the factor 1/2

$$\mathbf{E}'(\mathbf{r}_0) = -\frac{1}{2} F(z_0, \omega) \mu_x \hat{x} . \quad (9.32)$$

Equation (9.31) constitutes the central result in the study of the influence of a boundary on the dipole properties. It provides the induced field input in the calculation of the dielectric friction [13, 30],  $\xi_D(\omega)$ . The net friction is the sum of the bulk,  $\xi_D^{(b)}(\omega)$ , and the surface,  $\xi_D^{(s)}(\omega)$ , terms, and  $\xi_D^{(s)}(\omega)$  can be expressed through  $F(z_0, \omega)$  as follows:

$$\xi_D^{(s)}(\omega) = \frac{\mu^2}{I} \frac{F(z_0, \omega) - F(z_0, 0)}{-i\omega} , \quad (9.33)$$

where  $I$  is the moment of inertia of the dipole. For low frequencies such that  $\omega\tau \ll 1$  the rhs of Eq. (9.33) reduces to  $(\mu^2/I\omega) \text{Im } F(z_0, \omega)$ . The dielectric friction relates [12, 29] the frictional torque,  $\mathbf{T}$ , to the angular velocity,  $\Omega$ , of a dipole:

$$\mathbf{T}(\omega) = -\xi_D(\omega) \Omega(\omega) . \quad (9.34)$$

A frequency dependent rotational time,  $\tau_R(\omega)$ , can be defined through the dielectric friction [13, 29]:

$$\tau_R(\omega) = \xi_D(\omega)/2kT . \quad (9.35)$$

Generally in deriving the rotational relaxation in real systems a mechanical friction term has to be included [13, 29]. We however will concentrate on the dielectric contribution.

The influence of a surface on the optical absorption of the molecule is also determined by the induced field, Eq. (9.31). The net field acting on the dipole is the sum of the applied field  $\mathbf{E}_0$  and induced field  $\mathbf{E}'(\mathbf{r}_0)$ . Correspondingly the induced dipole moment  $\mu$  of a dipole with isotropic frequency-dependent  $\alpha_0(\omega)$ , is equal

$$\mu = \alpha_0(\omega)(\mathbf{E}_0 + \mathbf{E}'(\mathbf{r}_0)) = \alpha_0(\omega)[\mathbf{E}_0 - F(z_0, \omega)(\frac{1}{2}\mu_x \hat{x} + \mu_z \hat{z})] , \quad (9.36)$$

where we have assumed that  $\mathbf{E}_0$ , and hence  $\mathbf{E}'$ , lie in the  $x$ - $z$  plane. The solution of Eq. (9.36) can be written in the form

$$\mu_j = \alpha_j^{(\text{eff})}(\omega) E_{0j}, \quad j = x, z . \quad (9.37)$$

The quantities  $\alpha_j^{(\text{eff})}$  are components of the renormalized polarizability, i.e. the polarizability modified by the interaction of the dipole with its “image” in the substrate. They are equal

$$\alpha_j^{(\text{eff})}(\omega) = \frac{1}{\alpha_0^{-1}(\omega) + n_j F(z_0, \omega)} , \quad (9.38)$$

where  $n_x = 1/2$  and  $n_z = 1$ .

The dielectric friction,  $\xi_D(\omega)$ , determines the rotational diffusion properties of the dipole. The influence of boundary on the rotational relaxation can therefore be obtained by studying the change in the friction due to an interface. This change is also derived from the induced field,  $F(z_0, \omega)$ .

Let us focus on the limiting behaviors of the function  $F(z_0, \omega)$ :

(1)  $z_0 \gg \lambda$ , namely  $\tilde{\Gamma} \gg 1$ . This implies

$$F(z_0, \omega) = \frac{1}{4z_0^3} \frac{1}{\epsilon_b(\omega)} \frac{\epsilon_b(\omega) - \epsilon_{\text{sub}}}{\epsilon_b(\omega) + \epsilon_{\text{sub}}}, \quad (9.39)$$

which is the classical result obtained [31, 32] for a local representation of the liquid in contact with a substrate and is due to the effect of image charges.

(2)  $z_0 \ll \lambda$  and  $|\epsilon_b(\omega)| \gg |\epsilon_*(\omega)|$  (which typically holds)

$$F(z_0, \omega) = \frac{1}{4z_0^3} \frac{1}{\epsilon_*(\omega)} \frac{\epsilon_*(\omega) - \epsilon_{\text{sub}}}{\epsilon_*(\omega) + \epsilon_{\text{sub}}}. \quad (9.40)$$

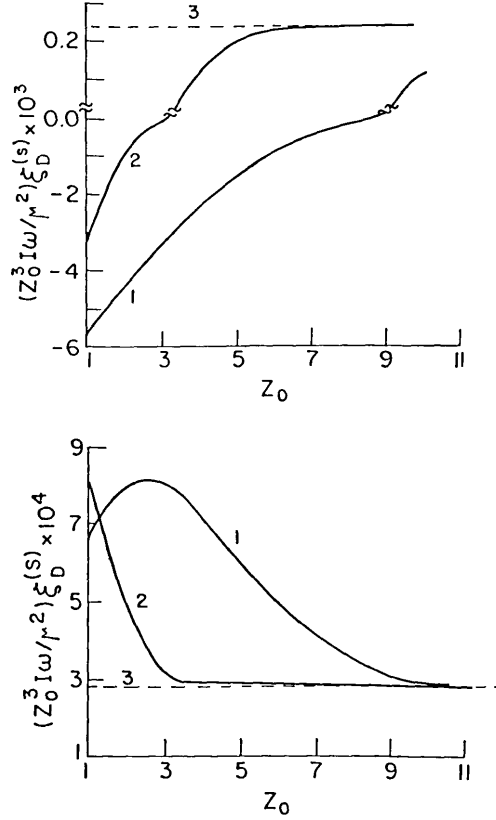
This result originates from our nonlocal description of the liquid and is essentially insensitive to the details of the boundary. (Boundary conditions, Eq. (9.24) as well as Eq. (9.17), lead to Eq. (9.40).) We see that at small distances from the substrate the function  $F(z_0, \omega)$  has the same “image force” form as for large distances, Eq. (9.39), but with a reduced effective dielectric constant,  $\epsilon_*$ . The leading terms of  $F(z_0, \omega)$  in the two limits, Eqs. (9.39) and (9.40), are  $1/4\epsilon_b z_0^3$  and  $1/4\epsilon_* z_0^3$  correspondingly. In qualitative terms we may conclude that the structure of the liquid, as reflected in the spatial correlation of polarization fluctuations, does not allow the liquid to respond fully at characteristic structure distances. Only beyond these distances are limits of macroscopic electrodynamics reached.

In the local model [31] of the liquid for  $|\epsilon_b(\omega)| > \epsilon_{\text{sub}}$  (a case which is the most interesting for us) the presence of the boundary increases the bulk dielectric friction and correspondingly the rotation time. The effect of nonlocality leads to some important qualitative consequences. Thus for  $|\epsilon_*| < (1 + \sqrt{2})\epsilon_{\text{sub}} < |\epsilon_b|$ , the boundary correction to the bulk dielectric friction,  $\xi_D^{(s)}(z_0, \omega)$ , changes sign as the distance from the substrate,  $z_0$ , changes (Fig. 9.1a). The net friction decreases (compare to the bulk value) in the immediate vicinity of the boundary,  $z_0 < \lambda \ln|\epsilon_b/\epsilon_*|$ , and increases at larger distances from the boundary. Under this condition the effect of nonlocality leads to the decreasing of the dielectric friction compared to the result of the local model at all distances from the boundary. For  $(1 + \sqrt{2})\epsilon_{\text{sub}} < |\epsilon_*| < |\epsilon_b|$  the boundary correction to the dielectric friction is positive in the whole range of distances from the surface and is larger than the result obtained in the local model (Fig. 9.1b).

In order to elucidate the relative role of the boundary correction to the bulk value of the friction,  $\xi_D^{(s)}$ , we have to evaluate the bulk friction,  $\xi_D^{(b)}$ . Following the cavity approach [13, 30, 33] the bulk friction,  $\xi_D^{(b)}$ , can be approximated by the expression (see Appendix)

$$\xi_D^{(b)} = -\frac{\mu^2}{\omega I R_c^3} \text{Im} \left( \frac{1}{\epsilon_{\text{eff}}(R_c, \omega)} \right), \quad (9.41)$$

where  $R_c$  is the radius of cavity. According to our model for the bulk dielectric



**Fig. 9.1a, b.** The dependence of the normalized dielectric friction at a given frequency,  $(z_0^3 I \omega / \mu)^2 \xi_D^{(s)}$ , on the distance between the dipole and the boundary. Curves 1 correspond to the correlation length,  $\Lambda = 3 \text{ \AA}$ ; curves 2 –  $\Lambda = 1 \text{ \AA}$  and curves 3 –  $\Lambda = 0$  (local limit). **a** The values of the parameters are:  $\epsilon_b = 80$ ,  $\omega\tau = 0.1$ ,  $\epsilon_{\text{sub}} = 5$ ,  $\epsilon_* = 3$ . At the same values of parameters the dielectric friction in the bulk liquid,  $(R^3 I \omega / \mu) \xi_D^{(b)}$ , is equal:  $1.8 \times 10^{-3}$  at  $R_c/\Lambda = \infty$ ;  $25 \times 10^{-3}$  at  $R_c/\Lambda = 3$ ;  $31 \times 10^{-3}$  at  $R_c/\Lambda = 1$ . **b** The values of the parameters are:  $\epsilon_b = 80$ ,  $\omega\tau = 0.1$ ,  $\epsilon_{\text{sub}} = 2$ ,  $\epsilon_* = 6$ . At the same values of parameters the dielectric friction in the bulk liquid,  $(R^3 I \omega / \mu^2) \xi_D^{(b)}$  is equal:  $1.8 \times 10^{-3}$  at  $R_c/\Lambda = \infty$ ;  $15 \times 10^{-3}$  at  $R_c/\Lambda = 3$ ;  $18 \times 10^{-3}$  at  $R_c/\Lambda = 1$ .

function, Eq. (9.8),

$$\xi_D^{(b)} = -\frac{\mu^2}{\omega I R_c^3} \text{Im} \left( \frac{2[\epsilon_1 - \epsilon_b(\omega)]}{\epsilon_1 [2\epsilon_b(\omega) + \epsilon_1]} - \frac{12\epsilon_b(\omega)[\epsilon_*(\omega) - \epsilon_b(\omega)]}{[2\epsilon_b(\omega) + \epsilon_1][2(2\epsilon_*(\omega) + \epsilon_1)\epsilon_b(\omega) + (2\epsilon_b(\omega) + \epsilon_1)\epsilon_*(\omega)f(R_c/\Lambda)]} \right). \quad (9.42)$$

In Eq. (9.42)  $\epsilon_1$  is the dielectric constant inside the cavity and the function  $f(R_c/\Lambda)$  is given by

$$f(R_c/\Lambda) = \frac{R_c^2}{\Lambda^2(1 + R_c/\Lambda)}. \quad (9.43)$$

From Eqs. (9.42) and (9.43) the following limiting relations can be obtained:

$$\xi_D^{(b)} = -\frac{\mu^2}{\omega I R_c^3} \times \begin{cases} \text{Im} \left( \frac{2[\varepsilon_1 - \varepsilon_b(\omega)]}{\varepsilon_1 [2\varepsilon_b(\omega) + \varepsilon_1]} \right) \cong -\frac{3 \text{Im}[\varepsilon_b(\omega)]}{[2 \text{Re} \varepsilon_b(\omega) + \varepsilon_1]^2}, & \text{at } R_c \gg \lambda; \\ \text{Im} \left( \frac{2[\varepsilon_1 - \varepsilon_*(\omega)]}{\varepsilon_1 [2\varepsilon_*(\omega) + \varepsilon_1]} \right) \cong -\frac{3 \text{Im} \varepsilon_*(\omega)}{[2 \text{Re} \varepsilon_*(\omega) + \varepsilon_1^2]}, & \text{at } R_c \ll \lambda. \end{cases} \quad (9.44a)$$

$$(9.44b)$$

Equation (9.44a) corresponds to the “traditional” behavior of the dielectric friction [13] and holds only for distances  $R_c \gg \lambda$ . In the opposite limit a similar relation holds, but with the high frequency dielectric constant,  $\varepsilon_*$ .

Comparing Eqs. (9.39), (9.40) and (9.44) we can conclude [34] that in both limiting cases,  $z_0 < \lambda$  and  $z_0 > \lambda$ , the boundary corrections to the dielectric friction in the liquid bulk are small, being of the relative order of  $R_c^3/z_0^3$ . The cavity size,  $R_c$ , is estimated to be of the order of a few molecular radii which limits the contribution of the boundary to the dielectric friction and consequently to the rotational time. However one expects the contribution to be significant for macromolecules near an interface where  $R_c$  is larger than the radius of the liquid molecules [31]. For such cases a more realistic approach is required in order to account for the detailed charge distribution in molecules.

#### 9.4 Effect of Substrate Modification on Dielectric Friction

There is some experimental and numerical evidence that a liquid near a substrate may have modified properties [4, 12, 18, 19, 35, 36]. Close to the interface the liquid may develop local structure due to interaction with the substrate. Such a structure will be characterized by different dielectric properties and can be observed, as proposed by Awschalom et al. [4] and by Zinsli [35], using rotational studies. The common observation has been that in the vicinity of the boundary there is a pronounced change of molecular reorientation time.

Here we extend our results of the previous section and describe the liquid side by two dielectric functions which correspond to the modified liquid in the close vicinity of the boundary,  $\varepsilon_s(\omega)$ , and the bulk solution,  $\varepsilon_b(\omega)$  (see Fig. 9.2).

Following the same type of calculations and boundary conditions as in Sect. 9.3, Eqs. (9.21) and (9.22), we arrive at the following expression for  $F(z_0, \omega)$  for a dipole in the bulk liquid:

$$F(z_0, \omega) = \frac{1}{\varepsilon_b(\omega) z_0^3} \int_0^\infty du u^2 \frac{w_{12} + w_{23} \exp(-2ud/z_0)}{1 + w_{12} w_{23} \exp(-2ud/z_0)} \exp(-2u), \quad (9.45)$$

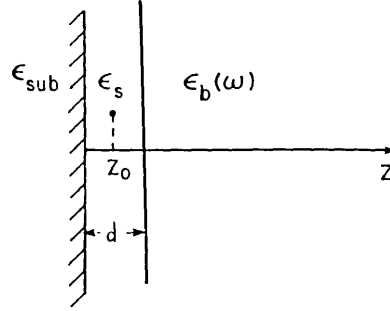


Fig. 9.2. The dipole is inside the modified liquid layer

where  $d$  is the layer thickness and

$$w_{ij} = \frac{\varepsilon_i - \varepsilon_j}{\varepsilon_i + \varepsilon_j}, \quad i, j = 1, 2, 3 \quad \text{and} \quad \varepsilon_1 = \varepsilon_b, \varepsilon_2 = \varepsilon_s, \varepsilon_3 = \varepsilon_{\text{sub}}. \quad (9.46)$$

An equation similar to Eq. (9.45) was used previously [32] for the description of radiation decay of the dipole near the surface covered by a film.

In the case of  $d \ll z_0$ , Eq. (9.45) reduces to Eq. (9.39); the dipole does not feel the presence of the layer. In the opposite case, when  $d \gg z_0$ , we obtain a similar expression for  $F(z_0, \omega)$  but with the dielectric function of the layer replacing the substrate one.

A more interesting situation arises for a dipole located within the surface layer. Now

$$F(z_0, \omega) = F_b(\omega) + F_s(z_0, \omega), \quad (9.47)$$

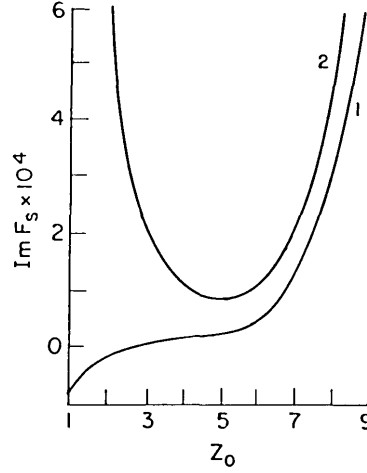
where

$$F_b(\omega) = \frac{1}{R^3} \left\{ \frac{2[\varepsilon_1 - \varepsilon_s(\omega)]}{\varepsilon_1[2\varepsilon_s(\omega) + \varepsilon_1]} \right\} - \frac{1}{R^3} \left\{ \frac{2[\varepsilon_1 - \varepsilon_b(\omega)]}{\varepsilon_1[2\varepsilon_b(\omega) + \varepsilon_1]} \right\} \quad (9.48)$$

and

$$F_s(z, \omega_0) = \frac{1}{\varepsilon_s z_0^3} \int_0^\infty du u^2 \frac{r_{23} \exp(-2u) - r_{12} \exp[-2u(d/z_0 - 1)] + 2r_{12}r_{23} \exp(-2ud/z_0)}{1 + r_{12}r_{23} \exp(-2ud/z_0)}. \quad (9.49)$$

The first term,  $F_b(\omega)$ , in Eq. (9.47) is the “bulk” contribution which determines the difference between dielectric frictions in two “bulk” liquids with different dielectric functions  $\varepsilon_b(\omega)$  and  $\varepsilon_s(\omega)$ . Usually due to the structuring effect of the substrate [12, 18] there is a lowering of the permittivity of the liquid near the boundary and  $|\varepsilon_s| \ll |\varepsilon_b|$ . The relative correction to the bulk dipole friction,  $\delta\xi_D$ ,



**Fig. 9.3.** The dependencies of the function  $\text{Im } F_s$  on the position of the dipole inside the layer. Curve 1 is obtained at  $\epsilon_b = 80$ ,  $\omega\tau = 0.1$ ,  $\epsilon_{\text{sub}} = 2$ ,  $\text{Re } \epsilon_s = 5$ ,  $L = 10$ ; at these values of the parameters the bulk contribution to the layer correction to the dipole damping is equal,  $R_c^3 \text{Im } F_b = 2.3 \times 10^{-2}$ . Curve 2 is obtained at  $\epsilon_b = 80$ ,  $\omega\tau = 0.1$ ,  $\epsilon_{\text{sub}} = 5$ ,  $\text{Re } \epsilon_s = 3$ ,  $L = 10$ ; at these values of parameters  $R_c^3 \text{Im } F_b = 3.5 \times 10^{-2}$ .

corresponding to the term  $F_b(\omega)$  is of the order of

$$\delta\zeta_D = \frac{\zeta_D^{(b)}(\epsilon_s) - \zeta_D^{(b)}(\epsilon_b)}{\zeta_D^{(b)}(\epsilon_b)} \cong - \frac{\text{Im} \left( \frac{1}{2\epsilon_s + \epsilon_1} \right) - \text{Im} \left( \frac{1}{2\epsilon_b + \epsilon_1} \right)}{\text{Im} \left( \frac{1}{2\epsilon_b + \epsilon_1} \right)}. \quad (9.50)$$

This correction may be large enough to be observable experimentally.

The second term,  $F_s(z_0, \omega)$ , takes into account the influence of the boundaries. The dependence of the dielectric friction,  $\zeta_D^{(s)}$ , on the position of the dipole inside the modified liquid layer are shown on Fig. 9.3.

The existence of two layers and their boundaries leads to a distribution of characteristic rotational times. However ignoring the boundary contributions (see previous section) we obtain two relaxation times which, if sufficiently separated, would be experimentally observed.

### 9.5 Dipole–Dipole Interactions near Interfaces

We now consider the model we use for the description of electromagnetic interaction of time-dependent point dipoles embedded in a liquid near a substrate. Let us denote the coordinates of the centers of dipoles with dipole moments  $\mu_d$  and  $\mu_a$  by  $\mathbf{r}_d = (0, 0, z_d)$  and  $\mathbf{r}_a = (R, z_a)$ , correspondingly, where  $z_d$  and  $z_a$  are the distances of dipoles from the substrate and  $R$  is the distance between dipoles along the surface (see Fig. 9.4).



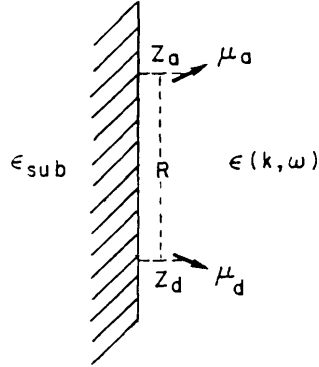


Fig. 9.4. Dipoles at the substrate-liquid interface

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

$$U = -\mu_d \frac{\partial^2 \Phi(\mathbf{r}_d, \mathbf{r}_a)}{\partial \mathbf{r}_d \partial \mathbf{r}_a} \mu_a = \mu_d (\mathbf{T}^{(\text{dip})} + \mathbf{T}^{(\text{ind})}) \mu_a \quad (9.51)$$

where  $\Phi(\mathbf{r}_d, \mathbf{r}_a)$  is the potential at a point  $\mathbf{r} = \mathbf{r}_a$  created by a point charge located at  $\mathbf{r} = \mathbf{r}_d$  near the interface and the tensors  $\mathbf{T}^{(\text{dip})}$  and  $\mathbf{T}^{(\text{ind})}$  describe direct interaction between dipoles and interaction induced by the presence of an interface correspondingly. It follows from Eq. (9.18) that in a *nonlocal* medium the tensor  $\mathbf{T}^{(\text{dip})}$  has the form [27]

$$\begin{aligned} \mathbf{T}_{ij}^{(\text{dip})} &= -\frac{2}{\pi} \frac{\partial^2}{\partial r_i \partial r_j} \int_0^\infty \frac{dk}{\varepsilon(k, \omega)} \frac{\sin kr}{kr} \\ &= -\frac{3r_i r_j - r^2 \delta_{ij}}{\varepsilon_b(\omega) r^5} \\ &\quad - C_2 \exp(-r/\Lambda) \left[ \frac{3r_i r_j - r^2 \delta_{ij}}{r^5} + \frac{2r_i r_j - r^2 \delta_{ij}}{\Lambda r^4} + \frac{r_i r_j}{\Lambda^2 r^3} \right]. \end{aligned} \quad (9.52)$$

Here  $\mathbf{r} = \mathbf{r}_a - \mathbf{r}_d$  is the vector connecting the two dipoles. The first term in Eq. (9.52) constitutes the classical result and the second term describes nonlocal effects. The second term, in contrast to the first, does not vanish after averaging over directions of the vector  $\mathbf{r}$ , and this leads to some important physical consequences [37], in particular to the existence of an electric field near a homogeneous dipole layer. It is evident from Eq. (9.52) that the effect of nonlocality does not change the energy of dipole–dipole interactions in the bulk liquid at distances larger than the characteristic correlation length,  $\Lambda$ , namely for  $r \gg \Lambda$ . The situation is quite different at interfaces.

The interaction tensor  $\mathbf{T}^{(\text{ind})}$  which arises due to the polarization at the interfacial region is

$$\begin{aligned} \mu_d \mathbf{T}^{(\text{ind})} \mu_a = & \frac{1}{2\pi} \int d\mathbf{k}_1 \left\{ \frac{C_1}{k_1} (\mu_a \mathbf{k})(\mu_d \mathbf{k}') \exp(-k_1(z_d + z_a)) \right. \\ & + \frac{C_2}{\Gamma} (\mu_a \Gamma)(\mu_d \Gamma') \exp(-\Gamma(z_d + z_a)) \\ & - \frac{2\varepsilon_{\text{sub}}}{k_1} \left[ C_1^2 (\mu_a \mathbf{k})(\mu_d \mathbf{k}') \exp(-k_1(z_d + z_a)) \right. \\ & + C_2^2 \frac{k_1^2}{\Gamma^2} (\mu_a \Gamma)(\mu_d \Gamma') \exp(-\Gamma(z_d + z_a)) \\ & + C_1 C_2 \frac{k_1}{\Gamma} ((\mu_a \mathbf{k})(\mu_d \Gamma') \exp(-\Gamma z_d - k_1 z_a) \\ & \left. \left. + (\mu_a \Gamma)(\mu_d \mathbf{k}') \exp(-\Gamma z_a - k_1 z_d)) \right] \right\} / \\ & [1 + C_1 \varepsilon_{\text{sub}} + C_2 \varepsilon_{\text{sub}} k_1 / \Gamma] \exp(i\mathbf{k}_1 R). \end{aligned} \quad (9.53)$$

In Eqs. (9.52) and (9.53) we introduced the following notations

$$\begin{aligned} \mathbf{k} &= (\mathbf{k}_1, ik_1), \quad \mathbf{k}' = (\mathbf{k}_1, -ik_1), \\ \Gamma &= (\mathbf{k}_1, i\Gamma), \quad \Gamma' = (\mathbf{k}_1, -i\Gamma). \end{aligned} \quad (9.54)$$

Let us analyze the dependence of the interaction tensor,  $\mathbf{T}$ , on the distance between the dipoles and on the substrate and liquid parameters. We will first consider the interaction between molecules with dipole moments  $\mu_d$  and  $\mu_a$  *perpendicular* to the surface. According to Eq. (9.53) the  $zz$ -component of the interaction tensor  $\mathbf{T}^{(\text{ind})}$  has the form

$$\begin{aligned} T_{zz}^{(\text{ind})} = & \int_0^\infty dk_1 k_1 \{ C_1 k_1 \exp(-k_1(z_d + z_a)) + C_2 \Gamma \exp(-\Gamma(z_d + z_a)) \\ & - 2\varepsilon_{\text{sub}} k_1 [C_1^2 \exp(-k_1(z_d + z_a)) + C_2^2 \exp(-\Gamma(z_d + z_a)) \\ & + C_1 C_2 (\exp(-\Gamma z_d - k_1 z_a) + \exp(-\Gamma z_a - k_1 z_d))] / \\ & [1 + C_1 \varepsilon_{\text{sub}} + C_2 \varepsilon_{\text{sub}} k_1 / \Gamma] \} J_0(k_1 R), \end{aligned} \quad (9.55)$$

where  $J_0(k_1 R)$  is the Bessel function of zero order. To follow the details of the dipole–dipole interaction near an interface we will study the behavior of the interaction tensor,  $T_{zz}^{(\text{ind})}$ , as a function of distances  $R$ ,  $z_d$  and  $z_a$ . In accordance with typical experimental conditions we consider the case where the distance between molecules in the direction along the interface,  $R$ , is larger than the other characteristic sizes,  $z_d$ ,  $z_a$  and  $\Lambda$ . In order to find the asymptotic behavior of

$T_{zz}^{(\text{ind})}$  for  $R \gg z_d, z_a, \Lambda$  it is convenient to carry out in Eq. (9.55) a transformation from the oscillating function,  $J_0(k_1 R)$ , to the modified Bessel function of third kind  $K_0(tR)$  which decreases exponentially for large values of  $tR$  [38]. Taking into account that  $J_0(k_1 R) = \text{Re } H_0^{(1)}(k_1 R)$ , where  $H_0^{(1)}$  is the Hankel function, and the fact that all functions in the integrand in Eq. (9.55) have no singularities in the region  $\{\text{Im } k_1 > 0, \text{Re } k_1 > 0\}$  we can move the integration contour to the imaginary axis where  $H_0^{(1)}(itR) = 2K_0(tR)/i\pi$ . After the transformation, Eq. (9.55) can be rewritten in the following form:

$$T_{zz}^{(\text{ind})} = -\frac{2}{\pi} \int_0^\infty dt \, t^2 K_0(tR) \{C_1 - 2\varepsilon_{\text{sub}}(1 + \varepsilon_{\text{sub}} C_1) \\ \times [C_1^2 + C_2^2 \exp(-(z_d + z_a)/\Lambda) + C_1 C_2 (\exp(-z_d/\Lambda) + \exp(-z_a/\Lambda))] / \\ [(1 + \varepsilon_{\text{sub}} C_1)^2 + (C_2 \varepsilon_{\text{sub}} \Lambda t)^2]\} . \quad (9.56)$$

In writing Eq. (9.56) it was taken into account that due to the presence of the exponentially decreasing function,  $K_0(tR)$ , the integral in Eq. (9.56) converges for values  $t \leq R^{-1}$ . Only the leading terms with respect to the parameter  $(tR)$  were conserved in the integrand in Eq. (9.56). Equations (9.52) and (9.56) have the following asymptotic behaviors of the interaction tensor  $T_{zz}$ :

(a) *at large distances between dipoles,  $R \gg z_d, z_a, g\Lambda$*

$$T_{zz} \approx \frac{2}{R^3} \frac{\varepsilon_{\text{sub}}}{\varepsilon_b \varepsilon_*^2 (\varepsilon_{\text{sub}} + \varepsilon_b)} \{ \varepsilon_*^2 + (\varepsilon_b - \varepsilon_*)^2 \exp(-(z_d + z_a)/\Lambda) + \varepsilon_* (\varepsilon_b - \varepsilon_*) \\ \times (\exp(-z_d/\Lambda) + \exp(-z_a/\Lambda)) \} , \quad (9.57)$$

where  $g = \varepsilon_b \varepsilon_{\text{sub}} / \{ \varepsilon_* (\varepsilon_{\text{sub}} + \varepsilon_b) \}$ . As an example, at the interface between silica and water  $\varepsilon_{\text{sub}} = 11.6$ ,  $\varepsilon_b = 80$  and  $\varepsilon_* = 1$  and for low frequencies  $\omega < 10^6$  Hz the parameter  $g = 10$ .

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

$$T_{zz} \approx \frac{2}{R\Lambda^2} \frac{(\varepsilon_{\text{sub}} + \varepsilon_b)}{\varepsilon_b \varepsilon_{\text{sub}} (\varepsilon_b - \varepsilon_*)^2} \{ \varepsilon_*^2 + (\varepsilon_b - \varepsilon_*)^2 \exp(-(z_d + z_a)/\Lambda) + \varepsilon_* (\varepsilon_b - \varepsilon_*) \\ \times (\exp(-z_d/\Lambda) + \exp(-z_a/\Lambda)) \} . \quad (9.58)$$

We can extend the domain of applicability of the intermediate asymptotics in Eq. (9.58) to smaller values of  $R$  (but bound by the condition  $R \gg z_a, z_d$ ) if we add to the expression at Eq. (9.58) the term at Eq. (9.52) which takes into account direct interaction between dipoles.

The region of intermediate asymptotics, Eq. (9.58), with anomalously slow (Coulomb-like) decrease of dipole–dipole interaction with distance  $R$  exists only in systems with high values of the dielectric constants of the substrate,  $\varepsilon_{\text{sub}}$ , and of the liquid,  $\varepsilon_b$ , when  $\varepsilon_{\text{sub}}/\varepsilon_* \gg 1$  and  $\varepsilon_b/\varepsilon_* \gg 1$ , and therefore correspondingly the coefficient  $g \gg 1$ . For instance at silica–water interface, as discussed in case (a), and for  $\Lambda \sim 4 \text{ \AA}$  [12] the limit in Eq. (9.58) can apply for a wide range of

distances,  $3 \text{ \AA} < R < 20 \text{ \AA}$ . Also at an interface between two immiscible liquids (for instance water–nitrobenzene system; for nitrobenzene  $\epsilon_b = 34.8$ ) the slow  $R$ -dependence of Eq. (9.58) can play an important role.

(c) *dipoles very close to the interface*,  $z_a, z_d < \Lambda$

When both dipoles are placed at small distances from the surface,  $z_d, z_a < \Lambda$ , Eqs. (9.57) and (9.58) are simplified to

$$T_{zz} = \begin{cases} \frac{2}{R^3} \frac{\epsilon_{\text{sub}} \epsilon_b}{\epsilon_*^2 (\epsilon_{\text{sub}} + \epsilon_b)}, & R \gg g\Lambda, \\ \frac{2}{R\Lambda^2} \frac{(\epsilon_{\text{sub}} + \epsilon_b)\epsilon_b}{\epsilon_{\text{sub}}(\epsilon_b - \epsilon_*)^2}, & z_d, z_a, \Lambda \ll R \ll g\Lambda. \end{cases} \quad (9.59)$$

$$(9.60)$$

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,  $z_a = z_d \simeq r_m$ , where  $r_m$  is the molecular size. In the limit of  $\epsilon_{\text{sub}} \rightarrow \infty$  Eqs. (9.59) and (9.60) reduce to the results obtained for metal–electrolyte interface [7]. It should be noted that in this case the expression of the dipole–dipole interaction energy at large  $R$  is directly proportional to the bulk dielectric constant of a liquid,  $\epsilon_b$ , in contrast to the traditional description obtained for a local representation of the liquid in contact with a substrate, in which the energy,  $\mu_a \mathbf{T}_{zz}^0 \mu_d$ , is inversely proportional to  $\epsilon_b$ ,

$$T_{zz}^0 \approx \frac{2}{R^3} \frac{\epsilon_{\text{sub}}}{\epsilon_b (\epsilon_{\text{sub}} + \epsilon_b)}, \quad R \gg z_a, z_d. \quad (9.61)$$

When the bulk dielectric constant of a liquid,  $\epsilon_b$ , is larger than both  $\epsilon_{\text{sub}}$  and  $\epsilon_*$  Eqs. (9.59) and (9.60) can be written as

$$T_{zz} \approx \begin{cases} \frac{2}{R^3} \frac{\epsilon_{\text{sub}}}{\epsilon_*^2} & \text{at } R \gg g\Lambda, z_d, z_a, \\ \frac{2}{R\Lambda^2} \frac{1}{\epsilon_{\text{sub}}} & \text{at } z_d, z_a, \Lambda \ll R \ll g\Lambda. \end{cases} \quad (9.62)$$

$$(9.63)$$

The different behavior in Eqs. (9.59)–(9.60) and (9.62)–(9.63) originates solely from our nonlocal description of the liquid and is essentially insensitive to the details of the imposed boundary conditions [11, 28]. At large distances between dipoles (and  $\epsilon_b > \epsilon_{\text{sub}}$ ) the interaction tensor, Eq. (9.62), has the same form as the traditional expression,  $T_{zz}^0$ , but with a reduced effective dielectric constant,  $\epsilon_*$ .

Our results demonstrate that nonlocal description of liquids leads to a nonuniform 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 in a liquid  $\Lambda$ , appears in the problem. Comparison of Eqs. (9.59)–(9.63) with the results obtained in the model of the modified liquid layer at the substrate surface [7]

(see also the results of next section) shows that this effect corresponds to the formation of the interface layer with reduced dielectric constant,  $\epsilon_*$ . The presence of such a layer reflects the structuring effect of a substrate [12, 18]. The thickness of the layer is of the order of the characteristic liquid structure distance,  $\Lambda$ . Only when the dipoles are placed far beyond the interfacial layer the traditional description of Eq. (9.61) applies. 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 [18, 23].

We see that *for all distances* between dipoles our results differ from the corresponding local behavior, Eq. (9.61). The effect of nonlocality may lead to an enhancement in the interaction between dipoles. At large distances,  $R \gg g\Lambda$ , the ratio of interaction tensors is  $T_{zz}/T_{zz}^0 \approx (\epsilon_b/\epsilon_*)^2$  which for water is of the order of  $10^2$ – $10^3$ . Similar nonlocal enhancement of dipole–dipole interaction at large distances  $R$  was predicted in [39]. The interaction at the substrate–liquid interface can be larger than the interaction near a free substrate, as described by the following ratio,  $(T_{zz}/T_{zz}^0(\epsilon_b = 1)) = (\epsilon_b(\epsilon_{\text{sub}} + 1)/\{\epsilon_*^2(\epsilon_{\text{sub}} + \epsilon_b)\})$ . We see 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,  $\epsilon_*$ . It should also be mentioned that in a non-local medium instead of the general law (at  $R \gg z_d, z_a$ ), Eq. (9.61), we have a more complicated behavior of the dipole–dipole interaction. This behavior shows a significant change of the form of  $T_{zz}(R)$  at a new characteristic length  $g\Lambda$ . The dependencies of the interaction on the distance between dipoles,  $R$ , calculated using Eq. (9.56) over the whole range of distances  $R$  and for different values of the system parameters are shown on Fig. 9.5.

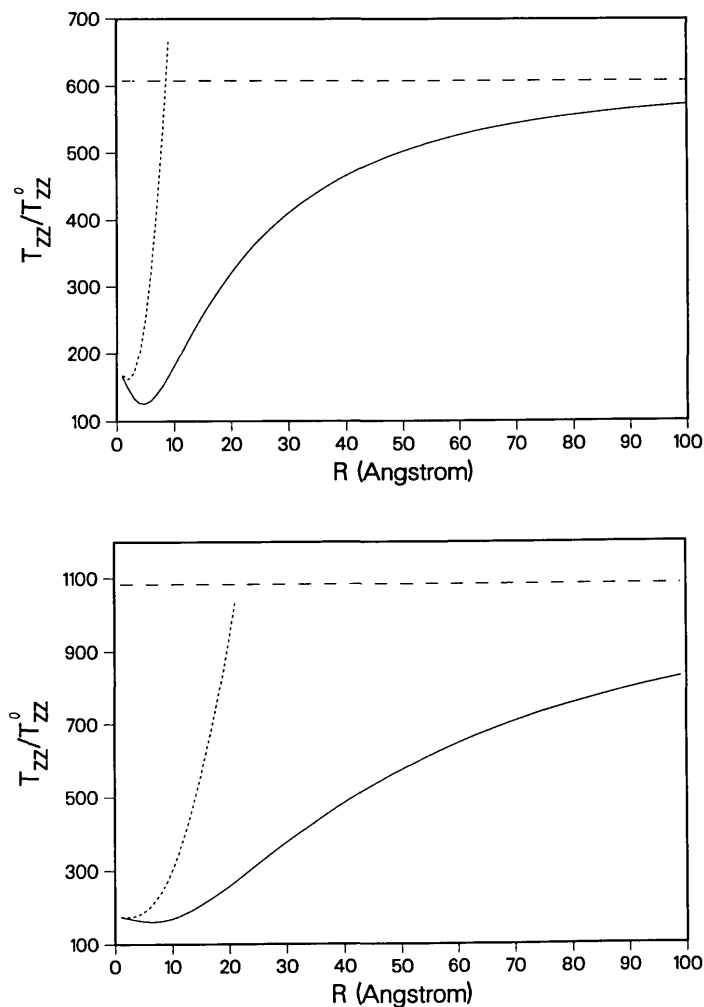
Equations (9.57) and (9.58) also describe the interaction between dipoles placed beyond the microscopic surface layer with thickness  $\Lambda$ . For instance, when one of the dipoles  $\mu_d$  is inside this layer ( $z_d < \Lambda$ ) and the second  $\mu_a$  is outside ( $z_a \geq \Lambda$ ) we have

$$T_{zz} \approx \frac{2}{R^3} \frac{\epsilon_{\text{sub}}}{\epsilon_*(\epsilon_{\text{sub}} + \epsilon_b)} \left\{ 1 + \frac{\epsilon_b - \epsilon_*}{\epsilon_*} \exp(-z_a/\Lambda) \right\}, \quad \text{at } R \gg g\Lambda, z_d, z_a \quad (9.64)$$

again a result which differs from Eq. (9.61).

The interaction between dipoles with other orientations of the dipole moments  $\mu_d$  and  $\mu_a$  can be found similarly from Eqs. (9.52) and (9.53). In the case of dipoles with dipole moments *parallel* to the surface plane and to the vector  $\mathbf{R}$  and placed at small distances from the substrate ( $z_d \approx z_a < \Lambda$ ), the long range asymptotic behavior of the interaction has the form

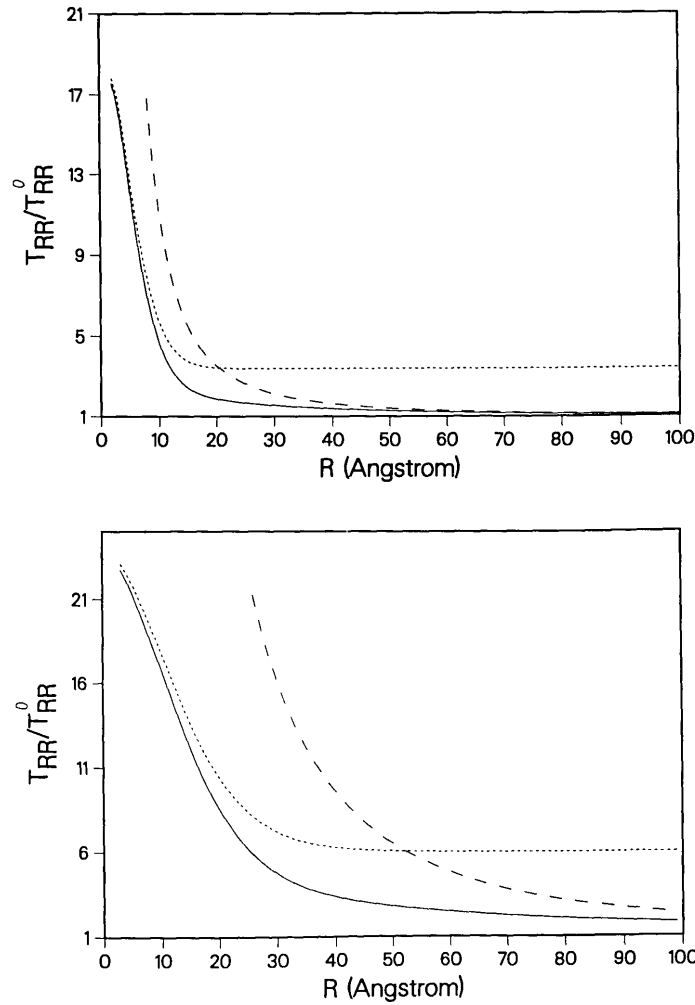
$$T_{RR} = -\frac{4}{R^3} \frac{1}{(\epsilon_{\text{sub}} + \epsilon_b)} - 24 \frac{z_d^2}{R^5} \frac{\epsilon_{\text{sub}} - \epsilon_b}{\epsilon_b(\epsilon_{\text{sub}} + \epsilon_b)} + 24 \frac{\Lambda^2}{R^5} \frac{\epsilon_{\text{sub}}(\epsilon_{\text{sub}} - \epsilon_b)(\epsilon_* - \epsilon_b)^2}{\epsilon_*^2 \epsilon_b(\epsilon_{\text{sub}} + \epsilon_b)^2} \\ \times \left\{ 1 + 2 \frac{z_d}{\Lambda} \frac{\epsilon_b^2}{(\epsilon_{\text{sub}} - \epsilon_b)(\epsilon_b - \epsilon_*)} - \frac{z_d^2}{\Lambda^2} \frac{2\epsilon_b^2 + \epsilon_{\text{sub}}(\epsilon_b + \epsilon_*)}{(\epsilon_{\text{sub}} - \epsilon_b)(\epsilon_b - \epsilon_*)} \right\}, \quad R \gg g\Lambda. \quad (9.65)$$



**Fig. 9.5.** Dependence of the energy of interaction between dipoles perpendicular to the interface,  $U = \mu_d T_{zz} \mu_a$ , on the distance between them. The energy is normalized by the function  $U^0 = \mu_d T_{zz}^0 \mu_a$  representing the traditional expression for the energy of dipole–dipole interaction (in perpendicular orientation) inside a local medium near a substrate ( $T_{zz}^0$  is given by Eq. (9.61)). *Solid lines* are the results of exact calculations on the base of Eqs. (9.52) and (9.56); *dashed lines* are long range asymptotes, Eq. (9.59), and *dotted lines* are intermediate asymptotes, Eq. (9.60), with account of direct interaction between dipoles Eq. (9.52). The calculations were carried out for the following values of parameters:  $\epsilon_{\text{sub}} = 10$ ,  $\epsilon_* = 2$ ,  $\epsilon_b = 80$ ,  $z_d = z_a = 1$  Å, (a)  $-\Lambda = 2$  Å and (b)  $-\Lambda = 5$  Å

The first two terms in Eq. (9.65) constitute the classical result describing an attraction (for  $\epsilon_{\text{sub}} > \epsilon_b$ ) of two dipoles parallel to the interface between local media. The third term takes into account the influence of the liquid structure as mimicked by the length  $\Lambda$ . In contrast to the previous case, Eq. (9.59), here the interaction energy depends on the correlation length,  $\Lambda$ , even at large distances

between dipoles. A comparison of Eqs. (9.59) and (9.65) shows that for large values of dielectric constants of the liquid,  $\epsilon_b$ , or of a substrate,  $\epsilon_{\text{sub}}$ , the interaction between dipoles with moments parallel to the surface is weaker than the interaction between dipoles perpendicular to the surface. In the limiting cases  $\epsilon_{\text{sub}} \gg 1$  or  $\epsilon_b \gg 1$ , Eq. (9.65) shows  $R^{-5}$  dependence of the interaction on



**Fig. 9.6.** Dependence of the energy of interaction between dipoles parallel to the interface,  $U = \mu_d T_{RR} \mu_a$ , on the distance between them. The energy is normalized by the function  $U^0 = \mu_d T_{RR}^0 \mu_a$  representing the energy of interaction between dipoles in planar orientation inside a local medium near a substrate ( $T_{RR}^0$  is given by the first two terms in Eq. (9.65)). Solid lines are the results of exact calculations on the base of Eqs. (9.52) and (9.53); dashed lines are long range asymptotes Eq. (9.65) and dotted lines are intermediate asymptotes. The calculations were carried out for the following values of parameters:  $\epsilon_{\text{sub}} = 10$ ,  $\epsilon_* = 2$ ,  $\epsilon_b = 80$ ,  $z_d = z_a = 1$  Å, (a)  $-l = 2$  Å and (b)  $-l = 5$  Å

distance between dipoles, different from the case of dipoles perpendicular to the surface where interaction energy decreases as  $R^{-3}$ . Again the inclusion of nonlocal dielectric properties leads to an enhancement of dipole–dipole interaction. But in this case the effect of enhancement is not so pronounced. In contrast to the case of perpendicular dipoles when for all values of parameters ( $\epsilon_b, \epsilon_{\text{sub}}, \epsilon_*$ ,  $A$ ,  $R$ ,  $z_d$  and  $z_a$ ) we had the usual repulsion between dipoles now the type of interaction (repulsive or attractive) depends on these parameters. For given parameters characterizing the liquid and substrate ( $\epsilon_b, \epsilon_{\text{sub}}, \epsilon_*$ ,  $A$ ) the interaction energy may change sign as a function of the distance between dipoles,  $R$ . The typical dependencies of the interaction between dipoles parallel to the surface on the distance  $R$  are presented at Fig. 9.6. Interaction between dipoles with other directions of dipole moments can be considered in a similar way.

## 9.6 The Effect of Substrate Modification on Dipole–Dipole Interactions

Here we extend our results of the previous section and describe the liquid side by two dielectric functions which correspond to the modified liquid in the close vicinity of the boundary,  $\epsilon_s(\omega)$ , and the bulk solution,  $\epsilon_b(\omega)$ .

Following the same type of calculations as previously, we arrive at the following expression for the dielectric tensor,  $\mathbf{T}$ , for dipoles in the surface layer

$$\mathbf{T}_{ij}^{(\text{dip})} = -\frac{3r_i r_j - r^2 \delta_{ij}}{\epsilon_s(\omega) r^5} \quad (9.66)$$

and

$$\begin{aligned} \mu_d \mathbf{T}^{(\text{ind})} \mu_a &= \frac{1}{2\pi\epsilon_s(\omega)} \int d\mathbf{k}_1 k_1^{-1} [1 + \omega_{12}\omega_{23} \exp(-2k_1 d)]^{-1} \\ &\times \{ (\mu_a \mathbf{k}')(\mu_d \mathbf{k}') \omega_{12}\omega_{23} \times \exp(-k_1(2d + z_d - z_a)) + (\mu_a \mathbf{k})(\mu_d \mathbf{k}) \omega_{12}\omega_{23} \\ &\times \exp(-k_1(2d - z_d + z_a)) + (\mu_a \mathbf{k}')(\mu_d \mathbf{k}) \omega_{12} \exp(-k_1(2d - z_d - z_a)) \\ &- (\mu_a \mathbf{k})(\mu_d \mathbf{k}') \omega_{23} \exp(-k_1(z_d + z_a)) \} \exp(i\mathbf{k}_1 R), \end{aligned} \quad (9.67)$$

where  $d$  is the layer thickness and

$$\omega_{ij} = \frac{\epsilon_i - \epsilon_j}{\epsilon_i + \epsilon_j}, \quad i, j = 1, 2, 3 \quad \text{and} \quad \epsilon_1 = \epsilon_b, \epsilon_2 = \epsilon_s, \epsilon_3 = \epsilon_{\text{sub}}. \quad (9.68)$$

The asymptotic behavior of Eq. (9.67) can be studied along the same procedure as in the previous section. For instance, the interaction tensor for two dipoles perpendicular to the surface in the region of large distances  $R$ , between them, has the form

$$T_{zz} \approx \frac{2}{R^3} \frac{\epsilon_{\text{sub}} \epsilon_b}{\epsilon_s^2 (\epsilon_{\text{sub}} + \epsilon_b)}, \quad R \gg d\epsilon_b/\epsilon_s, \quad (9.69)$$



which behaves as the corresponding Eq. (9.69) obtained in the framework of nonlocal description of a liquid. The comparison of these two equations shows again that the inclusion of a liquid structure even on a phenomenological level leads to the creation of the surface layer of modified liquid with dielectric constant,  $\varepsilon_s$  and with the thickness,  $d$ . This means that the nonlocal case discussed in the previous section leads essentially to an equivalent behavior but with a surface layer of a thickness of the order of the correlation length  $\Lambda$  with a reduced dielectric constant  $\varepsilon_s = \varepsilon_*$ . Other limits of Eq. (9.67) can be derived as well following the previous sections.

## 9.7 Conclusions

We have investigated the influence of a nonmetallic interface on the rotational relaxation and on the interaction between point dipoles located near the interface in the liquid side. Both the liquid and the boundary are described in terms of the continuum approach by their dielectric properties. We have assumed that the substrate is given by a local dielectric function and the liquid by a nonlocal dielectric function which introduces a typical length  $\Lambda$  into the problem.

Although the relaxation may be nonexponential in time we have calculated the dielectric friction for a given frequency as a function of  $z_0$ , the distance of the dipole from the boundary. The effect of the boundary has been shown to be small unless the properties of the liquid itself are drastically changed due to the presence of the interface. The nonlocal nature of dielectric function modifies the dielectric friction derived within the local approximation. The results show some new limits of the dipole–dipole interaction which originate from the nonlocal nature of the liquid. The results strongly depend on the embedding and neighboring dielectric functions and display a rich range of behaviors which may be amenable to experimental tests. In more realistic cases one also has to account for the finite size of molecules. This will introduce higher multipolar contributions. Estimates along this line have been done for interacting ions [20] showing small corrections to the point ion approximation.

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 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 between dipoles,  $R$ , 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 nonlocal properties of both liquids in terms of their structure parameter  $\Lambda$ . In such cases the functional

form of the induced field, Eq. (9.31), and the interaction tensor, Eqs. (9.57)–(9.60) are retained. Based on the calculations in Sect. 9.3, we believe that the parameter  $\lambda$  should, however, be replaced by an effective length characterizing the thickness of the surface layer of both liquids.

Examples for cases where the modification of the dipole–dipole interaction due to the presence of a boundary directly related to experimental observables are direct electronic energy transfer of the Förster type [40] and adsorption isotherms of molecules carrying dipole moments. The relationship between the energy transfer rate,  $w_{tr}$ , from a donor molecule to an acceptor and the nature dipole–dipole interaction can be obtained on the basis of the Golden Rule expression (to be summed over all possible transitions)

$$w_{tr} = (2\pi/\hbar) |\mu_d \mathbf{T} \mu_a|^2 \delta(E_f - E_i). \quad (9.70)$$

Here  $\mu_d$  is the dipole moment for the transition from the donor state  $|\Psi_{di}\rangle$  to the acceptor state  $|\Psi_{df}\rangle$ ,  $\mu_a$  is the transition dipole moment of the acceptor;  $E_f - E_i$  is the net change in total energy of the donor–acceptor pair and  $\mathbf{T}$  is the dipole–dipole interaction energy tensor. All those limits discussed above which lead to an incoherent energy transfer process (which excludes the slowly decaying Coulomb-like behavior) should apply to the energy transfer calculations through Eq. (9.70) and may therefore make it a method to relate the microscopic process of donor to acceptor energy transfer to the macroscopic dielectric behavior at the interface. However for most realistic cases the contribution of the dipole–dipole interaction tensor to Eq. (9.70) will be in the high frequency range where the effects of liquid structures and molecules are less pronounced. This may explain recent observation on energy transfer at silica interfaces which do not show marked differences when compared to energy transfer in bulk liquids [41]. The effect of the dipole–dipole interaction on adsorption isotherms comes through the contribution to the chemical potential of the surface layer ( $\lambda$  or  $d$ ). 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  $\lambda$  and the dielectric functions in the interface region. For dipoles perpendicular to the surface the slope decreases as a result of the nonlocal nature of the liquid.

The formalism developed in this paper can also be applied to the calculation of the van der Waals and hydration forces in atomic force microscopy (AFM) operating in liquids. Recent AFM studies in polar solvents [42] have demonstrated some new features arising in liquids. Particularly it has been shown that AFM operates more stably in water than in air or in a vacuum. Most previous attempts to devise a theory of atomic force microscopy [43, 44] neglected the solvent structure effect. However, the latter gives rise to a hydration force which together with steric repulsion are probably responsible for the strong repulsive forces between polar surfaces at small distances (less than 2 nm [45]). The first attempt to take into account the interfacial hydration in AFM has been done in [46].

### 9.8 Appendix

In order to calculate the dielectric friction in the bulk liquid we will follow the cavity approach [13, 30, 33]. Consider a dielectric sphere of radius  $R_c$  and dielectric constant  $\varepsilon_1$  at the center of which a dipole is located. Outside the sphere there is a liquid with dielectric function  $\varepsilon(\mathbf{k}, \omega)$ , Eq. (9.8). For this model the electrostatic potential,  $\Phi$ , can be written by expanding the solution of the Poisson equation, Eq. (9.10), in spherical coordinates. The potential in the liquid,  $r > R_c$ , should vanish at infinite distance, and the homogeneous part of the potential inside the sphere,  $r < R_c$ , has to be analytic at the origin. The nonhomogeneous part of the potential in the sphere arises from the point dipole with the dipole moment  $\mu$  at the center. Thus we have

$$\Phi_{\text{dip}} = \frac{(\mu \mathbf{r})}{\varepsilon_1 r^3} + A(\mu \mathbf{r}), \quad \text{at } r < R_c \quad (9.71)$$

$$\Phi_{\text{dip}} = B \frac{(\mu \mathbf{r})}{\varepsilon_b r^3} + C \left( \frac{1}{\varepsilon_*} - \frac{1}{\varepsilon_b} \right) (\mu \mathbf{r}) \frac{\exp(-r/\Lambda)}{r^3} \left( 1 + \frac{r}{\Lambda} \right), \quad \text{at } r > R_c. \quad (9.72)$$

The coefficients  $A$ ,  $B$  and  $C$  are obtained from the boundary conditions at  $r = R_c$  which are similar to the conditions, Eqs. (9.23), (9.24) and (9.25), used for the plane interface. As a result the field induced at the surface of dielectric sphere,  $r = R_c$ , has the form

$$\mathbf{E}' = -A\mu = -\frac{\mu}{R_c^3} \left\{ \frac{2[\varepsilon_1 - \varepsilon_b(\omega)]}{\varepsilon_1 [2\varepsilon_b(\omega) + \varepsilon_1]} - \frac{12\varepsilon_b(\omega)[\varepsilon_* - \varepsilon_b(\omega)]}{[\varepsilon_b(\omega) + \varepsilon_1][2(2\varepsilon_* + \varepsilon_1)\varepsilon_b(\omega) + (2\varepsilon_b(\omega) + \varepsilon_1)\varepsilon_* f(R_c/\Lambda)]} \right\} \quad (9.73)$$

with  $f(R_c/\Lambda)$  given by Eq. (9.43).

The similar approach for the calculation of the dipole damping in the liquid (with the same boundary conditions) was adopted by van der Zwan and Hynes in [30]. Our results however differ from theirs.

### 9.9 References

1. Klafter J, Drake JM (eds) (1989) Molecular dynamics in restricted geometries, Wiley, New York
2. Drake JM, Klafter J, Kopelman R (eds) (1990) Dynamics in small confining systems, MRS, Pittsburgh
3. Evans R (1990) J Phys: Condens Matt 2: 8989
4. Awschalom DD, Warnock J, In: Ref [1]
5. Granick S (1991) Science 253:1374
6. Vorotyntsev MA, Kornyshev AA (1980) Sov Phys JETP 51:509
7. Vorotyntsev MA (1988) In: Advances of science and engineering, electrochemistry, 26:3 (in Russian)
8. Drake JM, Klafter J (1990) Physics Today 43:46
9. Urbakh M, Klafter J (1992) J Phys Chem 96:3480
10. Urbakh M, Klafter J (1993) J Phys Chem 97:3344

11. Agranovich VM, Ginzburg VL (1976) Spatial dispersion in crystal optics and the theory of excitons, Interscience, New York
12. Dogonadze RR, Kalman E, Kornyshev AA, Ulstrup J (eds) (1988) The chemical physics of solvation, Parts A and C. Elsevier, Amsterdam
13. Nee Tsu-Wei, Zwanzig R (1970) J Chem Phys 52:6353
14. Alavi DS, Waldeck DH (1991) J Chem Phys 94:6196
15. Enderby JE, Neilson GW (1981) Rep Progr Phys 44:953
16. Pollock EL, Alder BJ (1981) Phys Rev Lett 46:950
17. Bagchi B, Chandra A (1991) In: Prigogine I, Rice SA (eds) Advances in chemical physics, vol 80. Wiley, New York, p 1
18. Israelachvili JN (1985) Intermolecular and surface forces with applications to colloidal and biological systems, Academic, London
19. (a) Davis HT, Somers SA, Tirrell M, Bitsanis I (1990) In: Drake JM, Klafter J, Kopelman R (eds) Dynamics in small confining systems, Extended Abstract of 1990 Fall Meeting of the MRS, p73; (b) Lupkowski M, van Swol F (1990). In: Drake JM, Klafter J, Kopelman R (eds) Dynamics in small confining systems, Extended Abstract of 1990 Fall Meeting of the MRS, p19
20. Vorotyntsev MA (1988). In: R.R. Dogonadze, Kalman E, Kornyshev AA, Ulstrup J (eds) The chemical physics of solvation, Part C Elsevier, Amsterdam, p 401
21. Zubarev ND (1974) Nonequilibrium statistical thermodynamics, Plenum, New York
22. Marcelja S, Radic N (1976) Chem Phys Lett 42:129
23. Kornyshev AA, Leikin S (1989) Phys Rev B 40:6431
24. Li H, Kardar M (1991) Phys Rev Lett 67:3275
25. Kliewer KL, Fuchs R (1974). In: Prigogine I, Rice SA (eds) Advances in chemical physics, vol 27, Wiley, New York
26. Fuchs R, Barrera RG (1981) Phys Rev B 24:2940
27. Harrison W (1970) Solid state theory, McGraw-Hill, New York
28. Kornyshev AA, Rubinstein AI, Vorotyntsev MA (1978) J Phys C Solid State Phys 11:3307
29. Bottcher CJF, Bordewijk P (1979) Theory of electric polarization, Elsevier, Amsterdam
30. van der Zwan G, Hynes JT (1983) Physica 121 A:227
31. van der Zwan G, Mazo RM (1985) J Chem Phys 82:3344
32. Chance RR, Prock A, Silbey R (1978) in: Prigogine I, Rice SA (eds) Advances in chemical physics, vol 37. Wiley, New York, p 1
33. Gersten J, Nitzan A (1991) J Chem Phys:686
34. Here we assume that the distance of the dipole from the boundary,  $z_0$ , is larger than the cavity radius,  $R_c$ . In principal in the opposite limit the conclusion may be different but in that case it is necessary to take into account the modification of the dielectric properties of the cavity by the substrate. Similar effect is considered in the next section
35. Zinsli PE (1979) J Phys Chem 83:3223
36. Derjaguin BV, Churaev NV, Muller VM (1987) Surface forces, Consultants Bureau, New York
37. Belaya ML, Levadnyi VG, Feigel'man MV (1986) Sov. Phys. JETP 64:787
38. Abramovitz M, Stegun I (eds) Handbook of mathematical functions, Dover, New York, 1965
39. Kornyshev AA (1988) J Electroanal Chem 255:297
40. Agranovich VM, Galanin MD (1982) Electronic excitation energy transfer in condensed matter, North-Holland, Amsterdam
41. Levitz P, Drake JM, Klafter J (1988) J Chem Phys 89:5224
42. Manne S, Hasma PK, Massie J, Elings VB, Gewirth AA (1991) Science 251:133
43. Goodman F, Garcia N (1991) Phys Rev B 43:4728
44. Garcia N, Binh Vu Thien (1992) Phys Rev B 46:7946
45. Rand RP, Parsegian VA (1990) Biochim Biophys Acta, 988:351
46. Cevc G, Kornyshev A (1992) J Electroanal Chem 330:407

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ISBN 3-540-57327-5 Springer-Verlag Berlin Heidelberg New York  
ISBN 0-387-57327-5 Springer-Verlag New York Berlin Heidelberg

Library of Congress Cataloging-in-Publication Data

Disorder effects on relaxation processes / R. Richert, A. Blumen, eds. Includes bibliographical references and index.

ISBN 3-540-57327-5 (Berlin : alk. paper). — ISBN 0-387-57327-5 (New York : alk. paper) 1. Relaxation phenomena. 2. Order-disorder models. 3. Condensed matter, I. Richert, R. (Ranko), 1957– II. Blumen, Alexander. QC173.4.R44D58 1994

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Printed in Germany

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Typesetting: Macmillan India Ltd, Bangalore-25;  
Printing: Saladruck, Berlin; Bookbinding: Lüderitz & Bauer, Berlin  
SPIN: 100 98 550 02/3020-5 4 3 2 1 0 – Printed on acid-free paper