## Static and dynamic theory of polarization under internal and directing electric fields: Fixed-charge and fixed-potential conditions

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We present a continuum theory on statics and dynamics of polar fluids, where the orientational polarization  $p_1$  and the induced polarization  $p_2$  are governed by the Onsager directing field  $E_d$ and the Lorentz internal field F, respectively. We start with a dielectric free energy functional  $\mathcal{F}$  with a cross term  $\propto \int d\mathbf{r} \ \mathbf{p}_1 \cdot \mathbf{p}_2$ , which was proposed by Felderhof [J. Phys. C: Solid State Phys. 12, 2423 (1979)]. With this cross-coupling, our theory can yield the theoretical results by Onsager and Kirkwood. We also present dynamic equations using the functional derivatives  $\delta \mathcal{F}/\delta p_i$ to calculate the space-time correlations of  $p_i$ . We then obtain analytic expressions for various frequency-dependent quantities including the Debye formula. We find that the fluctuations of the total polarization drastically depend on whether we fix the electrode charge or the applied potential difference between parallel metal electrodes. In the latter fixed-potential condition, we obtain a nonlocal (long-range) polarization correlation inversely proportional to the cell volume V, which is crucial to understand the dielectric response. It is produced by nonlocal charge fluctuations on the electrode surfaces and is sensitive to the potential drops in the Stern layers in small systems. These nonlocal correlations in the bulk and on the surfaces are closely related due to the global constraint of fixed potential difference. We also add some results in other boundary conditions including the periodic one, where nonlocal correlations also appear.

#### I. INTRODUCTION

The dielectric properties of polar fluids have long been studied since the pioneering work by Debye<sup>1</sup>, which is based on the Lorentz internal field F. Onsager<sup>2</sup> introduced the directing field<sup>3,4</sup>  $E_d$ , which governs the orientational polarization  $p_1$ . Remarkably,  $E_d$  is much smaller than F in magnitude for highly polar fluids, whereas  $E_d = F$  in Debye's theory. In contrast, the induced polarization  $p_2$  is proportional to F, where the proportionality constant is the polarizability related to the high-frequency dielectric constant  $\epsilon_{\infty}$  via the Clausius-Mossotti relation. Accounting for the long-range dipolar interaction, Onsager derived the so-called Onsager equation, which relates the dipole moment  $\mu_0$  to  $\epsilon_{\infty}$  and the static dielectric constant  $\epsilon$ . Soon afterwards, Kirkwood<sup>5</sup> included the short-range dipole-dipole correlation in the dielectric response. Fröhlich<sup>3</sup> combined these two theories in the Kirkwood-Fröhlich (KF) equation.

Later, Felderhof<sup>6</sup> presented a free energy including a cross-coupling term  $\propto p_1 \cdot p_2$ , which is called the Lorentz term in this paper. It yields the Lorentz field F for  $p_2$  and the Onsager directing field  $E_d$  for  $p_1$ . However, many other authors<sup>7–13</sup> did not include the Lorentz term in their free energies. In this study, we derive Onsager's results and the KF equation from a continuum theory based on Felderhof's free energy by expressing the polarization correlation functions in simple forms.

A number of theories<sup>14–27</sup> have been presented on the frequency-dependent dielectric constant  $\epsilon^*(\omega)$  at frequency  $\omega$ . In particular, Cole<sup>14</sup> assumed deformable

molecular bonds giving rise to atomic  $p_2$ , while Fatuzzo and Mason<sup>16</sup> derived a frequency-dependent KF equation. We also mention well-developed research on the wave-vector-dependent dielectric response<sup>21,22,24–26</sup>, to which the time-correlations of the Fourier components of  $\boldsymbol{p}$  are related. In dielectric measurements<sup>3,27</sup>,  $\epsilon^*(\omega)$  has been well approximated by the Debye formula<sup>1,3</sup>,

$$\epsilon^*(\omega) = \epsilon_{\infty} + (\epsilon - \epsilon_{\infty})/(1 + i\omega\tau_{\rm D}),$$
 (1)

which involves a single relaxation time  $\tau_{\rm D}$ . However, this formula is inadequate at high  $\omega$  for complex polar molecules. In this study, we present dynamic equations for  $\boldsymbol{p}_1$  and  $\boldsymbol{p}_2$  using Felderhof's free energy. They give three relaxation times<sup>25–30</sup>,  $\tau_{\rm D}$ ,  $\tau_{\rm L}$ , and  $\tau_{\rm f}$ , for the transverse part of  $\boldsymbol{p}_1$ , the longitudinal part of  $\boldsymbol{p}_1$ , and  $\boldsymbol{p}_2$ , respectively, at fixed electric charges. Here,  $\tau_{\rm D} > \tau_{\rm L} = \tau_{\rm D} \epsilon_{\infty}/\epsilon \gg \tau_{\rm f}$ . Then, calculating the time-correlation functions of  $\boldsymbol{p}_i$  analytically, we obtain various dielectric relations including the Debye formula (1).

We should understand the dielectric response in the frame of Kubo's linear response theory<sup>31,32</sup>. He supposed an externally applied time-dependent force F(t) and its conjugate internal variable A with the interaction energy  $\mathcal{H}_{\rm int}(t) = -\mathcal{A}F(t)$  in the Hamiltonian formalism. In the dielectric theory, however, it is not clear how to determine F(t) and A due to the long-range electrostatic interactions among the dipoles and the electrode charges. In the geometry of parallel metal plates, we can control the surface charge  $Q_0$  on one electrode or the applied potential difference  $\Phi_a$ . The physical consequences in these two conditions are very different in statics and dynamics. A number of simulations have been performed at fixed  $\Phi_a^{33-50}$ . Recently,  $\epsilon^*(\omega)$  was calculated at fixed  $\Phi_a^{49}$ . Simulations have also been performed by Sprik's group<sup>51,52</sup> when the space average of the Maxwell field

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 $\boldsymbol{E}$  or that of the electric induction  $\boldsymbol{D}$  vanishes, where the former is realized in the periodic boundary condition<sup>53</sup>. To remove the effects of the surfaces and the sample shape, some authors supposed applied fields varying sinusoidally in space and time for dielectric fluids<sup>22,24</sup> and electrolytes<sup>54</sup>, where the periodic boundary condition can be used without electrodes in simulation<sup>55–59</sup>.

In this paper, we determine F(t) and A to calculate the relaxation functions<sup>31</sup> of  $p_1$ ,  $p_2$ , and  $p = p_1 + p_2$ , where F(t) is homogeneous in space but can oscillate in time. We use the parallel plate geometry with a separation length H, where the z axis is perpendicular to the electrode surfaces. (i) First,  $Q_0$  is controlled, where  $\mathcal{A}$  is the integration of  $p_z$  in the cell, written as  $M_z^{\text{tot}}$ . In this case, the relaxation functions decay with  $\tau_{L}$ . (ii) Second, a mesoscopic sphere in the bulk in the cell is under an oscillating directing field, where A is the integration of  $p_{1z}$ in the sphere. We then obtain a frequency-dependent KF equation. (iii) Third, a mesoscopic sphere is under an oscillating cavity field, where A is the integration of  $p_z$  in the sphere. Then, we express  $\epsilon^*(\omega)$  in terms of the time correlation of p in the long wavelength limit. (iv) Fourth, we control  $\Phi_a$  with  $\mathcal{A} = M_z^{\text{tot}}/H$ . In this case, the space-time correlation of  $p_z$  contains a nonlocal (longrange) part inversely proportional to the cell volume V, which is induced by small fluctuations of  $Q_0$ . Previously, nonlocal polarization correlations were discussed in different contexts<sup>18,19,53</sup>. In fluid mixtures, nonlocal density correlations  $\propto V^{-1}$  generally appear in the canonical and isobaric-isothermal ensembles.

It is known that a significant potential drop appears in the Stern layers on solid-fluid surfaces<sup>33,38,42,43,62-67</sup>. It gives rise to the effective dielectric constant,

$$\epsilon_{\text{eff}} = 4\pi Q_0 H^2 / V \Phi_a = \epsilon / (1 + \ell_{\text{w}} / H). \tag{2}$$

Here,  $\ell_{\rm w}$  is a surface electric length<sup>43,65,66</sup>, which is enlarged for  $\epsilon \gg 1$  and is of order 10 nm for liquid water. The relation (2) holds both at fixed  $Q_0$  and at fixed  $\Phi_a$  and agrees with an experiment by Geim's group<sup>68</sup>. See a recent review on the dielectric response in nanoconfined water by Mondal and Bagchi<sup>69</sup>. We further present a frequency-dependent generalization of Eq.(2). We shall see that the variance and the lifetime of  $M_z^{\rm tot}$  at fixed  $\Phi_a$  are larger than those at fixed  $Q_0$  by factors of  $\epsilon_{\rm eff}$  and  $\epsilon_{\rm eff}/\epsilon_{\infty}$ , respectively.

We also calculate the in-plane correlation of the electrode charge density  $\sigma_0(x,y,t)$ . At fixed  $Q_0 = \int dx dy \, \sigma_0$ , it has a nonlocal term proportional to the inverse surface area H/V. At fixed  $\Phi_a$ , it additionally acquires a nonlocal term proportional to  $1/V(1+\ell_{\rm w}/H)$  and equal to the variance of  $M_z^{\rm tot}$ . which is small but greatly alters the overall dielectric response. These aspects have been overlooked in previous papers on the surface charge fluctuations  $^{39,44,47}$ .

The organization of this paper is as follows. In Sec.II, the statics of dielectrics will be discussed, where the relationship of our theory and Onsager's theory will be elucidated. In Sec.III, the equal-time polarization correlations will be calculated for wave lengths longer than the molecular length and shorter than H, while Sec.IV will present those of the total polarizations. In Sec.V, the solvation free energy<sup>7–11</sup> will be examined in the presence of solute charges. In Sec.VI, the dynamics of  $p_1$  and  $p_2$  and their time-correlations will be studied. In Sec.VII, the dynamical linear response relations will be given. In Sec.VIII, the dielectric response and the fluctuations in the polarizations and the surface charges will be studied at fixed  $\Phi_a$ . In Secs.IV, VI, and VIII, the fluctuations of the total polarizations and the nonlocal correlations will be studied in other boundary conditions.

#### II. POLARIZATION IN LINEAR REGIME

In the continuum approach, we treat a nearly incompressible, one-component polar liquid with a permanent dipole moment  $\mu_0$ . Electric charges are present only one the electrode surfaces (which will be supposed in the fluid in Sec.V). There is no chemical reaction in the fluid and on the surfaces. The net polarization  $\boldsymbol{p}$  consists of orientational, atomic, and electronic contributions<sup>3,6–8</sup>. The orientational one  $\boldsymbol{p}_1$  is dominant at low frequencies in highly polar fluids. The sum of the atomic and electronic ones is written as  $\boldsymbol{p}_2$  and is called the induced polarization. The Maxwell electric field  $\boldsymbol{E} = -\nabla \Phi$  is produced by  $\boldsymbol{p} = \boldsymbol{p}_1 + \boldsymbol{p}_2$  and the electrode charges, where  $\Phi$  is the electric potential. The electric induction is given by  $\boldsymbol{D} = \boldsymbol{E} + 4\pi \boldsymbol{p}$  in the cgs units.

#### A. Dielectric free energy

As in Fig.1, the fluid is confined between parallel metal plates with surface charges  $Q_0$  and  $Q_H(=-Q_0)$  at z=0 and H, respectively. The lateral cell length L much exceeds H and the edge effect is negligible. The average charge density is written as  $\bar{\sigma}_0 = Q_0/L^2$ . The cell volume is  $V = L^2H$ . In simulations, the periodic boundary condition can be imposed in the xy plane. In this section,  $Q_0$  is stationary, but it can be oscillatory from Sec.VII.

W start with a continuum dielectric free energy  $\mathcal{F}$  bilinear in  $\boldsymbol{p}_i$  and  $\boldsymbol{E}$  in the linear response regime. It is given by the space integral  $\mathcal{F} = \int_V d\boldsymbol{r} f$  in the cell with

$$f = \frac{1}{8\pi} |\mathbf{E}|^2 + \frac{1}{2} a_{11} |\mathbf{p}_1|^2 + a_{12} \mathbf{p}_1 \cdot \mathbf{p}_2 + \frac{1}{2} a_{22} |\mathbf{p}_2|^2, \quad (3)$$

where  $a_{ij} = a_{ji}$  are constants and the fluid-solid interaction terms are not written. The first electrostatic term sensitively depends on the boundary condition. The third cross term ( $\propto a_{12}$ ), called the Lorentz term, was introduced by Felderhof<sup>6</sup>. We can further add the gradient terms (such as const. $|\nabla \cdot \boldsymbol{p}|^2$ )<sup>71–74</sup> and the elastic coupling terms for elastic dielectrics<sup>75</sup>.

To seek equilibrium from Eq.(3), we superimpose small increments  $\delta \mathbf{E}$  and  $\delta \mathbf{p}_i$  on  $\mathbf{E}$  and  $\mathbf{p}_i$  at fixed  $a_{ij}$ 

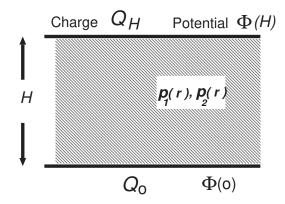


FIG. 1: Dielectric fluid with orientational polarizations  $p_1(r)$  and induced one  $p_2(r)$  between parallel metal plates, where  $Q_0$  and  $\Phi(0)$  are the electric charge and potential, respectively, at z=0, while  $Q_H(=-Q_0)$  and  $\Phi(H)$  are those at z=H. The z axis is perpendicular to the plates. We control  $Q_0$  in the fixed-charge condition and  $\Phi_a$  in Eq.(17) in the fixed-potential condition.

as70,73,75,76

$$\delta \mathcal{F} = \int_{V} d\mathbf{r} \left[ \frac{1}{4\pi} \mathbf{E} \cdot \delta \mathbf{D} - \mathbf{E} \cdot \delta \mathbf{p} + \sum_{i,j} a_{ij} \mathbf{p}_{i} \cdot \delta \mathbf{p}_{j} \right], \quad (4)$$

where  $\delta \mathbf{D} = \delta \mathbf{E} + 4\pi \delta \mathbf{p}$ . Since  $\mathbf{E} = -\nabla \Phi$  and  $\nabla \cdot \mathbf{D} = 0$ , we find  $\int_V d\mathbf{r} \mathbf{E} \cdot \delta \mathbf{D} = 0$  in the fixed-charge condition  $(\delta Q_0 = 0)$ . Thus, minimization of  $\mathcal{F}$  yields

$$\delta \mathcal{F}/\delta \boldsymbol{p}_1 = a_{11}\boldsymbol{p}_1 + a_{12}\boldsymbol{p}_2 - \boldsymbol{E} = \boldsymbol{0}, \tag{5}$$

$$\delta \mathcal{F}/\delta \boldsymbol{p}_2 = a_{22}\boldsymbol{p}_2 + a_{12}\boldsymbol{p}_1 - \boldsymbol{E} = \boldsymbol{0},\tag{6}$$

which are solved to give  $p_i = \chi_i E$  with the susceptibilities  $\chi_i$  for the two polarizations. The net susceptibility is given by  $\chi = (\epsilon - 1)/4\pi = \chi_1 + \chi_2$ . Using the inverse matrix  $\{a^{ij}\}$  of  $\{a_{ij}\}$  we obtain

$$\chi_1 = \sum_j a^{1j} = (a_{22} - a_{12})/(a_{11}a_{22} - a_{12}^2),$$

$$\chi_2 = \sum_j a^{2j} = (a_{11} - a_{12})/(a_{11}a_{22} - a_{12}^2).$$
 (7)

In equilibrium Eqs.(5) and (6) give the thermodynamic dielectric free energy  $\mathcal{F} = V \mathbf{E} \cdot \mathbf{D}/8\pi$ .

We introduce the Lorentz internal field  $\mathbf{F}$  by  $^{1}$ 

$$F = E + \frac{4\pi}{3}p,\tag{8}$$

which becomes  $\mathbf{F} = [(\epsilon + 2)/3]\mathbf{E}$  in equilibrium. Then, following Felderhof<sup>6</sup>, we assume that  $\mathbf{p}_2$  is given by

$$\mathbf{p}_2 = \bar{\alpha} \mathbf{F} = \frac{1}{4\pi} (\epsilon_{\infty} - 1) \left( \mathbf{E} + \frac{4\pi}{3} \mathbf{p}_1 \right), \tag{9}$$

where  $\epsilon_{\infty} - 1 = 4\pi \bar{\alpha}/(1 - 4\pi \bar{\alpha}/3)$ . Between  $\bar{\alpha}$  and  $\epsilon_{\infty}$  we have the Clausius-Mossotti relation,

$$\bar{\alpha} = n\alpha_0 = \frac{3}{4\pi} \cdot \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2},\tag{10}$$

where  $\bar{\alpha}$  is the dimensionless scalar polarizability,  $\alpha_0$  is the molecular polarizability, and n is the average dipole density. For polarizable polar fluids,  $\epsilon_{\infty}$  is the dielectric constant at relatively high frequencies for which  $p_1$  is negligibly small due to its slow relaxation (see Eq.(95)).

We assume that Eqs.(6) and (9) both hold in general situations, where  $p_1$  can differ from  $\chi_1 E$ . Then,

$$a_{12} = -\frac{4\pi}{3}, \quad a_{22} = \frac{4\pi}{\epsilon_{\infty} - 1}.$$
 (11)

From Eq.(7) we can express  $\chi$  in terms of  $a_{ij}$ . Using  $\chi - 1/a_{22} = (\epsilon - \epsilon_{\infty})/4\pi$ , we then find

$$a_{11} = \frac{4\pi}{9} \cdot \frac{\epsilon_{\infty} + 2}{\epsilon - \epsilon_{\infty}} (\epsilon + 2) - \frac{4\pi}{3}.$$
 (12)

Now,  $\chi_1$  and  $\chi_2$  are expressed in terms of  $\epsilon$  and  $\epsilon_{\infty}$  as

$$\chi_1 = \frac{3(\epsilon - \epsilon_\infty)}{4\pi(\epsilon_\infty + 2)} = \frac{3\chi}{\epsilon_\infty + 2} - \bar{\alpha}, \quad \chi_2 = \frac{\epsilon + 2}{3}\bar{\alpha}.$$
 (13)

Then, for  $\epsilon \gg \epsilon_{\infty}$ , we have  $\chi_1 \cong 3\chi/(\epsilon_{\infty} + 2)$  and  $\chi_2 \cong (\epsilon_{\infty} - 1)\chi/(\epsilon_{\infty} + 2) \gg (\epsilon_{\infty} - 1)/4\pi$ . With Eqs.(11)-(13) we can also express f in a symmetrical form,

$$f = \frac{1}{8\pi} |\mathbf{E}|^2 - \frac{2\pi}{3} |\mathbf{p}|^2 + \frac{\epsilon + 2}{6} \left[ \frac{1}{\chi_1} |\mathbf{p}_1|^2 + \frac{1}{\chi_2} |\mathbf{p}_2|^2 \right]. \tag{14}$$

We have fixed the surface charge  $Q_0$  to derive Eqs.(5) and (6). If the applied potential difference  $\Phi_a$  is fixed at a stationary value, we should perform the Legendre transformation of the free energy<sup>70,76,77</sup>,

$$\tilde{\mathcal{F}} = \mathcal{F} - \frac{1}{4\pi} \int_{V} d\mathbf{r} \mathbf{E} \cdot \mathbf{D} = \mathcal{F} - Q_0 \Phi_a, \qquad (15)$$

where the surface free energy is not written and use is made of  $\nabla \cdot \mathbf{D} = 0$  without ions in the fluid. For small changes in  $\mathbf{p}_i$  and  $\Phi_a$ ,  $\tilde{\mathcal{F}}$  changes infinitesimally as

$$\delta \tilde{\mathcal{F}} = \int_{V} d\mathbf{r} \Big[ -\mathbf{E} \cdot \delta \mathbf{p} + \sum_{i,j} a_{ij} \mathbf{p}_{i} \cdot \delta \mathbf{p}_{j} \Big] + Q_{0} \delta \Phi_{a}. \quad (16)$$

Thus,  $\delta \tilde{\mathcal{F}}/\delta \boldsymbol{p}_i$  at fixed  $\Phi_a$  are equal to  $\delta \mathcal{F}/\delta \boldsymbol{p}_i$  at fixed  $Q_0$ . As a result, minimization of  $\tilde{\mathcal{F}}$  at fixed  $\Phi_a$  also gives Eqs.(5) and (6). In equilibrium we have  $\tilde{\mathcal{F}} = -V\boldsymbol{E} \cdot \boldsymbol{D}/8\pi$ . Previously, the transformation (15) has been performed for electrolytes<sup>39,76,77</sup>.

#### B. Effect of surface potential drop

We remark the effect of the potential drop in the Stern layer on a solid-fluid surface  $^{33,38,41-43,62,63,69}$ , where the layer thickness d is microscopic and the electric field is very strong. The drop at  $z\cong 0$  consists of an intrinsic one  $\Phi^0_0$  without electric charges and an induced one  $\sigma_0/C_0$ , where  $\sigma_0$  is the local surface charge density and  $C_0$  is the

surface capacitance. The intrinsic drop arises from the molecular anisotropy (see Fig.1 in our previous paper<sup>42</sup>).

We also write the surface drop in the upper Stern layer region H-d < z < H as  $-\Phi_0^H - \sigma_H/C_H$  along the z axis. Then, removing the net charge-free potential drop  $\Phi_0^0 - \Phi_0^H$ , we define the applied potential difference  $\Phi_a$  as

$$\Phi_a = E_a H = \bar{\Phi}(d) - \bar{\Phi}(H - d) + \bar{\sigma}_0 / C$$

$$= H \int_V d\mathbf{r} E_z(\mathbf{r}) / V + \bar{\sigma}_0 / C, \tag{17}$$

where  $1/C = 1/C_0 + 1/C_H$  and  $\bar{\Phi}(z)$  and  $\bar{\sigma}_0$  are the lateral averages of the electric potential  $\Phi(r)$  and  $\sigma_0(x, y)$ , respectively. In this paper, the cell integration  $\int_V dr$  is performed outside the Stern layers, leading to the second line of Eq.(17) (which will be a key relation in Sec.VIII).

In the bulk region d < z < H - d, the electric field assumes a bulk value  $E_b$ , where  $\Phi(d) - \Phi(H - d) = (H - 2d)E_b$  and  $4\pi\bar{\sigma}_0 = \epsilon E_b$ . From Eq.(17) we find

$$E_b = E_a/(1 + \ell_{\rm w}/H).$$
 (18)

Here,  $\ell_{\rm w}$  is the surface electric length  $^{43,65,66}$ .

$$\ell_{\rm w} = \epsilon/(4\pi C) - 2d,\tag{19}$$

where the first term is amplified by  $\epsilon$  for  $\epsilon \gg 1$ . We then obtain the effective dielectric constant (2). Note that Eq.(19) can be used in the static limit. We will discuss the frequency-dependent surface effect in Appendix A.

At metal-water surfaces in the ambient condition (at  $T \cong 300 \,\mathrm{K}$  and  $p \cong 1 \,\mathrm{atm}$ ), the surface capacitance was in a range of 5-50  $\mu\mathrm{F/cm^2}$  (0.45 – 4.5/nm) in experiments<sup>62</sup> and around 10  $\mu\mathrm{F/cm^2}$  in simulations<sup>33,38,43</sup>. These indicate  $1/4\pi C \sim 1 \,\mathrm{\mathring{A}}$  and  $\ell_\mathrm{w} \sim 10 \,\mathrm{nm}$  for water, where  $\ell_\mathrm{w} \cong \chi/C$ . Thus, the situation  $d \ll H \lesssim \ell_\mathrm{w}$  can well be realized in simulations<sup>33,38,43</sup> and experiments<sup>68</sup>. See Appendix A and Sec.VIII for more discussions.

#### C. Directing field and Onsager theory

Felderhof<sup>6</sup> introduced a coefficient  $\lambda_{11}$  by

$$\lambda_{11} = 1/\chi_d - a_{11} = 1/\chi_d - (\epsilon + 2)/3\chi_1 + 4\pi/3,$$
 (20)

where  $a_{11}$  is given in Eq.(12) and  $\chi_d$  is the orientational susceptibility. He required the relation  $\delta \mathcal{F}/\delta \mathbf{p}_1 = \chi_d^{-1} \mathbf{p}_1 - \mathbf{E}_d$  using the simplest form  $\chi_d = n\mu_0^2/3k_BT$ . From Eq.(4) we express  $\mathbf{E}_d$  as

$$E_d = E + \lambda_{11} p_1 - a_{12} p_2 = F - \left(\frac{4\pi}{3} - \lambda_{11}\right) p_1,$$
 (21)

where F is the Lorentz field (8). In equilibrium we have

$$\mathbf{p}_1 = \chi_1 \mathbf{E} = \chi_d \mathbf{E}_d, \tag{22}$$

Thus,  $E_d$  is called the directing field<sup>4</sup> governing the dipole orientation. Debye<sup>1</sup> originally assumed  $E_d = F$  and  $p_1 = (n\mu_0^2/3k_BT)F$ .

Onsager assumed  $p_2 = \bar{\alpha} F$  with Eq.(10) and expressed  $E_d$  and F in terms of E and  $p_1$  as

$$\boldsymbol{E}_d = \frac{\epsilon(\epsilon_{\infty} + 2)}{2\epsilon + \epsilon_{\infty}} \boldsymbol{E},\tag{23}$$

$$F = E_d + \frac{8\pi(\epsilon - 1)(\epsilon_{\infty} + 2)}{9(2\epsilon + \epsilon_{\infty})} p_1,$$
 (24)

See Appendix B for more explanations of his theory. He argued that the second term in Eq.(24) is parallel to  $p_1$  and irrelevant in orienting the dipoles and hence the first term  $E_d$  governs the dipole orientation. Furthermore, let us set  $p_i = \chi_i E$  in equilibrium within Onsager's theory. Then, these  $\chi_1$  and  $\chi_2$  coincide with those in Eq.(13) (see Eq.(B5)). Now, Eqs.(22) and (23) yield

$$\chi_d = \chi_1 \frac{|\mathbf{E}|}{|\mathbf{E}_d|} = \frac{3(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{4\pi\epsilon(\epsilon_\infty + 2)^2},$$
 (25)

which is the Onsager equation if  $\chi_d = n\mu_0^2/3k_BT$ . From Eqs.(13), (20), and (25)  $\lambda_{11}$  is also calculated as<sup>6</sup>

$$\lambda_{11} = \frac{4\pi}{3} - \frac{8\pi(\epsilon - 1)(\epsilon_{\infty} + 2)}{9(2\epsilon + \epsilon_{\infty})}.$$
 (26)

With this expression, Felderhof's Eq.(21) and Onsager's Eq.(24) are identical self-consistently. We stress that  $\chi_1$  and  $\chi_2$  in Eq.(13) are fundamental theoretical elements, but use has been made of different expressions for them in the literature (see Appendix C)<sup>3,7–12,17,29</sup>.

In Onsager's theory the short-range dipole-dipole interaction is neglected. To account for it, Kirkwood<sup>5</sup> set

$$\chi_d = g\mu_0^2 n/3k_B T. (27)$$

With g in  $\chi_d$ , Eq.(25) is the Kirkwood-Fröhlich (KF) equation<sup>3</sup>. In this paper, we define  $\chi_d$  by Eq.(27) with g, while  $\lambda_{11}$  is given by Eq.(26) for any g. In Sec.IIIB, we shall see that Onsager's results and the KF equation follow from the free energy density (3).

We make remarks. (i) For  $\epsilon \gg \epsilon_{\infty}$  we have

$$|E| \sim |E_d| \ll |F| \sim [2\epsilon/3(\epsilon_{\infty} + 2)]|E|$$

from Eqs.(23) and (24). (ii) In equilibrium with  $p_1 = \chi_1 E$ , Eq.(24) is rewritten in the Lorentz form  $F = [(\epsilon + 2)/3]E$ . Namely, Onsager's F in Eq.(24) and Lorentz's F in Eq.(8) coincide for  $p_1 = \chi_1 E$ , but they differ for  $p_1 \neq \chi_1 E$ . The same statement can be made for Onsager's  $E_d$  in Eq.(23) and Felderhof's  $E_d$  in Eq.(21). However, Eqs.(21) and (24) give the same difference  $F - E_d$ . (iii) In general situations, we should define F by Eq.(8) and  $E_d$  by Eq.(21) or Eq.(24). (iv) The dipole orientation is in the nonlinear regime for  $\mu_0 |E_d| \gtrsim k_B T$ , which has been studied extensively  $^{76,78-81}$ .

Let us estimate the parameters introduced so far. If we set  $\epsilon = 78.5$ ,  $\epsilon_{\infty} = 1.77$ , and  $\mu_0 = 1.85$  D for ambient liquid water<sup>79</sup>, Eqs.(12), (13), and (25)-(27) give

$$\chi = 6.17, \quad \bar{\alpha} = 0.049, \quad \chi_1 = 4.86, \quad \chi_2 = 1.31,$$
 $a_{11} = 1.33, \quad \lambda_{11} = -0.95, \quad \chi_d = 2.61, \quad g = 2.80,$ 
 $n\mu_0^2/3k_BT = 0.92, \quad |\boldsymbol{E}_d| = 0.070|\boldsymbol{F}| = 1.86|\boldsymbol{E}|.$ 

#### III. STATIC POLARIZATION FLUCTUATIONS

In this section, we examine the static polarization correlations treating  $\mathbf{p}_i = (p_{ix}, p_{iy}, p_{iz})$  as thermal fluctuations. Their wave numbers are in the intermediate range  $\pi/H < q < \pi/a_m$ , where  $a_m$  is the molecular length. They obey the Gaussian distribution  $\propto \exp(-\mathcal{F}/k_BT)$  at  $Q_0 = 0$ . However, the variances of these inhomogeneous fluctuations with  $q \neq 0$  do not depend on the boundary condition in the linear regime.

#### A. Correlations of Fourier components

Introducing a variable s we rewrite f in Eq.(3) as

$$f = \frac{1}{8\pi} |\mathbf{E}|^2 + \frac{1}{2\chi} |\mathbf{p}|^2 + \frac{1}{2} A_0 |\mathbf{s}|^2, \tag{28}$$

where s is decoupled from  $p = p_1 + p_2$  and is defined by

$$s = \sum_{i} (a_{1i} - a_{2i}) \boldsymbol{p}_{i} = \frac{\epsilon + 2}{3} \left( \frac{\boldsymbol{p}_{1}}{\chi_{1}} - \frac{\boldsymbol{p}_{2}}{\chi_{2}} \right). \tag{29}$$

We also have  $\mathbf{s} = \delta \mathcal{F}/\delta \mathbf{p}_1 - \delta \mathcal{F}/\delta \mathbf{p}_2$  from Eq.(14). The linear response of  $\mathbf{s}$  to  $\mathbf{E}$  vanishes in the static limit. We express  $\mathbf{p}_1$  and  $\mathbf{p}_2$  in terms of  $\mathbf{p}$  and  $\mathbf{s}$  as

$$p_1 = \frac{1}{\chi} \chi_1 p + A_0 s, \quad p_2 = \frac{1}{\chi} \chi_2 p - A_0 s.$$
 (30)

The coefficient  $A_0$  is given by

$$A_0 = \bar{\alpha}\chi_1/\chi = 3\chi_1\chi_2/[\chi(\epsilon+2)],\tag{31}$$

which is close to  $\bar{\alpha}$  for  $\epsilon \gg \epsilon_{\infty} \sim 1$ .

The Fourier components of  $p_i$  and s are written as

$$\hat{\boldsymbol{p}}_{i}(\boldsymbol{q}) = \int_{V} d\boldsymbol{r} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \boldsymbol{p}_{i}(\boldsymbol{r}), \ \hat{\boldsymbol{s}}(\boldsymbol{q}) = \int_{V} d\boldsymbol{r} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \boldsymbol{s}(\boldsymbol{r}), \ (32)$$

where  $\mathbf{q} = 2\pi(n_x/L, n_y/L, n_z/H)$  with  $(n_x, n_y, n_z)$  being integers. We consider the correlations,

$$\hat{G}_{\alpha\beta}^{ij}(\mathbf{q}) = \langle \hat{p}_{i\alpha}(\mathbf{q})\hat{p}_{j\beta}(\mathbf{q})^* \rangle / Vk_B T, \qquad (33)$$

where the Greek indices refer to the Cartesian coordinates (x, y, z) and  $\langle \cdots \rangle$  represents the equilibrium average at  $Q_0 = 0$ . The inverse Fourier transformations of  $\hat{G}_{\alpha\beta}^{ij}(q)$  give the space correlations,

$$G_{\alpha\beta}^{ij}(\mathbf{r}) = \frac{\langle p_{i\alpha}(\mathbf{r}_1)p_{j\beta}(\mathbf{r}_2)\rangle}{k_B T} = \frac{1}{V} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \hat{G}_{\alpha\beta}^{ij}(\mathbf{q}), \quad (34)$$

where  $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$  and the sum  $\sum_{\mathbf{q}}$  is taken in the range  $\pi/H < q < \pi/a_m$ . The positions  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are located in the bulk region (far from the boundaries), where the translational symmetry nearly holds.

We express  $\mathcal{F}$  in terms of  $\hat{p}(q) = \sum_i \hat{p}_i(q)$  and  $\hat{s}(q)$  as

$$\mathcal{F} = \frac{1}{2V} \sum_{q} \left[ 4\pi |\hat{p}_{\parallel}(q)|^2 + \frac{1}{\gamma} |\hat{p}(q)|^2 + A_0 |\hat{s}(q)|^2 \right], (35)$$

where the Fourier components of E are equated to  $-4\pi p_{\parallel}(q)$ . Here,  $\hat{p}_{\parallel} = (\hat{q} \cdot \hat{p})\hat{q}$  and  $\hat{p}_{\perp} = \hat{p} - \hat{p}_{\parallel}$  are the longitudinal and transverse parts of  $\hat{p}$ , respectively, with  $\hat{q} \equiv q^{-1}q$  being the unit vector along q. Then,

$$\hat{G}_{\alpha\beta}(\mathbf{q}) = \sum_{i,j} \hat{G}_{\alpha\beta}^{ij}(\mathbf{q}) = \chi(\delta_{\alpha\beta} - \hat{q}_{\alpha}\hat{q}_{\beta}) + \frac{\chi}{\epsilon} \hat{q}_{\alpha}\hat{q}_{\beta}, (36)$$

$$\langle \hat{s}_{\alpha}(\boldsymbol{q})\hat{s}_{\beta}(\boldsymbol{q})^{*}\rangle \frac{1}{V} = \frac{k_{B}T}{A_{0}}\delta_{\alpha\beta}, \quad \langle \hat{p}_{\alpha}(\boldsymbol{q})\hat{s}_{\beta}(\boldsymbol{q})^{*}\rangle = 0, \quad (37)$$

where Eq.(36) is well known<sup>19,86,87</sup> and Eq.(37) shows that  $\boldsymbol{s}$  and  $\boldsymbol{p}$  are *orthogonal* to each other.

From Eqs.(30) and (36) we now obtain

$$\hat{G}_{\alpha\beta}^{ij}(\boldsymbol{q}) = (2\delta_{ij} - 1)\delta_{\alpha\beta}A_0 + (\chi_i\chi_j/\chi^2)\hat{G}_{\alpha\beta}(\boldsymbol{q})$$
$$= \chi_{\perp}^{ij}(\delta_{\alpha\beta} - \hat{q}_{\alpha}\hat{q}_{\beta}) + \chi_{\parallel}^{ij}\hat{q}_{\alpha}\hat{q}_{\beta}. \tag{38}$$

Here,  $\chi_{\perp}^{ij}$  and  $\chi_{\parallel}^{ij}$  are the transverse and longitudinal variances of  $\hat{\boldsymbol{p}}_i$  and  $\hat{\boldsymbol{p}}_j$ , which are the inverse matrices of  $a_{ij}$  and  $a'_{ij} = a_{ij} + 4\pi$ . respectively. From Eq.(7) we find  $a'_{11}a'_{22} - a'_{12}^2 = \epsilon(a_{11}a_{22} - a_{12}^2)$ , and  $a'_{22} = \epsilon_{\infty}a_{22}$ . Thus,

$$\chi_{\perp}^{11} = \frac{3\chi_1}{\epsilon_{\infty} + 2} = \frac{9(\epsilon - \epsilon_{\infty})}{4\pi(\epsilon_{\infty} + 2)^2}, \quad \chi_{\parallel}^{11} = \frac{\epsilon_{\infty}}{\epsilon} \chi_{\perp}^{11}, \quad (39)$$

$$\chi_{\perp}^{12} = -\frac{\epsilon}{2}\chi_{\parallel}^{12} = \frac{4\pi}{3}\bar{\alpha}\chi_{1},$$
(40)

$$\chi_{\perp}^{22} - \bar{\alpha} = -\frac{\epsilon}{2} (\chi_{\parallel}^{22} - \bar{\alpha}) = \frac{4\pi}{3} \bar{\alpha} \chi_2,$$
 (41)

where we have the sum relations,

$$\sum_{j} \chi_{\perp}^{ij} = \chi_i, \quad \sum_{j} \chi_{\parallel}^{ij} = \frac{1}{\epsilon} \chi_i. \tag{42}$$

Here, the longitudinal parts are suppressed by the dipolar interaction. In particular,  $\chi_{\parallel}^{11}/\chi_{\perp}^{11}=\epsilon_{\infty}/\epsilon$ . From the trace  $\sum_{\alpha}\hat{G}_{\alpha\alpha}^{11}(\boldsymbol{q})$ , we find another noteworthy relation,

$$2\chi_{\perp}^{11} + \chi_{\parallel}^{11} = (2 + \epsilon_{\infty}/\epsilon)\chi_{\perp}^{11} = 3\chi_d, \tag{43}$$

where  $\chi_d$  is given by Eq.(25). For  $\epsilon_{\infty}=1$ , we simply have  $\chi_{\perp}^{11}=\chi_1=\chi$ . For water, we have  $\chi_{\perp}^{11}=3.87$  and  $\chi_{\parallel}^{11}=0.087$  from the last paragraph in Sec.IIC.

"We make remarks. (i) The first line of Eq.(38) is equivalent to Felderhof's formal expression  $(3.11)^6$ . (ii) In Appendix C, we will present  $\hat{G}^{ij}_{\alpha\beta}(\boldsymbol{q})$  omitting the Lorentz term. (iii) Fulton<sup>86</sup> and Felderhof<sup>87</sup> examined the space-time polarization correlations including the radiation field, where the light speed appears.

#### B. Space correlations and g factor

We consider the space-correlation functions  $G_{\alpha\beta}^{ij}(\mathbf{r})$  in Eq.(34) and  $G_{\alpha\beta}(\mathbf{r}) = \sum_{i,j} G_{\alpha\beta}^{ij}(\mathbf{r})$ . From Eqs.(36) and (38) they are expressed in the range  $a_m < r < H$  as

$$G_{\alpha\beta}^{ij}(\mathbf{r}) = (2\delta_{ij} - 1)\delta_{\alpha\beta}A_0\delta(\mathbf{r}) + (\chi_i\chi_j/\chi^2)G_{\alpha\beta}(\mathbf{r}),$$
  

$$G_{\alpha\beta}(\mathbf{r}) = \chi\delta_{\alpha\beta}\delta(\mathbf{r}) + (4\pi\chi^2/\epsilon)\nabla_{\alpha}\nabla_{\beta}\psi(r),$$
(44)

where  $\delta(\mathbf{r})$  represents localized functions with  $\int d\mathbf{r}\delta(\mathbf{r}) = 1$ ,  $\nabla_{\alpha}$  is the  $\alpha$  component of  $\nabla$ , and  $\psi(r) = (4\pi r)^{-1}$  for  $r \gg a_m$ . From  $\nabla^2 \psi = -\delta(\mathbf{r})$  the traces (inner products)  $\sum_{\alpha} G_{\alpha\alpha}^{ij}(\mathbf{r})$  are short-ranged. The short-range behaviors of  $\delta(\mathbf{r})$  and  $\psi(r)$  can be known only from microscopic simulations. The expressions in Eq.(44) can be used in the bulk and are independent of the boundary condition, so they are the correlations in infinite systems. For finite systems, we should add the nonlocal terms to the right hand sides of Eq.(44), which will be discussed in Sec.IV.

We suppose a mesoscopic sphere embedded in the same fluid<sup>3-5</sup>. Its center is at the origin  $\mathbf{0}$  in the bulk, its radius R is in the range  $a_m \ll R \ll H$ , and its volume  $v = 4\pi R^3/3$  is in the range  $1/n \ll v \ll V$ . We integrate  $p_i(r)$  and p(r) within the sphere as

$$M_i = \int_{r < R} d\mathbf{r} \ \mathbf{p}_i(\mathbf{r}), \ M = \sum_i M_i = \int_{r < R} d\mathbf{r} \ \mathbf{p}(\mathbf{r}).$$
 (45)

Because the integration region is spherical, we have  $\langle M_{i\alpha}M_{j\beta}\rangle = \langle \mathbf{M}_i \cdot \mathbf{M}_j\rangle \delta_{\alpha\beta}/3$ . Thus, Eq.(44) gives

$$\langle M_{i\alpha} M_{j\beta} \rangle / v k_B T = (2\chi_{\perp}^{ij} + \chi_{\parallel}^{ij}) \delta_{\alpha\beta} / 3,$$
  
$$\langle M_{\alpha} M_{\beta} \rangle / v k_B T = \chi (2 + 1/\epsilon) \delta_{\alpha\beta} / 3,$$
 (46)

where we neglect corrections of order v/V from the nonlocal correlations. We also find Eq.(46) if the integration region is a cube. If it is a spheroid with the symmetry axis along the z axis<sup>43,70</sup>, the right-hand sides of Eq.(46) become uniaxial, tending to those of Eq.(53) in the pancake limit. For  $v \ll V$ , Eqs.(43) and (46) give

$$\langle |\boldsymbol{M}_1|^2 \rangle / 3vk_B T = \chi_d, \tag{47}$$

where  $\chi_d$  is given in Eq.(25). See Eq.(58) for a generalization of Eq.(47) with the long-range correction added.

Microscopically,  $M_1$  is expressed as  $M_1 = \sum_{k}' \mu_0 \omega_k$ , where we sum over the dipoles in the sphere with  $\omega_k$  being the unit vector along the direction of the k-th dipole. Then, the g factor in Eq.(27) is expressed as<sup>5</sup>

$$g = \langle |\boldsymbol{M}_1|^2 \rangle / (nv\mu_0^2) = 1 + \sum_{k \neq m}' \langle \boldsymbol{\omega}_k \cdot \boldsymbol{\omega}_m \rangle / nv, \quad (48)$$

which accounts for the short-range orientational correlation for  $a_m \ll R \ll H$ . With Eqs.(47) and (48) we recognize that the Felderhof free energy density (3) can yield the KF equation.

Fröhlich<sup>3</sup> expressed  $\langle |M_1|^2 \rangle$  in his Eq.(7.38) in the form of Eq.(C7), which is larger than  $\chi_d$  in Eq.(25) by a factor of  $(\epsilon_{\infty} + 3)^2/9$ . To derive it, he assumed  $p_2 = [(\epsilon_{\infty} - 1)/4\pi] E$  and  $p_1 = [(\epsilon - \epsilon_{\infty})/4\pi] E$  in his Eqs.(7.35) and (7.36), which are invalid in the static limit (see below Eq.(13)). He then introduced the effective dipole moment  $\mu \equiv \mu_0(\epsilon_{\infty} + 2)/3$  in his Eq.(8.1) to obtain the KF equation (25). In contrast, using  $\chi_1$  and  $\chi_2$  in Eq.(13), we do not modify the dipole moment  $\mu_0$ .

## C. Static linear response: Embedded sphere

From Eq.(46) we find the linear response relations in terms of the variances among  $M_i$  in the static limit,

$$\mathbf{p}_{i} = \chi_{i} \mathbf{E} = [\langle \mathbf{M}_{i} \cdot \mathbf{M} \rangle / 3vk_{B}T] \mathbf{E}_{c} \quad (i = 1, 2),$$
$$\mathbf{p} = \chi \mathbf{E} = [\langle |\mathbf{M}|^{2} \rangle / 3vk_{B}T] \mathbf{E}_{c}, \tag{49}$$

where  $\chi_2/\chi_1 = \langle \boldsymbol{M}_2 \cdot \boldsymbol{M} \rangle / \langle \boldsymbol{M}_1 \cdot \boldsymbol{M} \rangle$  follows from Eq.(30). The  $\boldsymbol{E}_c$  is the cavity field in the sphere<sup>2-5</sup>,

$$\boldsymbol{E}_c = [3\epsilon/(2\epsilon + 1)]\boldsymbol{E}.\tag{50}$$

which is produced by the electrode charges and the exterior dipoles. We can see that  $E_c$  is the applied field and the interior M is its conjugate variable.

From Eqs.(22) and (46) we write  $p_1$  in another form,

$$\mathbf{p}_1 = \chi_d \mathbf{E}_d = [\langle |\mathbf{M}_1|^2 \rangle / 3v k_B T] \mathbf{E}_d. \tag{51}$$

where  $E_d$  is the applied field and its conjugate variable is the interior  $M_1$ . Here,  $E_d$  is a modified cavity field including the reaction effect due to the interior  $p_2$ . Thus,  $p_2$  cannot be calculated in this scheme.

## IV. TOTAL POLARIZATIONS AND NONLOCAL CORRELATIONS

We consider the total polarizations in the cell,

$$\boldsymbol{M}_{i}^{\mathrm{tot}} = \int_{V} d\boldsymbol{r} \ \boldsymbol{p}_{i}(\boldsymbol{r}), \quad \boldsymbol{M}^{\mathrm{tot}} = \sum_{i} \boldsymbol{M}_{i}^{\mathrm{tot}},$$
 (52)

which are the Fourier components,  $\hat{p}_i(0)$  and  $\hat{p}(0)$ , with q=0 in Eq.(32). The contributions from the polarizations in the Stern layers are negligible for  $d \ll H$ . These homogeneous components are sensitive to the boundary condition. We introduce the nonlocal correlations, which are written as  $\chi_i \chi_j D_{\alpha\beta}/\chi^2 V$  in  $G_{\alpha\beta}^{ij}(r)$  and  $D_{\alpha\beta}/V$  in  $G_{\alpha\beta}(r)$  from Eq.(30), where the coefficients  $D_{\alpha\beta}$  depend on the boundary condition. They yield additional contributions to the variances  $\langle M_{i\alpha}^{\rm tot} M_{j\beta}^{\rm tot} \rangle$ . Some discussions on their dynamics will be given in Sec.VIC. The case of fixed  $\Phi_a$  will be studied in Sec.VIII.

(i) First, setting  $Q_0 = 0$  with  $H \ll L$ , we integrate  $G_{\alpha\beta}^{ij}(\mathbf{r}_1 - \mathbf{r}_2)$  in Eq.(44) over  $\mathbf{r}_1$  and  $\mathbf{r}_2$  to find<sup>81,82</sup>

$$\langle M_{i\alpha}^{\text{tot}} M_{j\beta}^{\text{tot}} \rangle / V k_B T = \chi_{\perp}^{ij} (\delta_{\alpha\beta} - \delta_{\alpha z} \delta_{\beta z}) + \chi_{\parallel}^{ij} \delta_{\alpha z} \delta_{\beta z},$$
  
$$\langle M_{\alpha}^{\text{tot}} M_{\beta}^{\text{tot}} \rangle / V k_B T = \chi (\delta_{\alpha\beta} - \delta_{\alpha z} \delta_{\beta z}) + \frac{\chi}{\epsilon} \delta_{\alpha z} \delta_{\beta z}, \quad (53)$$

For  $H \ll L$  the integration of the dipolar term in Eq.(44) can be performed if use is made of the equation,

$$\int \! d\mathbf{r}'_{\perp} \nabla_{\alpha} \nabla_{\beta} \psi(|\mathbf{r} - \mathbf{r}'|) \cong -\delta(z - z') \delta_{\alpha z} \delta_{\beta z}, \qquad (54)$$

where we integrate over  $\mathbf{r}'_{\perp} = (x'.y')$  and  $\psi(r)$  in Eq.(44) is set equal to  $1/4\pi r$ . Here, Eq.(54) is obtained from

 $\int \!\! d{m r}'_\perp \nabla_z \psi(|{m r}-{m r}'|) \cong -(z-z')/2|z-z'|$  for  $|z-z'| \ll L$ . Here, the dipolar interaction suppresses the z components  $M_{iz}^{\rm tot}$ . In this case, no nonlocal correlation appears (see the last paragraph in Sec.VIIIB).

We can derive Eq.(53) even for not small H/L if we assume the periodic boundary condition along the x and y axes. To show this, we present another derivation of Eq.(53) assuming  $Q_0 = 0$  and the lateral periodicity. In this case, the cell integrals of  $D_z = E_z + 4\pi p_z$ ,  $E_x$ , and  $E_y$  vanish. Then, Eq.(28) yields the free energy from the Fourier components with q = 0 in the form,

$$\mathcal{F}_{\text{tot}} = \frac{2\pi}{V} |\hat{p}_z(\mathbf{0})|^2 + \frac{1}{2V\chi} |\hat{p}(\mathbf{0})|^2 + \frac{1}{2V} A_0 |\hat{s}(\mathbf{0})|^2. \quad (55)$$

Here,  $\hat{\boldsymbol{p}}(\mathbf{0}) = \boldsymbol{M}^{\text{tot}}$  and  $\hat{\boldsymbol{s}}(\mathbf{0}) = \int_{V} d\boldsymbol{r} \boldsymbol{s}(\boldsymbol{r})$  obey the distribution  $\propto \exp(-\mathcal{F}_{\text{tot}}/k_B T)$ , so we are led to Eq.(53).

(ii) Second, we consider the case of the periodic boundary condition along the three axes<sup>23,51,55–59</sup>, where we have  $\int_V d\mathbf{r} \mathbf{E} = \mathbf{0}$ . Then, the first term in Eq.(55) is absent, leading to the isotropic variance relations<sup>23,53–55</sup>,

$$\langle M_{i\alpha}^{\text{tot}} M_{j\beta}^{\text{tot}} \rangle / V k_B T = \chi_{\perp}^{ij} \delta_{\alpha\beta},$$
  
 $\langle M_{\alpha}^{\text{tot}} M_{\beta}^{\text{tot}} \rangle / V k_B T = \chi \delta_{\alpha\beta} \text{ (periodic)}, (56)$ 

which hold for  $L_x \times L_y \times L_z$  rectangular cells. We also find Eq.(56) if a polar fluid is enclosed by an equi-potential surface or by a metal<sup>53,83</sup>. For finite V,  $G_{\alpha\beta}^{ij}(\mathbf{r})$  consist of those in Eq.(44) and the nonlocal parts given by  $4\pi\chi_i\chi_j\delta_{\alpha\beta}/3\epsilon V$  for cubic cells. For example, we find

$$\sum_{\alpha} G_{\alpha\alpha}(\mathbf{r}) = \langle \mathbf{p}(\mathbf{r}) \cdot \mathbf{p}(\mathbf{0}) \rangle / k_B T$$

$$= \frac{\chi}{\epsilon} (2\epsilon + 1)\delta(\mathbf{r}) + \frac{\chi(\epsilon - 1)}{\epsilon V} \text{ (periodic)}, (57)$$

where the first term arises from Eq.(44). The cell integration of Eq.(57) is  $3\chi$  in accord with Eq.(56).

(iii) Third, Sprik's group<sup>51,52</sup> imposed the global condition,  $\int_V d\boldsymbol{r} \boldsymbol{D} = \int_V d\boldsymbol{r} \boldsymbol{E} + 4\pi \hat{\boldsymbol{p}}(\mathbf{0}) = \mathbf{0}$ , in their simulation. In this case, the first term in Eq.(55) is replaced by  $2\pi |\hat{\boldsymbol{p}}(\mathbf{0})|^2/V$ , so the counterpart of Eq.(56) is obtained by replacements:  $\chi^{ij}_{\perp} \to \chi^{ij}_{\parallel}$  and  $\chi \to \chi/\epsilon$ . For cubic cells, the nonlocal parts in  $G^{ij}_{\alpha\beta}(\boldsymbol{r})$  are  $-8\pi\chi_i\chi_j\delta_{\alpha\beta}/3\epsilon V$  and the second term in Eq.(57) is replaced by  $-2\chi(\epsilon-1)/\epsilon V$ , leading to  $\langle |\boldsymbol{M}^{\text{tot}}|^2 \rangle/Vk_BT = 3\chi/\epsilon$ .

In addition, the nonlocal correlations change the variance of the sphere integral  $M_1$  in Eq.(47) to<sup>53</sup>

$$\langle |\boldsymbol{M}_1|^2 \rangle / 3vk_B T = \chi_d + C_{\rm nl}\chi_1^2 v / 3\epsilon V.$$
 (58)

The Kirkwood g factor should be determined without the second term. The coefficient  $C_{\rm nl}$  is equal to  $4\pi$  for  $\int_V d\mathbf{r} \mathbf{E} = \mathbf{0}$  (in the periodic case) and to  $-8\pi$  for  $\int_V d\mathbf{r} \mathbf{D} = \mathbf{0}$ , which agree with simulations<sup>51,56</sup>. In the parallel plate geometry, it vanishes at fixed  $Q_0$  and becomes  $\epsilon/\chi(1+\ell_{\rm w}/H)-1/\chi$  at fixed  $\Phi_a$  (see Sec.VIII).

The nonlocal correlations generally appear under global constraints. In fluid mixtures, the space correlations of the number densities have nonlocal parts  $\propto V^{-1}$ 

in the canonical and isothermal-isobaric ensembles  $^{60,61}$ , which do not exist in the grand-canonical ensemble. For example, the pair correlation of the density fluctuation  $\delta \hat{n}(\mathbf{r})$  in pure fluids behaves in the canonical ensemble as

$$\langle \delta \hat{n}(\mathbf{r}) \delta \hat{n}(\mathbf{0}) \rangle = n \delta(\mathbf{r}) + n^2 [g(r) - 1] - n^2 k_B T \kappa_T / V, (59)$$

Here, n is the mean density, g(r) is the radial distribution function, and  $\kappa_T$  is the isothermal compressibility. The cell integration of Eq.(59) vanishes due to the thermodynamic relation  $nk_BT\kappa_T = 1 + n \int d\mathbf{r}[g(r) - 1]$ .

## V. SOLVATION FREE ENERGY WITH A CHARGE DENSITY

Marcus<sup>7</sup> studied the electron transfer kinetics in a polar solvent, where the solvent polarization around ions was assumed to obey the classical electrostatics. In this approach, various chemical reactions in a polar solvent have been studied<sup>9–12,26,30,84,85</sup>. Marcus wrote the fastest electronic polarization as  $\boldsymbol{p}_e$  and the sum of the slower orientational and atomic ones as  $\boldsymbol{p}_u$ . He then expressed  $\boldsymbol{p}_e$  in terms of  $\boldsymbol{p}_u$  and the bare electric field  $\boldsymbol{E}_0$  produced by the solute charge density  $\rho_s$  and the electrode charges in local equilibrium. In these papers, however, the Lorentz term in the free energy has been missing. Hence, it is included in this section. In our theory,  $\boldsymbol{p}_1$  denotes the orientational polarization and  $\boldsymbol{p}_2$  the sum of the atomic and electronic ones. The relations here will be used in Secs.VI-VIII.

The bare field  $E_0$  does not include the polarization contribution and is determined by<sup>7,8</sup>

$$E_0 = -\nabla \Phi_{\text{bare}}, \quad \nabla \cdot E_0 = -\nabla^2 \Phi_{\text{bare}} = 4\pi \rho_{\text{s}}, \quad (60)$$

where  $\Phi_{\text{bare}}$  is the bare potential and the electrode charges appear in the boundary conditions.

We divide  $p_i(r)$  into the longitudinal part  $p_{i\parallel}(r)$  and the transverse part  $p_{i\perp}(r)$ , where their Fourier components are  $\hat{p}_{i\parallel}(q)$  and  $\hat{p}_{i\perp}(q)$ , respectively (see below Eq.(35)). If  $p_i$  depends only on z, we have  $p_{i\parallel}=(0,0,p_{iz})$ . From  $\nabla \cdot D=4\pi \rho_{\rm sol}$  we find

$$\boldsymbol{E}_0 = \boldsymbol{E} + 4\pi \boldsymbol{p}_{\parallel} = \boldsymbol{D} - 4\pi \boldsymbol{p}_{\perp}, \tag{61}$$

where  $p_{\parallel}=p-p_{\perp}=p_{1\parallel}+p_{2\parallel}$ . The fields  $E_0$  and E are longitudinal. Thus,  $E_0=D$  for  $p_{\perp}=0$ .

Minimization of  $\mathcal{F}$  with respect to  $p_2$  at fixed  $p_1$  and  $Q_0$  is attained at  $p_2 = p_2^{\text{eq}}$  as in Eqs.(6) and (9). Using Eq.(61) we rewrite this  $p_2^{\text{eq}}$  in terms of  $p_1$  and  $E_0$  as

$$\boldsymbol{p}_{2}^{\mathrm{eq}} = \frac{\epsilon_{\infty} - 1}{4\pi\epsilon_{\infty}} \left[ \boldsymbol{E}_{0} - \frac{8\pi}{3} \boldsymbol{p}_{1\parallel} \right] + \frac{\epsilon_{\infty} - 1}{3} \boldsymbol{p}_{1\perp}. \tag{62}$$

Then,  $\mathcal{F}$  at  $\boldsymbol{p}_2 = \boldsymbol{p}_2^{\text{eq}}$  is written as

$$\mathcal{F}_{\mathrm{s}} = \int_{V} d\boldsymbol{r} \left[ \frac{|\boldsymbol{E}_{0}|^{2}}{8\pi\epsilon} + \frac{1}{2\chi_{\parallel}^{11}} \left| \boldsymbol{p}_{1\parallel} - \boldsymbol{p}_{1}^{\mathrm{eq}} \right|^{2} + \frac{|\boldsymbol{p}_{1\perp}|^{2}}{2\chi_{\perp}^{11}} \right], \quad (63)$$

where  $\chi_{\perp}^{11}$  and  $\chi_{\parallel}^{11}$  are given in Eqs.(39) and (43) and

$$p_1^{\text{eq}} = \frac{\chi_1}{\epsilon} E_0. = \frac{3(\epsilon - \epsilon_\infty)}{4\pi(\epsilon_\infty + 2)\epsilon} E_0.$$
 (64)

Here,  $p_{1\parallel}$  and  $E_0$  evolve slowly, to which  $p_{1\perp}$  is uncoupled in the linear order.

We are interested in the thermal fluctuation of  $p_2$  around  $p_2^{\text{eq}}$  in Eq.(62), so we consider its deviation,

$$\boldsymbol{\xi} = \boldsymbol{p}_2 - \boldsymbol{p}_2^{\text{eq}},\tag{65}$$

which will be important in the next section. Retaining  $\xi$  we express E in Eq.(61) and  $p = p_1 + p_2$  as

$$E = \frac{1}{\epsilon_{\infty}} \left[ E_0 - \frac{4\pi}{3} (\epsilon_{\infty} + 2) p_{1\parallel} \right] - 4\pi \xi_{\parallel}, \tag{66}$$

$$\boldsymbol{p} = \frac{\epsilon_{\infty} - 1}{4\pi\epsilon_{\infty}} \boldsymbol{E}_0 + \frac{\epsilon_{\infty} + 2}{3\epsilon_{\infty}} \left( \boldsymbol{p}_{1\parallel} + \epsilon_{\infty} \boldsymbol{p}_{1\perp} \right) + \boldsymbol{\xi}. \tag{67}$$

The free energy increase due to  $\xi$  is calculated as

$$\mathcal{F}_{\xi} = \mathcal{F} - \mathcal{F}_{s} = \frac{1}{2} a_{22} \int_{V} d\mathbf{r} \left[ \epsilon_{\infty} |\boldsymbol{\xi}_{\parallel}|^{2} + |\boldsymbol{\xi}_{\perp}|^{2} \right], \quad (68)$$

where  $\boldsymbol{\xi}_{\parallel}$  and  $\boldsymbol{\xi}_{\perp}$  are the longitudinal and transverse parts of  $\boldsymbol{\xi}$ , respectively. Thus,  $\int d\boldsymbol{r} \langle \boldsymbol{\xi}_{\alpha}(\boldsymbol{r}) p_{1\beta}(\boldsymbol{0}) \rangle = 0$ , so  $\boldsymbol{\xi}$  is *orthogonal* to  $\boldsymbol{p}_{1}$ . From the above  $\mathcal{F}_{\xi}$  we obtain the variances of the Fourier components  $\hat{\boldsymbol{\xi}}(\boldsymbol{q})$  of  $\boldsymbol{\xi}(\boldsymbol{r})$ :

$$\frac{\langle \hat{\xi}_{\alpha}(\boldsymbol{q})\hat{\xi}_{\beta}(\boldsymbol{q})^{*}\rangle}{Vk_{B}T} = \frac{\epsilon_{\infty} - 1}{4\pi} \left[ (\delta_{\alpha\beta} - \hat{q}_{\alpha}\hat{q}_{\beta}) + \frac{\hat{q}_{\alpha}\hat{q}_{\beta}}{\epsilon_{\infty}} \right]. \quad (69)$$

In E in Eq.(66), the last term  $-4\pi \xi_{\parallel}$  serves as a rapidly varying random noise (see Eqs.(74) and (75)).

Lee and Hynes<sup>8</sup> presented the solvation free energy  $\mathcal{F}_s$  in their Eq.(2.4), which is equivalent to that of Marcus<sup>7</sup>. Let us rewrite the second term in Eq.(63) as

$$\frac{1}{2\chi_{\parallel}^{11}} \left| \boldsymbol{p}_{1\parallel} - \boldsymbol{p}_{1}^{\text{eq}} \right|^{2} = \frac{\epsilon - \epsilon_{\infty}}{8\pi\epsilon\epsilon_{\infty}} \left| \boldsymbol{E}_{0} - \frac{\epsilon_{\infty} + 2}{3} \cdot \frac{4\pi\epsilon\boldsymbol{p}_{1\parallel}}{\epsilon - \epsilon_{\infty}} \right|^{2},$$

where use is made of Eq.(39). We can see that the factor  $(\epsilon_{\infty}+2)/3$  in the above expression does not appear in Lee-Hynes'  $\mathcal{F}_s$ . In Appendix C, we will give more comments on the previous linear theories.

#### VI. POLARIZATION DYNAMICS

## A. Dynamic equations

We now investigate the linear dynamics of the time-dependent polarizations  $p_i(r,t)$  at long wavelengths, where the translational motions are negligible. The temperature T and the dipole density n are homogeneous constants. We set up simple relaxation equations<sup>74,88</sup>,

$$\frac{\partial}{\partial t} \boldsymbol{p}_{1} = -L_{1} \frac{\delta}{\delta \boldsymbol{p}_{1}} \mathcal{F} = \frac{\chi_{1}}{\tau_{L} \epsilon} \boldsymbol{E}_{0} - \frac{1}{\tau_{L}} \boldsymbol{p}_{1 \parallel} - \frac{1}{\tau_{D}} \boldsymbol{p}_{1 \perp} 
- (4\pi/3) L_{1} (2\boldsymbol{\xi}_{\parallel} - \boldsymbol{\xi}_{\perp}),$$
(70)

$$\frac{\partial}{\partial t} \boldsymbol{p}_2 = -L_2 \frac{\delta}{\delta \boldsymbol{p}_2} \mathcal{F} = -\frac{1}{\tau_{\rm f}} (\epsilon_{\infty} \boldsymbol{\xi}_{\parallel} + \boldsymbol{\xi}_{\perp}), \tag{71}$$

where  $L_1$  and  $L_2$  are kinetic coefficients with  $L_1 \ll L_2$  and  $\delta \mathcal{F}/\delta \boldsymbol{p}_i = \sum_j a_{ij} \boldsymbol{p}_j - \boldsymbol{E}$  at fixed  $Q_0$ . We should replace  $\mathcal{F}$  by  $\tilde{\mathcal{F}}$  in Eq.(15) at fixed  $E_a$  to obtain the same equations (see below Eq.(16)). The right hand sides are expressed in terms of  $\boldsymbol{p}_1$ ,  $\boldsymbol{\xi}$ , and  $\boldsymbol{E}_0$  using  $\mathcal{F}_s$  and  $\mathcal{F}_{\xi}$  in Eqs.(63) and (68). For stationary  $\boldsymbol{E}_0$ , we have

$$\frac{d}{dt}\mathcal{F} = -\sum_{i} L_{i} |\delta \mathcal{F} / \delta \mathbf{p}_{i}|^{2} \le 0,$$

so the equilibrium determined by  $\delta \mathcal{F}/\delta \mathbf{p}_i = \mathbf{0}$  is approached as  $t \to \infty$ .

In Eqs.(70) and (71) we define  $\tau_D$ ,  $\tau_L$ , and  $\tau_f$  as

$$\tau_{\rm D} = \chi_{\perp}^{11}/L_1, \quad \tau_{\rm L} = \chi_{\parallel}^{11}/L_1 = \tau_{\rm D}\epsilon_{\infty}/\epsilon,$$
  
$$\tau_{\rm f} = (\epsilon_{\infty} - 1)/(4\pi L_2). \tag{72}$$

At fixed  $E_0$ ,  $\tau_D$  is the relaxation time of  $p_{1\perp}$  and  $\tau_L$  is that of  $p_{1\parallel}$ , while  $\tau_f$  is that of  $\xi$ . The  $\tau_D$  is the Debye relaxation time in Eqs.(1) and (89) below. The dynamical relation  $\tau_L/\tau_D = \epsilon_\infty/\epsilon$  is well known in the literature<sup>22–30</sup>. In our theory, it follows from the static relation  $\chi_{\parallel}^{11}/\chi_{\perp}^{11} = \epsilon_\infty/\epsilon$  in Eq.(39). In the limit  $\tau_f/\tau_L \to 0$ , we are led to  $\xi = p_2 - p_2^{\rm eq} = 0$ . The relaxation equation (67) is convenient to take this limit in the time-correlation functions below, though its Markovian form is a very crude approximation for microscopic  $\tau_f$ .

Using Eqs.(13), (64), and (66), we can rewrite Eq.(70) into Hubbard-Onsager's Eq.(2.9)<sup>29</sup>:

$$\tau_{\rm D} \frac{\partial \boldsymbol{p}_1}{\partial t} = \chi_1 \boldsymbol{E} - \boldsymbol{p}_1, \tag{73}$$

where we set  $\boldsymbol{\xi} = \boldsymbol{0}$  in Eq.(70). However, these authors assumed  $\chi_1 = (\epsilon - \epsilon_{\infty})/4\pi$  and  $\chi_2 = (\epsilon_{\infty} - 1)/4\pi$ , which also lead to  $\tau_{\rm L}/\tau_{\rm D} = \epsilon_{\infty}/\epsilon$  (see Appendix C).

As is well known, a moving ion and a rotating dipole are exerted by a relaxing electric field produced by the surrounding dipoles, resulting in a dielectric friction<sup>16,17,25,29,89–94</sup>, If this effect is included,  $L_1$  in Eq.(70) can be frequency-dependent on the scale of  $\tau_L^{-1}$ . In this paper, we treat  $L_1$  as a constant as a first step.

We should also generalize Eqs.(70) and (71) accounting for the diffusion and the convection at finite  $q^{17,29}$ . Some authors<sup>19,26,91,95</sup> examined the dynamics of the positionangle distribution  $\rho(\mathbf{r}, \boldsymbol{\omega}, t)$  of the dipoles for  $\epsilon_{\infty} = 1$ .

#### B. Short-range time-correlation functions

We calculate the polarization time-correlations at long wavelengths with  $E_0 = \mathbf{0}$  in the bulk region, neglecting the nonlocal correlations. In this case, we should treat Eqs.(70) and (71) as Langevin equations<sup>74,88</sup> describing the polarization dynamics, though we do not write the random source terms for simplicity.

First, we consider the time-correlation of  $\xi$  in Eq.(65):

$$G_{\rm f}(t) = \int d\mathbf{r} \frac{\langle \boldsymbol{\xi}(\mathbf{r}, t) \cdot \boldsymbol{\xi}(\mathbf{0}, 0) \rangle}{3k_B T} = \frac{2}{3} G_{\perp}^{\rm f}(t) + \frac{1}{3} G_{\parallel}^{\rm f}(t), \tag{74}$$

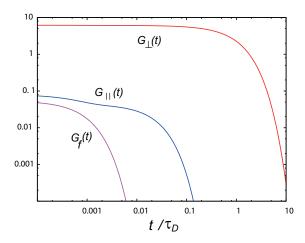


FIG. 2:  $G_f(t)$ ,  $G_{\perp}(t)$ , and  $G_{\parallel}(t)$  vs  $t/\tau_{\rm D}$  on a log-log scale for water, where  $\epsilon=78.5$ ,  $\epsilon_{\infty}=1.77$ , and  $\tau_{\rm f}/\tau_{\rm D}=10^{-2}$ . In this case  $G_{\perp}(t)$  is much larger than the others and  $G(t)\cong 2G_{\perp}(t)/3$ .

where  $G_{\perp}^{\rm f}(t)$  arises from  $\boldsymbol{\xi}_{\perp}$  and  $G_{\parallel}^{\rm f}(t)$  from  $\boldsymbol{\xi}_{\parallel}$ . For  $0 < t \lesssim \tau_{\rm f}$ ,  $\boldsymbol{p}_{1}$  is unchanged and  $\partial \boldsymbol{p}_{2}/\partial t$  can be equated to  $\partial \boldsymbol{\xi}/\partial t$  in Eq.(71). Thus, Eq.(71) is integrated to give

$$G_{\perp}^{\rm f}(t) = \frac{\epsilon_{\infty} - 1}{4\pi} e^{-t/\tau_{\rm f}}, \quad G_{\parallel}^{\rm f}(t) = \frac{\epsilon_{\infty} - 1}{4\pi\epsilon_{\infty}} e^{-\epsilon_{\infty}t/\tau_{\rm f}}, \quad (75)$$

which decay rapidly with  $\tau_{\rm f}$ . However, in experiments and simulations  $^{30,57,58,96}$ , the polarization time-correlations decayed non-exponentially at short times.

Second, Eq.(70) gives the time-correlation of  $p_1$ :

$$G_{\text{or}}(t) = \int d\mathbf{r} \langle \mathbf{p}_{1}(\mathbf{r}, t) \cdot \mathbf{p}_{1}(\mathbf{0}, 0) \rangle / 3k_{B}T$$
$$= 2\chi_{\perp}^{11} e^{-t/\tau_{\text{D}}} + \chi_{\parallel}^{11} e^{-t/\tau_{\text{L}}}, \tag{76}$$

where  $G_{\rm or}(0) = \chi_d$  from Eq.(43). This function is continuous at t = 0 even in the limit  $\tau_{\rm f} \to 0$ .

Third, we examine the time-correlation of p:

$$G(t) = \int d\mathbf{r} \langle \mathbf{p}(\mathbf{r}, t) \cdot \mathbf{p}(\mathbf{0}, 0) \rangle / 3k_B T$$

$$= G_{\rm f}(t) + \frac{\epsilon - \epsilon_{\infty}}{12\pi} \left[ 2e^{-t/\tau_{\rm D}} + \frac{1}{\epsilon \epsilon_{\infty}} e^{-t/\tau_{\rm L}} \right], \quad (77)$$

where  $G(0) = \chi(2+1/\epsilon)/3$  and use is made of Eq.(67). Since  $G_{\rm f}(t)$  decays rapidly, G(t) decreases in the time interval  $0 < t \lesssim \tau_{\rm f}$  by  $G_{\rm f}(0) = (\epsilon_{\infty} - 1)(2+1/\epsilon_{\infty})/12\pi$ .

In  $G_{\rm or}(t)$  and G(t), the transverse parts are much larger than the longitudinal parts for  $\epsilon \gg \epsilon_{\infty}$ . We write the transverse and longitudinal parts of G(t) as  $G_{\perp}(t)$  and  $G_{\parallel}(t)$ , respectively. Some calculations give

$$G_{\perp}(t) = \int d\mathbf{r} \langle \mathbf{p}_{\perp}(\mathbf{r}, t) \cdot \mathbf{p}_{\perp}(\mathbf{0}, 0) \rangle / 2k_{B}T,$$

$$= G_{\perp}^{f}(t) + [(\epsilon - \epsilon_{\infty})/4\pi]e^{-t/\tau_{D}}, \qquad (78)$$

$$G_{\parallel}(t) = \int d\mathbf{r} \langle \mathbf{p}_{\parallel}(\mathbf{r}, t) \cdot \mathbf{p}_{\parallel}(\mathbf{0}, 0) \rangle / k_{B}T$$

$$= G_{\parallel}^{f}(t) + [(\epsilon - \epsilon_{\infty})/4\pi\epsilon\epsilon_{\infty}]e^{-t/\tau_{L}}. \qquad (79)$$

where  $G(t) = [2G_{\perp}(t) + G_{\parallel}(t)]/3$ ,  $G_{\perp}(0) = \chi$ , and  $G_{\parallel}(0) = \chi/\epsilon$ . Thus,  $G_{\perp}(t)$  and  $G_{\parallel}(t)$  decrease by  $G_{\perp}^{\rm f}(0)$  and  $G_{\parallel}^{\rm f}(0)$  in the time range  $t \lesssim \tau_{\rm f}$  and subsequently decay with  $\tau_{\rm D}$  and  $\tau_{\rm L}$ , respectively. Previously, Madden and Kivelson<sup>25</sup> predicted the long-time behaviors of  $G_{\perp}(t)$  and  $G_{\parallel}(t)$  for  $\epsilon_{\infty} = 1$ . In Fig.2, we plot  $G_f(t)$ ,  $G_{\perp}(t)$ , and  $G_{\parallel}(t)$  vs  $t/\tau_{\rm D}$  for water.

Furthermore, at finite wave number q, we can introduce the q-dependent time-correlation functions,

$$G_{\perp}(q,t) = \langle \hat{\boldsymbol{p}}_{\perp}(\boldsymbol{q},t) \cdot \hat{\boldsymbol{p}}_{\perp}(\boldsymbol{q},0)^* \rangle / 2V k_B T,$$
  

$$G_{\parallel}(q,t) = \langle \hat{\boldsymbol{p}}_{\parallel}(\boldsymbol{q},t) \cdot \hat{\boldsymbol{p}}_{\parallel}(\boldsymbol{q},0)^* \rangle / V k_B T,$$
 (80)

where  $\hat{p}_{\perp}(q,t)$  and  $\hat{p}_{\parallel}(q,t)$  are the transverse and longitudinal parts of the Fourier component  $\hat{p}(q,t)$ , respectively. To find the q-dependence of these functions, however, we should perform microscopic simulations or introduce the gradient free energy<sup>71–74</sup>. Then, the time-correlation of  $\hat{p}(q,t)$  is written as

$$\hat{G}_{\alpha\beta}(\boldsymbol{q},t) = \langle \hat{p}_{\alpha}(\boldsymbol{q},t)\hat{p}_{\beta}(\boldsymbol{q},0)^{*}\rangle/Vk_{B}T$$

$$= G_{\perp}(q,t)(\delta_{\alpha\beta} - \hat{q}_{\alpha}\hat{q}_{\beta}) + G_{\parallel}(q,t)\hat{q}_{\alpha}\hat{q}_{\beta}. \tag{81}$$

In the small q range  $q \ll a_m^{-1}$  we have  $G_{\perp}(q,t) \cong G_{\perp}(t)$  and  $G_{\parallel}(q,t) \cong G_{\parallel}(t)$ . Thus, Eq.(81) yields the spacetime correlation for  $a_m \ll r < H$ :

$$G_{\alpha\beta}(\mathbf{r},t) = \langle p_{\alpha}(\mathbf{r},t)p_{\beta}(\mathbf{0},0)\rangle/k_{B}T$$
  
=  $G_{\perp}(t)\delta_{\alpha\beta}\delta(\mathbf{r}) + [G_{\perp}(t) - G_{\parallel}(t)]\nabla_{\alpha}\nabla_{\beta}\psi(r),$  (82)

which tends to  $G_{\alpha\beta}(\mathbf{r})$  in Eq.(44) as  $t \to 0$  and gives  $\sum_{\alpha} G_{\alpha\alpha}(\mathbf{r}, t) = 3G(t)\delta(\mathbf{r})$  in accord with Eq.(77).

In the above time-correlation functions, we take the inner products of the two vectors, for which the long-range dipolar correlation is cancelled (see below Eq.(44)). We integrate them in a region much smaller than V to neglect the nonlocal correlations. If the integration is in a sphere r < R, the integrals are well defined for  $R_c < R \ll H$ , where  $R_c \sim 1$  nm in massive simulations by Alvarez et al.<sup>97</sup> (with dipole numbers  $\gtrsim 10^6$ ).

## C. Time correlations of total polarizations

In Sec.IV we have calculated the variances of the total polarizations  $M_i^{\text{tot}}$ . Here, we consider their time-correlation functions. (i) At fixed  $Q_0$ , we integrate Eq.(82) in the cell using Eq.(54) to find

$$\langle M_{\alpha}^{\text{tot}}(t)M_{\beta}^{\text{tot}}(0)\rangle/Vk_{B}T = \int_{V} d\mathbf{r}G_{\alpha\beta}(\mathbf{r},t)$$
$$= G_{\perp}(t)(\delta_{\alpha\beta} - \delta_{\alpha z}\delta_{\beta z}) + G_{\parallel}(t)\delta_{\alpha z}\delta_{\beta z}, \quad (83)$$

which tends to the last equation in Eq.(53) as  $t \to 0$ .

(ii) Second, in the periodic boundary condition, we have  $\int_V d\mathbf{r} \mathbf{E}(\mathbf{r},t) = \mathbf{0}$ , so Eqs.(73) and (78) give

$$\langle M_{1\alpha}^{\text{tot}}(t)M_{1\beta}^{\text{tot}}(0)\rangle/Vk_BT = \delta_{\alpha\beta}\chi_{\perp}^{11}e^{-t/\tau_D},$$
  
$$\langle M_{\alpha}^{\text{tot}}(t)M_{\beta}^{\text{tot}}(0)\rangle/Vk_BT = \delta_{\alpha\beta}G_{\perp}(t) \text{ (periodic)}. (84)$$

which tend to those in Eq.(56) as  $t \to 0$ . We will relate  $G_{\perp}(t)$  to  $\epsilon^*(\omega)$  in Eq.(97). In some simulations in the periodic boundary condition<sup>56,58,97</sup>,  $\langle \boldsymbol{M}^{\text{tot}}(t) \cdot \boldsymbol{M}^{\text{tot}}(0) \rangle$  decayed with  $\tau_D$ , which slightly deviated from the single-exponential Debye form due to dipole librations.

(iii) Third, in the Sprik condition  $\int_V d\mathbf{r} \mathbf{D}(\mathbf{r},t) = \mathbf{0}$ , the counterpart of Eq.(84) is obtained by replacements:  $\chi_{\perp}^{11} e^{-t/\tau_D} \to \chi_{\parallel}^{11} e^{-t/\tau_L}$  and  $G_{\perp}(t) \to G_{\parallel}(t)$ , which are consistent with the simulation<sup>46</sup>.

### VII. DYNAMICAL LINEAR RESPONSE

#### A. Frequency-dependent dielectric functions

In this subsection, we examine the dielectric response to an applied field oscillating with frequency  $\omega$  in the geometry of parallel metal plates. The deviations are the statistical averages and are written in complex numbers depending on time as  $e^{i\omega t}$ , where their real parts have their physical meaning.

The vector deviations are written as

$$p_i = p_i^* e_z, \quad p = p^* e_z, \quad E_0 = E_0^* e_z, \quad E = E^* e_z, \quad (85)$$

where  $e_z$  is the unit vector along the z axis. Here,  $p_i^*$  and  $E^*$  are homogeneous in the bulk but depend on z near the walls. We relate  $E_0^*$  and  $E^*$  as

$$E_0^* = \epsilon^*(\omega)E^* = 4\pi\bar{\sigma}_0 \propto e^{i\omega t}.$$
 (86)

where  $\epsilon^*(\omega) = 1 + 4\pi\chi^*(\omega)$  is the frequency-dependent dielectric constant. We define the frequency-dependent dielectric susceptibilities for E and  $E_0$  as

$$\chi_i^*(\omega) = p_i^*/E^*, \quad \alpha_i^*(\omega) = p_i^*/E_0^*.$$
 (87)

Their sums are the net susceptibilities  $\chi^*(\omega) = p^*/E = \sum_i \chi_i^*(\omega)$  and  $\alpha^*(\omega) = p^*/E_0 = \sum_i \alpha_i^*(\omega)$ , where

$$\alpha_i^*(\omega) = \chi_i^*(\omega)/\epsilon^*(\omega), \quad \alpha^*(\omega) = [1 - 1/\epsilon^*(\omega)]/4\pi.$$
 (88)

In the present situation,  $p_i$  are longitudinal (or  $p_{i\perp}=0$ ). Setting  $\boldsymbol{\xi}=0$ , we have  $(1+i\omega\tau_{\rm L})\alpha_1^*=\chi_1/\epsilon$  from Eq.(70) and  $\alpha_2^*=(1-1/\epsilon_\infty)(1-8\pi\alpha_1^*/3)/4\pi$  from Eq.(62). Then, we obtain all the susceptibilities as

$$\epsilon^*(\omega) = \epsilon \frac{1 + i\omega\tau_{\rm L}}{1 + i\omega\tau_{\rm D}} = \epsilon_{\infty} + \frac{\epsilon - \epsilon_{\infty}}{1 + i\omega\tau_{\rm D}},\tag{89}$$

$$\chi_1^*(\omega) = \frac{\chi_1}{1 + i\omega\tau_D} = \frac{3}{4\pi} \cdot \frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_\infty + 2},\tag{90}$$

$$\chi_2^*(\omega) = \frac{\epsilon_\infty - 1}{4\pi} \left[ 1 + \frac{4\pi}{3} \chi_1^*(\omega) \right],\tag{91}$$

$$\alpha^*(\omega) = \frac{\epsilon_{\infty} - 1}{4\pi\epsilon_{\infty}} + \frac{\epsilon - \epsilon_{\infty}}{4\pi\epsilon\epsilon_{\infty}(1 + i\omega\tau_{\mathrm{L}})},\tag{92}$$

$$\alpha_1^*(\omega) = \frac{\chi_1}{\epsilon(1 + i\omega\tau_L)} = \frac{3}{4\pi} \cdot \frac{\epsilon - \epsilon_\infty}{(\epsilon_\infty + 2)\epsilon(1 + i\omega\tau_L)}, \quad (93)$$

$$\alpha_2^*(\omega) = \frac{\epsilon_\infty - 1}{4\pi\epsilon\epsilon_\infty} \left[ \epsilon - \frac{8\pi\chi_1}{3(1 + i\omega\tau_L)} \right],\tag{94}$$

which hold for  $\omega \tau_{\rm f} \ll 1$ . Note that Eq.(89) is the Debye formula (1). Here,  $\epsilon^*(\omega)$  and  $\chi_i^*(\omega)$  are characterized by  $\tau_{\rm D}$ , while  $\alpha^*(\omega)$  and  $\alpha_i^*(\omega)$  by  $\tau_{\rm L}$ . See their relaxation functions in Eqs.(97)-(102) below.

For  $\epsilon \gg \epsilon_{\infty}$  and  $\epsilon_{\infty} - 1 \gtrsim 1$  we notice that  $\epsilon_{\infty}$  has the meaning of the high-frequency dielectric constant in the frequency range  $\tau_{\rm L}^{-1} \ll \omega \ll \tau_{\rm f}^{-1}$ , where  $|\boldsymbol{p}_2| \gg |\boldsymbol{p}_1|$  and

$$\chi^*(\omega) \cong \chi_2^*(\omega) \cong (\epsilon_{\infty} - 1)/4\pi.$$
(95)

See the sentences below Eq.(13) on the static limit  $\chi_2$ .

In addition, we note that Eq.(70) and (71) can be solved for general  $\omega$  under Eq.(85). For example, in the case  $L_1/L_2 \ll 1$ ,  $\epsilon^*(\omega)$  and  $\alpha^*(\omega)$  are calculated as

$$\epsilon^*(\omega) - 1 = \frac{\epsilon_{\infty} - 1}{1 + i\omega\tau_{\rm f}} + \frac{\epsilon - \epsilon_{\infty}}{1 + i\omega\tau_{\rm D}},$$

$$4\pi\alpha^*(\omega) = \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + i\omega\tau_{\rm f}} + \frac{\epsilon - \epsilon_{\infty}}{\epsilon\epsilon_{\infty}(1 + i\omega\tau_{\rm L})},$$
(96)

where the first terms involve  $\tau_{\rm f}$ .

#### B. Relaxation functions and previous theories

We express  $\chi^*(\omega)$  and  $\alpha^*(\omega)$  in Eqs.(89) and (92) in terms of  $G_{\perp}(t)$  and  $G_{\parallel}(t)$  in Eqs.(78) and (79) as<sup>31</sup>

$$\chi^*(\omega) = p^*/E^* = G_{\perp}(0) - i\omega \int_0^{\infty} dt e^{-i\omega t} G_{\perp}(t), \quad (97)$$

$$\alpha^*(\omega) = p^*/E_0^* = G_{\parallel}(0) - i\omega \int_0^{\infty} dt e^{-i\omega t} G_{\parallel}(t).$$
 (98)

Here, the right hand sides are the Fourier-Laplace (FL) transforms of the response functions  $-dG_{\perp}(t)/dt$  and  $-dG_{\parallel}(t)/dt$ , while  $G_{\perp}(t)$  and  $G_{\parallel}(t)$  are the relaxation functions<sup>31</sup>. We derive these relations using the explicit expressions of  $\chi^*$ ,  $\alpha^*$ ,  $G_{\perp}$ , and  $G_{\parallel}$ . Previously, they were derived in the Hamiltonian formalism<sup>21,22,24–26</sup>. See Appendix D for more discussions on our scheme.

We can also express  $\chi_i^*(\omega)$  and  $\alpha_i^*(\omega)$  in the same manner by replacements:  $G_{\perp}(t) \to G_{i\perp}(t)$  in Eq.(97) and  $G_{\parallel}(t) \to G_{i\parallel}(t)$  in Eq.(98), respectively, where we define

$$G_{i\perp}(t) \equiv \int d\mathbf{r} \langle \mathbf{p}_{i\perp}(\mathbf{r}, t) \cdot \mathbf{p}_{\perp}(\mathbf{0}, 0) \rangle / 2k_B T,$$
 (99)

$$G_{i\parallel}(t) = \int d\mathbf{r} \langle \mathbf{p}_{i\parallel}(\mathbf{r}, t) \cdot \mathbf{p}_{\parallel}(\mathbf{0}, 0) \rangle / k_B T.$$
 (100)

Here,  $\sum_i G_{i\perp}(t) = G_{\perp}(t)$ ,  $\sum_i G_{i\parallel}(t) = G_{\parallel}(t)$ ,  $G_{i\perp}(0) = \chi_i$ , and  $G_{i\parallel}(0) = \chi_i/\epsilon$ . For  $t \gg \tau_{\rm f}$  we find

$$G_{1\perp}(t) = \chi_1 e^{-t/\tau_D}, \quad G_{2\perp}(t) = \frac{\epsilon_{\infty} - 1}{3} \chi_1 e^{-t/\tau_D}, \quad (101)$$

$$G_{1\parallel}(t) = \frac{\chi_1}{\epsilon} e^{-t/\tau_L}, \quad G_{2\parallel}(t) = 2 \frac{1 - \epsilon_{\infty}}{3\epsilon \epsilon_{\infty}} \chi_1 e^{-t/\tau_L}. \quad (102)$$

where the initial rapid decreases of  $G_{2\perp}(t)$  and  $G_{2\parallel}(t)$  are  $(\epsilon_{\infty}-1)/4\pi$  and  $(1-1/\epsilon_{\infty})/4\pi$ , respectively. The FL

transforms of  $-dG_{i\perp}(t)/dt$  and  $-dG_{i\parallel}(t)/dt$  are equal to the right-hand sides of Eqs.(90) and (91) and those of Eqs.(93) and (94), respectively.

In statistical-mechanical theories<sup>22,24–26,54</sup>, inhomogeneous, oscillatory fields were applied fictitiously without electrodes. These fields are transverse or longitudinal, so the combined interaction energy is written as

$$\mathcal{H}_{\mathrm{ext}}^{\mathrm{inh}} = -\int \! d\boldsymbol{r} \left[ \mathrm{Re}(\boldsymbol{\mathcal{E}}_T) \cdot \boldsymbol{p}_{\perp} + \mathrm{Re}(\boldsymbol{\mathcal{E}}_L) \cdot \boldsymbol{p}_{\parallel} \right], \quad (103)$$

where  $\text{Re}(\cdots)$  denotes taking the real part. Here,  $\mathcal{E}_T$  is a transverse radiation field, while  $\mathcal{E}_L$  is a longitudinal field tending to  $\mathbf{E}_0$  in Eq.(85) in the homogeneous limit. Then, at wave number q and frequency  $\omega$ , the linear response relations for  $\mathbf{p}_{\perp}$  and  $\mathbf{p}_{\parallel}$  are given by

$$\langle \boldsymbol{p}_{\perp} \rangle = \chi^*(q,\omega)\boldsymbol{\mathcal{E}}_T, \quad \langle \boldsymbol{p}_{\parallel} \rangle = \alpha^*(q,\omega)\boldsymbol{\mathcal{E}}_L,$$
 (104)

where  $\chi^*(q,\omega)$  and  $\alpha^*(q,\omega)$  are the FL transforms of  $-\partial G_{\perp}(q,t)/\partial t$  and  $-\partial G_{\parallel}(q,t)/\partial t$ , respectively, with  $G_{\perp}(q,t)$  and  $G_{\parallel}(q,t)$  being defined in Eq.(80). Then, the  $(q,\omega)$ -dependent transverse and longitudinal dielectric constants can be defined by<sup>22,24–26,54</sup>

$$\epsilon_T(q,\omega) = 1 + 4\pi \chi^*(q,\omega), \tag{105}$$

$$\epsilon_L(q,\omega) = [1 - 4\pi\alpha^*(q,\omega)]^{-1}. \tag{106}$$

For large H, these results can be used for  $q \gg \pi/H$  in the bulk. As discussed below Eq.(81),  $\chi^*(q,\omega) \to \chi^*(\omega)$  and  $\alpha^*(q,\omega) \to \alpha^*(\omega)$  as  $q \to 0$ , leading to Eqs.(97) and (98). However, we have derived  $\chi^*(\omega)$  in Eq.(97) from  $\alpha^*(\omega)$  via Eq.(88) not using the transverse fields.

Chandra and Bagchi<sup>26</sup> calculated  $\epsilon_T(q,\omega)$  and  $\epsilon_L(q,\omega)$ . Skaf  $et~al.^{57}$  obtained  $G_{\perp}(q,t)$  and  $G_{\parallel}(q,t)$  for methanol, where  $G_{\perp}(q,t)$  was much larger and decayed much slower than  $G_{\parallel}(q,t)$  at the smallest wave number 0.24/Å in their simulation in accord with Eqs.(78) and (79). Bopp  $et~al.^{59}$  calculated  $G_{p\parallel}(q,t)$  for water.

## C. Linear response. I: Total polarization

In the parallel plate geometry, we can treat the bare field  $\boldsymbol{E}_0 = E_0^* \boldsymbol{e}_z$  as the applied field controlling the electrode charge  $Q_0 = L^2 \bar{\sigma}_0$ . Then, its conjugate variable is  $M_z^{\text{tot}}$  in Eq.(51). If  $E_0^* \propto e^{i\omega t}$ , we fix the amplitude  $|E_0^*|$ . We present the interaction energy in the form,

$$\mathcal{H}_{\text{ext}}^{\text{I}} = -\text{Re}(E_0^*) M_z^{\text{tot}} = -4\pi \text{Re}(\bar{\sigma}_0) M_z^{\text{tot}}.$$
 (107)

In our scheme at fixed  $Q_0$ , the polarization fluctuations obey the perturbed distribution  $(1-\mathcal{H}_{\rm ext}^{\rm I}/k_BT)\mathcal{P}_0$ , where  $\mathcal{P}_0 \propto \exp(-\mathcal{F}/k_BT)$  is the distribution at  $Q_0 = 0$ . Kubo himself derived Eqs.(98) and (107).

In our theory, Eqs.(30), (53), and (83) indicate that the relaxation functions of  $p_z$  and  $p_{iz}$  in the bulk are  $G_{\parallel}(t)$  in Eq.(79) and  $G_{i\parallel}(t)$  in Eq.(100), respectively. Namely,

$$\langle M_z^{\text{tot}}(t)M_z^{\text{tot}}(0)\rangle/Vk_BT = G_{\parallel}(t),$$
  
$$\langle M_{iz}^{\text{tot}}(t)M_z^{\text{tot}}(0)\rangle/Vk_BT = G_{i\parallel}(t),$$
 (108)

which decay with  $\tau_{\rm L}$  from Eqs.(79) and (102) with  $G_{\parallel}(0)=\chi/\epsilon$  and  $G_{i\parallel}(0)=\chi_i/\epsilon$ . As in Eq.(98),  $\langle p^* \rangle/E_0^*$  and  $\langle p_i^* \rangle/E_0^*$  are the FL transforms of  $-dG_{\parallel}(t)/dt$  and  $-dG_{i\parallel}(t)/dt$ , respectively.

The dielectric response is heterogeneous near a solid surface, a two-phase interface, a lipid bilayer, and so on, which was calculated in the static<sup>82,98,99</sup> and oscillatory cases<sup>69,100,101</sup> with  $\epsilon_{\infty} = 1$ . In these papers, a polar fluid is confined between nonconducting walls and the interaction energy is of the form  $\mathcal{H}_{\text{int}} = -\mathcal{E} \cdot \mathbf{M}^{\text{tot}}$ , where  $\mathcal{E} = (\mathcal{E}_x, \mathcal{E}_y, \mathcal{E}_z)$  is a homogeneous applied field. They obtained z-dependent dielectric constants,  $\epsilon_{\perp}(z)$  and  $\epsilon_{\parallel}(z)$ , where the subscripts  $\perp$  and  $\parallel$  denote the directions orthogonal and parallel to the surface, respectively. For example,  $1 - 1/\epsilon_{\perp}(z) = 4\pi \langle p_z(\mathbf{r}) M_z \rangle / k_B T$  at  $\omega = Q_0 = 0$ .

#### D. Linear response. II: Embedded sphere

Using  $\chi_d$  in Eq.(25) and the time-correlation function  $G_{\text{or}}(t)$  for  $\boldsymbol{p}_1$  in Eq.(76), we define a frequency-dependent orientational susceptibility by

$$\chi_d^*(\omega) = G_{\rm or}(0) - i\omega \int_0^\infty dt e^{-i\omega t} G_{\rm or}(t)$$

$$= \frac{\chi_d}{2 + \epsilon_\infty / \epsilon} \left[ \frac{2}{1 + i\omega \tau_{\rm D}} + \frac{\epsilon_\infty / \epsilon}{1 + i\omega \tau_{\rm L}} \right]. \quad (109)$$

Then, use of the Debye form of  $\epsilon^*(\omega)$  in Eq.(89) yields a frequency-dependent KF equation,

$$\frac{3(\epsilon^*(\omega) - \epsilon_{\infty})(2\epsilon^*(\omega) + \epsilon_{\infty})}{4\pi\epsilon^*(\omega)(\epsilon_{\infty} + 2)^2} = \chi_d^*(\omega), \tag{110}$$

which can be derived with the aid of the relation,

$$(\epsilon^* - \epsilon_{\infty}) \left( 2 + \frac{\epsilon_{\infty}}{\epsilon^*} \right) = \frac{\epsilon - \epsilon_{\infty}}{1 + i\omega\tau_{\rm D}} \left[ 2 + \frac{\epsilon_{\infty}}{\epsilon} \cdot \frac{1 + i\omega\tau_{\rm D}}{1 + i\omega\tau_{\rm L}} \right].$$

To understand Eq.(110) in the linear response theory, we introduce the frequency-dependent directing field,

$$E_d^* = \frac{\epsilon^*(\omega)(\epsilon_\infty + 2)}{2\epsilon^*(\omega) + \epsilon_\infty} E^*. \tag{111}$$

which gives Eq.(23) as  $\omega \to 0$ . As in Eq.(84), we have  $\mathbf{E} = E^* \mathbf{e}_z$  and  $\mathbf{E}_d = E_d^* \mathbf{e}_z$  in the parallel plate geometry. Using  $\chi_1^*(\omega)$  in Eq.(90) and  $\chi_d^*(\omega)$  in Eq.(109) we find

$$p_1^* = \chi_1^*(\omega)E^* = \chi_d^*(\omega)E_d^*, \tag{112}$$

which tends to Eqs.(22) and (50) as  $\omega \to 0$ .

If we suppose a mesoscopic sphere with volume  $v = 4\pi R^3/3 \ll V$  in the bulk,  $E_d = E_d^* e_z$  is the externally applied, oscillating field, whose conjugate variable is the interior  $M_{1z}$  in Eq.(45). Thus, we propose the effective interaction energy in the sphere,

$$\mathcal{H}_{\text{ext}}^{\text{II}} = -\text{Re}(\boldsymbol{E}_d) \cdot \boldsymbol{M}_1. = -\text{Re}(E_d^*) M_{1z}. \tag{113}$$

Then, the relaxation function of  $p_{1z}$  is given by  $G_{\rm or}(t)$  in Eq.(76). From Eqs.(109) and (112) we confirm

$$G_{\rm or}(t) = \frac{\langle M_{1z}(t)M_{1z}(0)\rangle}{vk_BT} = \frac{\langle \boldsymbol{M}_1(t)\cdot\boldsymbol{M}_1(0)\rangle}{3vk_BT}.$$
 (114)

As discussed below Eq.(50), we cannot calculate the linear response of  $p_2$  from Eq.(113).

Since Eq.(110) is a natural generalization of the KF equation, it has been presented by many authors (mostly for  $\epsilon_{\infty} = 1)^{14-17,19-24}$ , but the relaxation function  $G_{\rm or}(t)$  has not been calculated explicitly. Nee and Zwanzig<sup>17</sup> assumed  $\mathbf{p}_2 = \mathbf{p} - \mathbf{p}_1 = [(\epsilon_{\infty} - 1)/4\pi]\mathbf{E}$ , the effective dipole moment  $\mu = \mu_0(\epsilon_{\infty} + 2)/3$ , and a modified directing field (=  $[3/(\epsilon_{\infty} + 2)]\mathbf{E}_d$ ) to obtain Eq.(113), following Fröhlich<sup>3</sup> (see the last paragraph in Sec.IIIB).

## E. Linear response. III: Embedded sphere

To generalize Eq.(49) to a frequency-dependent one, we introduce the frequency-dependent cavity field,

$$E_c^* = \frac{3\epsilon^*(\omega)}{2\epsilon^*(\omega) + 1} E^*, \tag{115}$$

which gives  $E_c$  in Eq.(50) as  $\omega \to 0$ . Again we suppose a mesoscopic sphere in the bulk. Then,  $E_c = E_c^* e_z$  is the oscillating applied field, whose conjugate variable is the interior M in Eq.(45). We find the interaction energy,

$$\mathcal{H}_{\text{ext}}^{\text{III}} = -\text{Re}(\boldsymbol{E}_c) \cdot \boldsymbol{M} = -\text{Re}(E_c^*) M_z. \tag{116}$$

In the situation (80), use of Eqs.(97) and (98) gives

$$p^* = \chi^*(\omega)E^* = \alpha^*(\omega)E_0^* = \left[\frac{2\chi^*(\omega)}{3} + \frac{\alpha^*(\omega)}{3}\right]E_c^*.$$
(117)

Thus,  $p^*/E_c^*$  is equal to the FL transform of -dG(t)/dt, where  $G(t) = 2G_{\perp}(t)/3 + G_{\parallel}(t)/3$  is given in Eq.(77). Using Eqs.(89) and (92) we then obtain

$$(\epsilon^*(\omega) - 1) \frac{2\epsilon^*(\omega) + 1}{12\pi\epsilon^*(\omega)} = G(0) - i\omega \int_0^\infty dt e^{-i\omega t} G(t)$$
$$= G_{\rm f}(0) + \frac{\epsilon - \epsilon_\infty}{12\pi} \left[ \frac{2}{1 + i\omega\tau_{\rm D}} + \frac{1/\epsilon\epsilon_\infty}{1 + i\omega\tau_{\rm D}} \right], \tag{118}$$

where  $G_{\rm f}(0)=(\epsilon_\infty-1)(2+1/\epsilon_\infty)/12\pi$ . This equation coincides with Eq.(110) for  $\epsilon_\infty=1$ . We also confirm

$$G(t) = \frac{\langle M_z(t) \cdot M_z(0) \rangle}{v k_B T} = \frac{\langle \boldsymbol{M}(t) \cdot \boldsymbol{M}(0) \rangle}{3 v k_B T}.$$
 (119)

Fulton<sup>21</sup> derived the first line of Eq.(118) for  $\epsilon_{\infty} = 1$ . The relaxation functions of  $p_i$  are given by

$$G_i(t) = \frac{2}{3}G_{i\perp}(t) + \frac{1}{3}G_{i\parallel}(t) = \frac{\langle \mathbf{M}_i(t) \cdot \mathbf{M}(0) \rangle}{3vk_BT},$$
 (120)

where  $G_{i\perp}(t)$  and  $G_{i\parallel}(t)$  are defined in Eqs.(99) and (100). As in Eq.(117)  $p_i^*/E_c^* = [2\chi_i^*(\omega) + \alpha_i^*(\omega)]/3$  are equal to the FL transforms of  $-dG_i(t)/dt$ .

## VIII. FLUCTUATIONS AND LINEAR RESPONSE IN FIXED-POTENTIAL CONDITION

In simulations<sup>33–47</sup>, the applied electric field  $E_a = \Phi_a/H$  in Eq.(17) can be fixed between two metal plates. This is a typical experimental method, where the condition  $Q_H = -Q_0$  at fixed  $E_a$  is realized by attachment of an external circuit to the two metal electrodes. We assume this fixed-potential condition along the z axis, imposing the periodic boundary condition along the x and y axes. In the oscillatory case, the amplitude  $|E_a|$  is fixed. There are no electric charges in the fluid.

#### A. Interaction energy at fixed $E_a$

At fixed  $E_a$ , the mean surface charge density  $\bar{\sigma}_0 = Q_0/L^2$  fluctuates. Since the lateral average of  $D_z$  is independent of z from  $\nabla \cdot \mathbf{D} = 0$ , we find

$$4\pi\bar{\sigma}_0 = \bar{E}(z) + 4\pi\bar{p}(z) = \bar{\bar{E}} + 4\pi\bar{\bar{p}},\tag{121}$$

which holds at any z. Here,  $\bar{E}(z)$  and  $\bar{p}(z)$  are the lateral averages of the z components  $E_z(\mathbf{r})$  and  $p_z(\mathbf{r}) = p_{1z}(\mathbf{r}) + p_{2z}(\mathbf{r})$ , while  $\bar{E}$  and  $\bar{p}$  are their cell averages. Namely,

$$\bar{E}(z) = \frac{1}{L^2} \int d\mathbf{r}_{\perp} E_z(\mathbf{r}), \quad \bar{p}(z) = \frac{1}{L^2} \int d\mathbf{r}_{\perp} p_z(\mathbf{r}), 
\bar{\bar{E}} = \frac{1}{H} \int dz \ \bar{E}(z), \quad \bar{\bar{p}} = \frac{1}{H} \int dz \ \bar{p}(z) = \frac{1}{V} M_z^{\text{tot}}, \quad (122)$$

where  $\int d\mathbf{r}_{\perp}$  and  $\int dz$  denote the integrations with respect to  $\mathbf{r}_{\perp} = (x,y)$  and z, respectively, in the cell. To avoid confusion, the subscript z for the z components is not written for these space averages. The lateral and cell averages consist of the Fourier components with  $q_x = q_y = 0$  and  $\mathbf{q} = \mathbf{0}$ , respectively. The correlations with  $\mathbf{q} \neq \mathbf{0}$  are insensitive to the boundary condition.

Including the surface effect we rewrite Eq.(17) as

$$E_a = \bar{\bar{E}} + \bar{\sigma}_0/CH. \tag{123}$$

The statistical averages of  $\bar{E}$ ,  $\bar{p}$ , and  $\bar{\sigma}_0$  are given by

$$\langle \bar{\bar{E}} \rangle_a = E_b, \quad \langle \bar{\bar{p}} \rangle_a = \chi E_b, \quad \langle \bar{\sigma}_0 \rangle_a = \epsilon E_b / 4\pi, \quad (124)$$

in terms of  $E_b$  in Eq.(18). Hereafter,  $\langle \cdots \rangle_a$  denotes taking the statistical average at fixed  $E_a$ . From Eqs.(121) and (123) their fluctuation parts  $\delta \bar{E} = \bar{E} - E_b$ ,  $\delta \bar{p} = \bar{p} - \chi E_b$ , and  $\delta \bar{\sigma}_0 = \bar{\sigma}_0 - \epsilon E_b/4\pi$  are related by

$$\delta \bar{\sigma}_0 = \delta \bar{\bar{p}} / (1 + 1/4\pi CH) \cong \delta \bar{\bar{p}},$$
  
$$\delta \bar{\bar{E}} = -\delta \bar{\sigma}_0 / CH, \cong -\delta \bar{\bar{p}} / CH, \qquad (125)$$

where  $1/4\pi C = \ell_{\rm w}/\epsilon \ll H$  from Eq.(19) for  $\epsilon \gg 1$ .

For stationary  $E_a$ , the polarizations obey the distribution  $\propto \exp[-\tilde{\mathcal{F}}/k_BT]$  with  $\tilde{\mathcal{F}}$  in Eq.(15). This indicates that the interaction energy is given by

$$\mathcal{H}_{\text{ext}}^{\text{IV}} = -\text{Re}(\Phi_a)Q_0 = -\text{Re}(E_a)M_z^{\text{tot}}, \tag{126}$$

where the fluctuation parts of  $Q_0$  and  $L^2\bar{p} = M_z^{\rm tot}/H$  coincide for  $d \ll H$  from Eq.(125). In our scheme, the polarization fluctuations obey the perturbed distribution  $\mathcal{P}_a = [1 - \mathcal{H}_{\rm ext}^{\rm IV}/k_BT]\mathcal{P}_a^0$  in the linear order, where  $\mathcal{P}_a^0 \propto \exp(-\mathcal{F}/k_BT)$  is the distribution at  $E_a = 0$  under the global electrostatic constraints (121) and (123). We use Eqs.(121)-(126) even in the oscillatory case.

### B. Nonlocal correlations for stationary $E_a$

Because the problem is multifold, we first assume stationary  $E_a$  and neglect the surface effect. Then,  $\bar{E}=E_a=E_b$  and  $\bar{E}(z)=E_a-4\pi(\bar{p}(z)-\bar{p})$ .

In  $\tilde{\mathcal{F}} = \mathcal{F} - HE_a\bar{\sigma}_0$  we pick up the Fourier components of  $p_z(\mathbf{r})$  with  $q_x = q_y = 0$ . We then obtain the one-dimensional free energy density  $\mathcal{F}_{1D} = \tilde{\mathcal{F}}/L^2$  as

$$\mathcal{F}_{1D} = \int dz \left[ \frac{1}{8\pi} \bar{E}(z)^2 + \frac{1}{2\chi} \bar{p}(z)^2 \right] - H E_a \bar{\sigma}_0$$

$$= \int dz \frac{\epsilon}{2\chi} \left[ \delta \bar{p}(z) - \delta \bar{\bar{p}} \right]^2 + \frac{H}{2\chi} (\delta \bar{p})^2 - \frac{H\epsilon}{8\pi} E_a^2, \quad (127)$$

where  $\delta \bar{p}(z) = \bar{p}(z) - \chi E_a$ , The last term in the second line is the minimum of  $\mathcal{F}_{1D}$ . The variable s in Eq.(29) is decoupled from p, so its contribution is not written here.

The fluctuation part of  $\mathcal{F}_{1D}$  is written in the double integral form  $\int dz \int dz' c(z,z') \delta \bar{p}(z) \delta \bar{p}(z')/2$  with

$$c(z, z') = (\epsilon/\chi)\delta(z - z') - 4\pi/H. \tag{128}$$

Then, we find the one-dimensional correlation function,

$$G_{1D}(z,z') = \langle \delta \bar{p}(z) \delta \bar{p}(z') \rangle_a L^2 / k_B T$$
  
=  $(\chi/\epsilon) \delta(z-z') + 4\pi \chi^2 / \epsilon H,$  (129)

where we use  $\int dz'' c(z, z'') G_{1D}(z'', z') = \delta(z - z')$ . From Eq.(125) we obtain the variance relations at fixed  $E_a$ ,

$$V\langle (\delta\bar{\sigma}_0)^2\rangle_a = V\langle (\delta\bar{\bar{p}})^2\rangle_a = \frac{\langle (\delta M_z^{\rm tot})^2\rangle_a}{V} = k_B T \chi, (130)$$

Here, all  $\langle \delta M_{i\alpha}^{\rm tot} \delta M_{j\beta}^{\rm tot} \rangle$  are given by Eq.(56), but only the zz components  $G_{zz}^{ij}(r)$  acquire nonlocal parts given by  $4\pi \chi_i \chi_j / \epsilon V$  for  $H \ll L$ .

In contrast, at fixed  $Q_0$ , the relation  $\delta \bar{E} = -4\pi \delta \bar{p}$  gives  $G_{1D}(x, x') = (\chi/\epsilon)\delta(z - z')$  with no nonlocal correlation in the z direction. Furthermore, since Eq.(53) holds, we find no nonlocal correlation also in the xy plane,

#### C. Surface effect for stationary $E_a$

Next, to include the surface effect for stationary  $E_a$ , we add a surface free energy density to  $\mathcal{F}_{1D}$  in Eq.(127):

$$\mathcal{F}_{1D}^{\text{tot}} = \mathcal{F}_{1D} + \bar{\sigma}_0^2 / 2C = \int dz \frac{\epsilon}{2\chi} \left[ \delta \bar{p}(z) - \delta \bar{\bar{p}} \right]^2 + (H + \ell_{\text{w}}) (\delta \bar{\bar{p}})^2 / 2\chi - H \epsilon E_a E_b / 8\pi.$$
 (131)

where  $\delta \bar{p}(z) = \bar{p}(z) - \chi E_b$  and  $\delta \bar{p} = \delta \bar{\sigma_0}$ . The last term is equal to the thermodynamic free energy  $-\Phi_a \langle Q_0 \rangle_a / 2\pi$  divided by  $L^2$ . See Appendix A for a derivation of the surface free energy density  $\bar{\sigma}_0^2/2C$ .

With Eq.(131)  $G_{1D}(x, x')$  in Eq.(129) is changed to

$$G_{1D}(z.z') = \frac{\chi}{\epsilon} \left[ \delta(z - z') - \frac{1}{H} \right] + \frac{\chi}{H + \ell_w}.$$
 (132)

Then, we obtain the variance relations,

$$V\langle (\delta\bar{\sigma}_0)^2 \rangle_a = V\langle (\delta\bar{p})^2 \rangle_a = \langle (\delta M_z^{\text{tot}})^2 \rangle_a / V$$
$$= k_B T \chi / (1 + \ell_w / H). \tag{133}$$

The typical size of  $\delta \bar{\sigma}_0$  is small and is estimated as

$$|\delta \bar{\sigma}_0| \sim 0.3 e/(L\sqrt{\ell_B(H+\ell_w)}),$$

where  $\ell_B$  is the Bjerrum length. From Eq.(30) we find

$$\langle \delta M_{iz}^{\text{tot}} \delta M_{jz}^{\text{tot}} \rangle_a = V k_B T \left[ \chi_{\perp}^{ij} - \frac{\chi_i \chi_j}{\chi(H + \ell_{\text{w}})} \ell_{\text{w}} \right].$$
 (134)

These variances among the z components are very different from those in Eqs.(53) at  $Q_0 = 0$ , while those among the x and y components are commonly given by Eq.(53). Furthermore, let  $G_{\alpha\beta}^a(\mathbf{r}) = \langle p_{\alpha}(\mathbf{r})p_{\beta}(\mathbf{0})\rangle_a/k_BT$  be the space-correlation function of  $\mathbf{p}$  at  $E_a = 0$ , which differs from  $G_{\alpha\beta}(\mathbf{r})$  in Eq.(44) only for  $\alpha = \beta = z$  as<sup>43</sup>

$$G_{zz}^{a}(\mathbf{r}) = G_{zz}(\mathbf{r}) - \chi/\epsilon V + \chi/[V(1 + \ell_{w}/H)].$$
 (135)

Takae and the present author<sup>43</sup> performed a fixed-potential simulation. With  $\ell_{\rm w}=2H$ , they found Eq.(133) for the variance of  $M_z^{\rm tot}$ , Eq.(53) or Eq.(56) for those of  $M_x^{\rm tot}$  and  $M_y^{\rm tot}$ , and Eq.(135) for  $G_{zz}^a(r)$ .

## D. Surface charge fluctuations

The local surface charge densities  $\sigma_0$  and  $\sigma_H$  are equal to  $\pm D_z/4\pi$  at z=0 and H in the continuum electrostatics. In some simulations  $^{33-35,41-43}$ , this relation was used on smooth surfaces. Siepmann and Sprik  $^{102}$  presented an electrode model, where atomic particles in the electrodes have charges varying continuously to realize the metallic boundary condition. Here, we divide  $\sigma_0$  and  $\sigma_H$  into the lateral averages  $\bar{\sigma}_0$  and  $\bar{\sigma}_H (= -\bar{\sigma}_0)$  and the inhomogeneous parts  $\sigma_0^{\rm inh} = \sigma_0 - \bar{\sigma}_0$  and  $\sigma_H^{\rm inh} = \sigma_H - \bar{\sigma}_H$ , where  $\bar{\sigma}_0$  is coupled to  $M_z^{\rm tot}$  as in Eq.(125).

We consider the in-plane correlation of the deviation  $\delta \sigma_0(\mathbf{r}_\perp) = \sigma_0(\mathbf{r}_\perp) - \epsilon E_b/4\pi$  at z=0. It behaves as

$$\mathcal{G}_0(\mathbf{r}_{\perp} - \mathbf{r}_{\perp}') = \langle \delta \sigma_0(\mathbf{r}_{\perp}) \delta \sigma_0(\mathbf{r}_{\perp}') \rangle_a / k_B T$$
  
=  $S_0 \delta(\mathbf{r}_{\perp} - \mathbf{r}_{\perp}') - S_0 / L^2 + \chi / [L^2(H + \ell_{\rm w})], \quad (136)$ 

where  $\delta(\mathbf{r}_{\perp})$  is a localized function with  $\int d\mathbf{r}_{\perp}\delta(\mathbf{r}_{\perp}) = 1$ . The last two terms are nonlocal. We set  $S_0 = \int d\mathbf{r}_{\perp}\mathcal{G}_0(\mathbf{r}_{\perp})$  in the limit  $L \to \infty$  (see Appendix A). Then, the in-plane integral of  $\mathcal{G}_0(\mathbf{r}_{\perp})$  becomes

$$\int d\mathbf{r}_{\perp} \mathcal{G}_0(\mathbf{r}_{\perp}) = \frac{\langle (\delta Q_0)^2 \rangle_a}{L^2 k_B T} = \frac{\chi}{H + \ell_w}, \quad (137)$$

where  $\delta Q_0 = L^2 \delta \bar{\sigma}_0$ . This is in accord with Eq.(133). However, both at fixed  $Q_0$  and at fixed  $E_a$ , the in-plane correlation of  $\sigma_0^{\text{inh}} = \sigma_0 - \bar{\sigma}_0$  is given by

$$\langle \sigma_0^{\text{inh}}(\boldsymbol{r}_{\perp})\sigma_0^{\text{inh}}(\boldsymbol{r}_{\perp}')\rangle = \langle \sigma_0^{\text{inh}}(\boldsymbol{r}_{\perp})\sigma_0^{\text{inh}}(\boldsymbol{r}_{\perp}')\rangle_a$$
  
=  $k_B T [S_0 \delta(\boldsymbol{r}_{\perp} - \boldsymbol{r}_{\perp}') - S_0/L^2],$  (138)

which follows from Eq.(136) at fixed  $E_a$  and is suggested by the last paragraph in Sec.IV at fixed  $Q_0$ .

In our simulation<sup>42</sup>, the correlation length  $\xi_s$  of  $\mathcal{G}_0(r_\perp)$  was of order 1Å (for  $|r_\perp| \ll L$ ) and  $S_0$  was about 0.3/nm. Thus, in Eq.(136), the third term is comparable to the second one unless  $H \gg \ell_{\rm w}$ . We also found that the electric fields produced by  $\sigma_0^{\rm inh}$  and  $\sigma_H^{\rm inh}$  in the fluid decay rapidly outside the Stern layers. On the other hand, in the previous papers on the surface charges<sup>39,44,47</sup>, use has been made of  $\langle (\delta Q_0)^2 \rangle_a / L^2 k_B T = S_0 = C_0$  without the nonlocal terms in Eq.(136), where the global conditions (121) and (123) were not accounted for.

#### E. Dynamics for total polarizations

We examine dynamics for  $E_a \propto e^{i\omega t}$  with  $\omega \tau_{\rm f} \ll 1$  including the surface effect. We first assume  $\omega \tau_s \ll 1$ , where  $\tau_s$  is the relaxation time of the surface polarization (see Appendix A). Then, the surface potential drop is given by  $\bar{\sigma}_0/C$  and Eqs.(121) and (123) give

$$\bar{E}(z,t) = E_a(t) - \bar{\sigma}_0(t)/CH - 4\pi[\bar{p}(z,t) - \bar{\bar{p}}(t)], \quad (139)$$

where  $\bar{\sigma}_0 \cong \bar{p} + E_b/4\pi$  from Eq.(125). Hereafter, we suppress the space-time dependence of the variables if no confusion occurs. For  $\omega \tau_s \gtrsim 1$  we need to replace  $\ell_w$  by its frequent-dependent generalization (145) below.

We take the lateral and cell averages of the z component of Eq.(67) writing those of  $p_{1z}$  as  $\bar{p}_1$  and  $\bar{p}_1$ , where the lateral average of  $E_{0z}$  is  $4\pi\bar{\sigma}_0$ . Setting  $\boldsymbol{\xi} = \mathbf{0}$ , we find

$$\bar{p} - \bar{\bar{p}} = \frac{\epsilon_{\infty} + 2}{3\epsilon_{\infty}} (\bar{p}_1 - \bar{\bar{p}}_1), \quad \bar{\bar{p}} = \frac{\epsilon_{\infty} - 1}{4\pi} \bar{\bar{E}} + \frac{\epsilon_{\infty} + 2}{3} \bar{\bar{p}}_1.$$

Using these relations and assuming  $\epsilon \gg \epsilon_{\infty}$  we have

$$\chi_1 \bar{E} \cong \chi_1 E_a - \ell_w \bar{p}_1 / H - (\epsilon / \epsilon_\infty - 1)(\bar{p}_1 - \bar{p}_1), \quad (140)$$

where the second term is amplified by  $\chi_1$ . Then, the lateral average of the z component of Eq.(73) gives

$$\tau_{\rm D} \frac{\partial}{\partial t} \bar{p}_1 = \chi_1 E_a - (1 + \ell_{\rm w}/H) \bar{\bar{p}}_1 - \frac{\epsilon}{\epsilon_{\infty}} (\bar{p}_1 - \bar{\bar{p}}_1), \quad (141)$$

which gives  $\bar{p}_1 = \bar{p}_1 = \chi_1 E_b$  in equilibrium at  $\omega = 0$ .

From Eq.(141) the homogeneous variables  $\bar{p}_1$ ,  $\bar{p}$ , and  $\bar{\sigma}_0$  decay as  $\exp(-t/\tau'_D)$  with a modified relaxation time,

$$\tau_{\rm D}' = \tau_{\rm D}/(1 + \ell_{\rm w}/H) = \tau_{\rm L} \epsilon_{\rm eff}/\epsilon_{\infty}. \tag{142}$$

However, the inhomogeneous part  $\bar{p}_1 - \bar{\bar{p}}_1$  decays with  $\tau_{\rm L}$  as in the fixed charge condition. For example, at  $E_a = 0$ , the time-correlation of  $M_{1z}^{\rm tot}(t) = V\bar{\bar{p}}_1(t)$  decays as

$$\langle M_{1z}^{\text{tot}}(t)M_{1z}^{\text{tot}}(0)\rangle/Vk_BT = e^{-t/\tau_D'}D_{11},$$
 (143)

where  $D_{11} = \chi_{\perp}^{11} - \chi_{1}^{2} \ell_{\rm w} / [\chi(H + \ell_{\rm w})]$  from Eq.(134). This equation is similar to that in Eq.(84) for the periodic boundary condition. We generalize Eq.(76) to

$$\langle \boldsymbol{p}_{1}(\boldsymbol{r},t) \cdot \boldsymbol{p}_{1}(\boldsymbol{r}',0) \rangle / k_{B}T = 3G_{\text{or}}(t)\delta(\boldsymbol{r}-\boldsymbol{r}')$$
$$-e^{-t/\tau_{L}}\chi_{\perp}^{11}\epsilon_{\infty}/\epsilon V + e^{-t/\tau_{D}'}D_{11}/V.$$
(144)

In Appendix A, the Stern layers will be approximated as thin films with a thickness d and a dielectric constant  $\epsilon_s(\ll \epsilon)$ . Using the surface relaxation time  $\tau_s$  we will obtain the frequency-dependent surface electric length,

$$\ell_{\mathbf{w}}^*(\omega) = \ell_{\mathbf{w}}(1 + i\omega\tau_s\epsilon_s)/(1 + i\omega\tau_s),$$
 (145)

where  $\ell_{\rm w}=2d\epsilon/\epsilon_s$  is the static limit. For  $\omega\tau_s\gg 1$ , we have  $\ell_{\rm w}^*(\omega)\to 2d\epsilon$  (the value for empty films)<sup>35,38</sup>.

#### F. Linear response at fixed $E_a$

We examine the linear response for  $E_a \propto e^{i\omega t}$ . We use the static length  $\ell_{\rm w}$  assuming  $t \gg \tau_s$  in the time correlations and  $\omega \tau_s \ll 1$  in the frequency-dependent relations. For  $\tau_s^{-1} \lesssim \omega \ll \tau_{\rm f}^{-1}$ , we should use  $\ell_{\rm w}^*(\omega)$  in Eq.(145).

We consider the relaxation function of  $p_z$  at  $E_a = 0$ , written as  $K_a(t)$ . From Eq.(125) and (126) it is expressed in terms of the following correlations at  $E_a = 0$ :

$$K_a(t) = \frac{\langle M_z^{\text{tot}}(t) M_z^{\text{tot}}(0) \rangle_a}{V k_B T} = V \frac{\langle \bar{\sigma}_0(t) \bar{\sigma}_0(0) \rangle_a}{k_B T}. \quad (146)$$

We can then relate  $K_a(t)$  to  $G_{\perp}(t)$  in Eqs. (78) as

$$K_a(t) = G_{\perp}(t')/(1 + \ell_{\rm w}/H),$$
 (147)

where  $t' = t(1 + \ell_{\rm w}/H)$  and  $t'/\tau_D = t/\tau'_D$ , so  $K_a(t)$  decays with  $\tau'_{\rm D}$ . Notice that  $G_{\perp}(t)$  also appears in Eqs.(97), where the surface potential drop is irrelevant at fixed  $Q_0$ . However,  $K_a(t)$  much differs from the relaxation function  $G_{\parallel}(t)$  at  $Q_0 = 0$  in Eq.(108), though they are both expressed in the form of the time correlation of  $M_z^{\rm tot}$ . In the same manner, using  $G_{i\perp}(t)$  in Eq.(99), the relaxation function of  $p_{iz}$  are written as

$$K_{ia}(t) = \frac{\langle M_{iz}^{\text{tot}}(t)M_z^{\text{tot}}(0)\rangle_a}{Vk_BT} = \frac{G_{i\perp}(t')}{1 + \ell_w/H}, \quad (148)$$

which are very different from  $G_{i\parallel}(t)$  in Eq.(108).

The frequency-dependent susceptibilities are defined by  $\chi_a^*(\omega) = p^*/E_a$  and  $\chi_{ia}^*(\omega) = p_i^*/E_a$ , which are the FL transforms of  $-dK_a(t)/dt$  and  $-dK_{ai}(t)/dt$ , respectively. From Eqs.(78) and (101) they are written as

$$\chi_a^*(\omega) = \frac{1}{4\pi} \left[ \frac{\epsilon_{\infty} - 1}{1 + \ell_{\rm w}/H} + \frac{\epsilon - \epsilon_{\infty}}{1 + \ell_{\rm w}/H + i\omega\tau_{\rm D}} \right], \quad (149)$$

$$\chi_{1a}^*(\omega) = \frac{\chi_1}{1 + \ell_{\rm w}/H + i\omega\tau_{\rm D}},\tag{150}$$

$$\chi_{2a}^{*}(\omega) = \frac{\epsilon_{\infty} - 1}{4\pi} \left[ \frac{1}{1 + \ell_{w}/H} + \frac{4\pi}{3} \chi_{1a}^{*}(\omega) \right], \quad (151)$$

which also follow directly from Eqs.(9) and (140). In large cells with  $H \gg \ell_{\rm w}$ , these susceptibilities tend to  $\chi^*(\omega)$  and  $\chi_i^*(\omega)$  in Eqs.(89)-(91),

At  $E_a=0$  we also calculate the space-time correlation  $G_{\alpha\beta}^a(\mathbf{r},t)=\langle p_{\alpha}(\mathbf{r},t)p_{\beta}(\mathbf{0},0)\rangle_a/k_BT$ . It differs from  $G_{\alpha\beta}(\mathbf{r},t)$  in Eq.(82) only for  $\alpha=\beta=z$  as

$$G_{zz}^{a}(\mathbf{r},t) = G_{zz}(\mathbf{r},t) - [G_{\parallel}(t) - K_{a}(t)]/V.$$
 (152)

In the bulk region, the average electric field is  $E_b$  in Eq.(18) and the average electric induction is  $E_b + 4\pi\chi_a^*(\omega)E_a = 4\pi\bar{\sigma}_0$ . Then, we can define the frequency-dependent dielectric constant in the Debye form,

$$\epsilon_b^*(\omega) = 4\pi\bar{\sigma}_0/E_b = \epsilon_\infty + (\epsilon - \epsilon_\infty)/(1 + i\omega\tau_D'), \quad (153)$$

where the time constant is  $\tau'_{\rm D}$  in Eq.(142). On the other hand, in the capacitor experiments, the effective dielectric constant should be determined by

$$\epsilon_{\text{eff}}^*(\omega) = 4\pi\bar{\sigma}_0/E_a = \epsilon_b^*(\omega)/(1 + \ell_w/H),$$
 (154)

which tends to  $\epsilon_{\text{eff}}$  in Eq.(2) as  $\omega \to 0$ .

#### IX. SUMMARY AND REMARKS

We have studied statics and dynamics of dielectric fluids in the linear regime in the continuum theory. We have assumed the fixed-charge and fixed-potential conditions in a  $L \times L \times H$  cell with  $H \ll L$ . We have also revealed consequences for the total polarizations in other boundary conditions. We have found nonlocal polarization correlations, which are essential in electrostatic systems. Our main results are summarized below.

- (i) In Sec.IIA, we have started with Felderhof's dielectric free energy density f in Eq.(3)<sup>6</sup>. It contains the Lorentz term  $\propto p_1 \cdot p_2$  between the orientational polarization  $p_1$  and the induced one  $p_2$ , which yields the Lorentz internal field  $\mathbf{F}$  in Eq.(8) governing  $p_2$  as in Eq.(9). From this f we have obtained the susceptibilities  $\chi_1$  and  $\chi_2$  in Eq.(13), which also follow from Onsager's theory<sup>2</sup>. In Sec,IIB, we have examined the effect of the potential drop in the Stern layers to find the effective dielectric constant  $\epsilon_{\rm eff}$  in Eq.(2). In Sec.IIC, we have introduced the directing field  $\mathbf{E}_d$  governing  $\mathbf{p}_1$  in Eqs.(21)-(24) and the orientational susceptibility  $\chi_d$  by  $\mathbf{p}_1 = \chi_d \mathbf{E}_d$  to reproduce Onsager's results.
- (ii) In Sec.III, we have calculated the static polarization correlations in the wave number range  $\pi/H < q < \pi/a_m$  or in the distance range  $a_m < r < H$ , where  $a_m$  is the molecular length. These fluctuations are insensitive to the boundary condition. We have then obtained the Kirkwood-Fröhlich equation (25).
- (iii) In Sec.IV, we have calculated the variances of the total polarizations  $M_i^{\text{tot}}$ . They are given by Eq(53) at fixed  $Q_0$  and by Eq.(56) in the periodic boundary condition. We have also examined Sprik's case<sup>46,51,52</sup> with  $\int_V d\mathbf{r} \mathbf{D} = \mathbf{0}$ . The nonlocal polarization correlations have

also been examined. Their effects on the sphere integral  $M_1 = \int_{r < R} dr p_1$  has been shown in Eq.(58).

- (iv) In Sec.V, we have examined the solvation free energy for given  $p_1$  and bare electric field  $E_0$ , since the Lorentz term is missing in Marcus' free energy<sup>7</sup>.
- (v) In Sec.VI, we have studied polarization dynamics, where three relaxation times  $\tau_{\rm D},~\tau_{\rm L}=\tau_{\rm D}\epsilon_{\infty}/\epsilon$ , and  $\tau_{\rm f}$  appear with  $\tau_{\rm D}>\tau_{\rm L}\gg\tau_{\rm f}$ . Then, the polarization time-correlation functions have been calculated.
- (vi) In Sec.VII, we have given frequency-dependent linear response relations. The relaxation functions<sup>31</sup> have been calculated in analytic forms in typical situations.
- (vii) In Sec.VIII, we have controlled the applied field  $E_a = \Phi_a/H$  under the global constraints (121) and (123). Nonlocal polarization correlations are produced by surface-charge fluctuations. The variance and the lifetime of  $M_z^{\rm tot}$  at fixed  $E_a$  are larger than those at fixed  $Q_0$  by factors  $\epsilon_{\rm eff}$  and  $\epsilon_{\rm eff}/\epsilon_{\infty}$ , respectively. The nonlocal correlations in the surface charge density fluctuations have also been found, which are related to the bulk polarization fluctuations in Eq.(133). The frequency-dependent dielectric constant in small systems has been given in Eqs.(153) and (154).

We comment on future problems. (1) We should extend the present theory to study the dielectric response in electrolytes<sup>104</sup> and elastic dielectrics<sup>75</sup>. (2) The nonlinear dielectric response<sup>76,78–81</sup> should further be studied. In polar mixtures, the component with a larger dipole moment tends to accumulate in regions of higher electric field<sup>76,80</sup>. (3) In this paper, the dipole density is a constant, but it can be enriched around charged objects (electrostriction)<sup>70,76</sup>. This effect is enhanced in supercritical polar fluids. It even induces nucleation of liquid droplets around ions in metastable vapors<sup>103,104</sup>. (4) In fluid mixtures, the composition can be strongly heterogeneous around charged objects (preferential solvation). (5) The chemical reactions near surfaces are of great interest, where the image interaction can be relevant<sup>84</sup>.

Data availability: The data that support the findings of this study are available within the article.

#### Appendix A: Thin-film model of Stern layers

Here, we treat a Stern layer as a thin film with a low dielectric constant  $\epsilon_s(\ll \epsilon)$  in the region 0 < z < d ( $\ll H$ ). In the film, the surface charge density  $\sigma_0$  at z = 0 induces a polarization  $p_s$  along the z axis, where the electric field is given by  $E_s = 4\pi(\sigma_0 - p_s)$ . We then propose the dielectric free energy density in the film as

$$f_s = 2\pi(\sigma_0 - p_s)^2 + p_s^2 / 2\chi_s,$$
 (A1)

where  $\chi_s = (\epsilon_s - 1)/4\pi$ . For given  $\sigma_0$ , minimization of  $f_s$  with respect to  $p_s$  yields

$$p_s/\chi_s = E_s = 4\pi\sigma_0/\epsilon_s, \quad f_s = 2\pi\sigma_0^2/\epsilon_s.$$
 (A2)

The surface capacitance is then given by  $C_0 = \sigma_0/dE_s = \epsilon_s/4\pi d$ . If the dielectric constant varies smoothly as  $\epsilon = \epsilon(z)$ ,  $C_0$  is the z-integral of  $E_s(z)$  in the layer and

 $\Phi_a$  is given by<sup>69</sup>  $\Phi_a = 4\pi\sigma_0 \int_0^H dz \epsilon(z)^{-1}$ . The three-dimensional electric potential can be calculated if use is made of the Fourier transformation in the xy plane<sup>41,81</sup>. Note that the charge-free polarization and electric field<sup>62</sup>,  $p_{\rm int}$  and  $E_{\rm int}(=-4\pi p_{\rm int})$ , do not contribute to  $f_s$ .

The integral of  $f_s$  in the film 0 < z < d is given by

$$d \int d\mathbf{r}_{\perp} f_s = L^2 \bar{\sigma}_0^2 / 2C_0 + \int d\mathbf{r}_{\perp} (\sigma_0^{\text{inh}})^2 / 2C_0, \quad (A3)$$

where  $\sigma_0^{\text{inh}} = \sigma_0 - \bar{\sigma}_0$  is the inhomogeneous part of  $\sigma_0$  and the first term gives the surface free energy in Eq.(133). For  $C_H = C_0$ , Eq.(19) gives the surface electric length,

$$\ell_{\rm w} = 2d(\epsilon/\epsilon_s - 1) \cong 2d\epsilon/\epsilon_s \gg 2d.$$
 (A4)

There should be Coulombic repulsion among the surface charges, which is screened by the polarization deviation near the surface. Thus, we have an additional surface free energy density, written as  $(\sigma_0^{\rm inh})^2/2D_0$  at long wavelengths. Then, the short-range variance  $S_0$  of  $\sigma_0^{\rm inh}$  in Eq.(138) is given by

$$S_0 = (1/C_0 + 1/D_0)^{-1}.$$
 (A5)

We also propose a dynamic equation for  $p_s$ ,

$$\frac{\partial}{\partial t}p_s = -L_s \frac{\partial f_s}{\partial p_s} = -L_s \left[ \frac{\epsilon_s}{\gamma_s} p_s - 4\pi\sigma_0 \right], \tag{A6}$$

where  $L_s$  is a kinetic coefficient and the relaxation time of  $p_s$  is  $\tau_s = \chi_s/\epsilon_s L_s$ . For  $\bar{\sigma}_0 \propto e^{i\omega t}$ , the lateral averages of  $p_s$  and  $E_s$  in the film are given by

$$\bar{p}_s = 4\pi \chi_s \bar{\sigma}_0 / \epsilon_s (1 + i\omega \tau_s), \quad \bar{E}_s = 4\pi \bar{\sigma}_0 / \epsilon_s^*(\omega). \quad (A7)$$

We define the frequency-dependent film dielectric constant and surface capacitance by

$$\epsilon_s^*(\omega) = 1 + \frac{\epsilon_s - 1}{1 + i\omega\tau_s\epsilon_s}, \quad C^*(\omega) = \frac{1}{4\pi d}\epsilon_s^*(\omega).$$
 (A8)

The induced potential drop at z=0 is given by  $d\bar{E}_s=\bar{\sigma}_0/C^*(\omega)$ , Thus, we find Eq.(145).

## Appendix B: Onsager theory

Onsager<sup>2</sup> supposed a spherical cavity containing a single polarizable polar molecule, where its volume  $4\pi a^3/3$  was equated to the inverse density 1/n. He assumed the Clausius-Mossotti relation (10) for the induced polarization of the molecule  $n^{-1}\mathbf{p}_2 = \alpha_0 \mathbf{F}$ , where  $\alpha_0 = \bar{\alpha}/n$  is the molecular polarizability in Eq.(10) and  $\mathbf{F}$  is an internal electric field given by

$$\mathbf{F} = \bar{c}\mathbf{E} + \bar{r}\mathbf{p} = \bar{c}\mathbf{E} + \bar{r}\mathbf{p}_1 + \bar{r}\bar{\alpha}\mathbf{F}.$$
 (B1)

Here,  $\bar{c}$  is the cavity factor and  $\bar{r}$  is the reaction factor:

$$\bar{c} = 3\epsilon/(2\epsilon + 1), \quad \bar{r} = 8\pi(\epsilon - 1)/[3(2\epsilon + 1)], \quad (B2)$$

From his Eqs.(12), (13), and (20)  $\mathbf{F}$  and the directing field  $\mathbf{E}_d$  are expressed in terms of  $\bar{\alpha}$ ,  $\bar{c}$ , and  $\bar{r}$  as

$$F = E_{d} + (1 - \bar{r}\bar{\alpha})^{-1}\bar{r}p_{1}, \quad E_{d} = (1 - \bar{r}\bar{\alpha})^{-1}\bar{c}E, \quad (B3)$$

which give Eqs.(23) and (24) from Eq.(B2). Our n,  $\bar{\alpha}$ ,  $\epsilon_{\infty}$ ,  $\boldsymbol{p}_1$ ,  $\boldsymbol{p}_2$ , and  $\boldsymbol{E}_d$  correspond to N,  $N\alpha$ ,  $n^2$ ,  $N\mu_0\boldsymbol{u}$ ,  $N\alpha\boldsymbol{F}$ , and  $(\mu^*/\mu_0)\boldsymbol{E}$  in his paper, respectively.

Within Onsager's scheme, we introduce  $\chi_1$  and  $\chi_2$  by  $p_1 = \chi_1 E$  and  $p_2 = \chi_2 E = \bar{\alpha} F$ . Then, Eq.(B1) gives

$$\chi_1 + \chi_2 = \chi, \quad \chi_2 = \bar{\alpha}(1 - \bar{r}\bar{\alpha})^{-1}(\bar{c} + \bar{r}\chi_1).$$
 (B4)

These equations are solved to give

$$\chi_1 = \chi(1 - \bar{r}\bar{\alpha}) - \bar{\alpha}\bar{c}, \quad \chi_2 = \bar{\alpha}(\chi\bar{r} + \bar{c}),$$
(B5)

which yield Eq.(13) from Eqs.(10) and (B2). We also find  $\lambda_{11} = 4\pi/3 - \bar{r}/(1 - \bar{r}\bar{\alpha})$  in accord with Eq.(26).

Onsager assumed a microscopic sphere, which is allowable to take account of the long-range dipolar interaction. Kirkwood and Fröhlich assumed a mesoscopic sphere to include the short-range interactions. We have also assumed a mesoscopic sphere in Sec.IIIB,

## Appendix C: Previous linear theories

Many authors<sup>7–12</sup> started with the dielectric free energy without the Lorentz term, which is written as

$$\mathcal{F}_0 = \int_V d\mathbf{r} \left[ \frac{1}{8\pi} |\mathbf{E}|^2 + \frac{1}{2\chi_{01}} |\mathbf{p}_1|^2 + \frac{1}{2\chi_{02}} |\mathbf{p}_2|^2 \right]. \quad (C1)$$

Here,  $(\boldsymbol{p}_1, \boldsymbol{p}_2, \chi_{01}, \chi_{02})$  were written as  $(\boldsymbol{p}_u, \boldsymbol{p}_e, \alpha_u, \alpha_e)$  by Marcus<sup>7</sup> and as  $(\boldsymbol{p}_h, \boldsymbol{p}_e, \chi_h, \chi_e)$  by Lee and Hynes<sup>8</sup>. In equilibrium at fixed  $Q_0$ , this  $\mathcal{F}_0$  gives  $\boldsymbol{p}_i = \chi_{0i} \boldsymbol{E}$  with

$$\chi_{01} = (\epsilon - \epsilon_{\infty})/4\pi, \quad \chi_{02} = (\epsilon_{\infty} - 1)/4\pi, \quad (C2)$$

which differ from  $\chi_1$  and  $\chi_2$  in Eq.(13) not leading to Eq.(9). The expressions in Eq.(C2) were used also by Fröhlich<sup>3</sup>, Lee-Zwanzig<sup>17</sup>, and Hubbard-Onsager<sup>29</sup>.

Setting  $\delta \mathcal{F}_0/\delta \boldsymbol{p}_2 = \boldsymbol{0}$  at fixed  $\boldsymbol{p}_1$  and  $\boldsymbol{E}_0$  we find

$$p_2 = p_{2\parallel} = \frac{\epsilon_{\infty} - 1}{4\pi} E, \quad E = \frac{1}{\epsilon_{\infty}} (E_0 - 4\pi p_{1\parallel}). \quad (C3)$$

Substitution of the above E into Eq.(73) gives  $\tau_L/\tau_D = \epsilon_{\infty}/\epsilon^{29}$ . Under these relations we remove  $p_2$  from  $\mathcal{F}_0$  as

$$\mathcal{F}_{0} = \int_{V} d\mathbf{r} \left[ \frac{|\mathbf{E}_{0}|^{2}}{8\pi\epsilon_{\infty}} - \frac{\mathbf{p}_{1\parallel} \cdot \mathbf{E}_{0}}{\epsilon_{\infty}} + \frac{\epsilon |\mathbf{p}_{1\parallel}|^{2}}{2\epsilon_{\infty}\chi_{01}} + \frac{|\mathbf{p}_{1\perp}|^{2}}{2\chi_{01}} \right].$$
(C4)

Compare Eqs.(C3) and (C4) with Eqs.(63)-(67). From Eq.(C1) we calculate the correlations (33) as<sup>8,13</sup>

$$\hat{G}_{\alpha\beta}^{ij}(\mathbf{q}) = \chi_{0i}\delta_{ij}\delta_{\alpha\beta} - (4\pi\chi_{0i}\chi_{0j})/\epsilon)\hat{q}_{\alpha}\hat{q}_{\beta}, \qquad (C5)$$

which differ from those in Eq.(38) but give  $\hat{G}_{\alpha\beta}(q)$  in the form of Eq.(36). In particular, for i = j = 1, we have

$$\hat{G}_{\alpha\beta}^{11}(\mathbf{q}) = [\delta_{\alpha\beta} - \hat{q}_{\alpha}\hat{q}_{\beta} + (\epsilon_{\infty}/\epsilon)\hat{q}_{\alpha}\hat{q}_{\beta}](\epsilon - \epsilon_{\infty})/4\pi.$$
 (C6)

The variance of  $M_1$  in Eq.(45) is given by

$$\langle |\mathbf{M}_1|^2 \rangle / 3vk_B T = (\epsilon - \epsilon_\infty)(2 + \epsilon_\infty/\epsilon)/12\pi,$$
 (C7)

which is larger than in Eq.(47) by a factor of  $(\epsilon_{\infty} + 2)^2/9$ . Fröhlich<sup>3</sup> derived Eq.(C7) as remarked in Sec.IIIB.

Dinpajooh et al.<sup>12</sup> expressed  $\hat{G}_{\alpha\beta}^{ij}(q)$  differently from those in Eqs.(38) and (C5). For example, they found  $\chi_{\perp}^{11}=(\epsilon/\epsilon_{\infty}-1)/4\pi$  and  $\chi_{\parallel}^{11}=(1-1/\epsilon)/4\pi$  (written as  $\chi_{nn}^{T}$  and  $\chi_{nn}^{L}$  in their paper). Their theory does not yield the KF equation for  $\epsilon_{\infty}\neq 1$ .

# Appendix D: Fourier-Laplace transforms of relaxation functions in linear dynamics

We show how Eqs.(97) and (98) follow in our continuum theory. For the longitudinal parts of  $p_i$  and  $p_j$  we consider the time-correlation functions in the bulk:

$$G_{\parallel}^{ij}(t) = \int d\mathbf{r} \langle \mathbf{p}_{i\parallel}(\mathbf{r}, t) \cdot \mathbf{p}_{j\parallel}(\mathbf{0}, 0) \rangle / k_B T,$$
 (D1)

where  $G^{ij}_{\parallel}(0)=\chi^{ij}_{\parallel}$  in Eq.(38) and Eqs.(70) and (71) give

$$\frac{\partial}{\partial t}G_{\parallel}^{ij}(t) = -\sum_{\ell} \mathcal{L}_{i\ell}G_{\parallel}^{\ell j}(t). \tag{D2}$$

Here,  $\mathcal{L}_{ij} = L_i(a_{ij} + 4\pi)$ . Then, the FL transform of  $G^{ij}_{\parallel}(t)$  is written as  $\sum_{\ell} U^*_{i\ell}(\omega) \chi^{\ell j}_{\parallel}$ , where  $U^*_{ij}(\omega)$  is the inverse of the matrix  $i\omega \delta_{ij} + \mathcal{L}_{ij}$ . Here,  $\sum_{\ell} \mathcal{L}_{i\ell} \chi^{\ell j}_{\parallel} = L_i \delta_{ij}$ , since  $\chi^{ij}_{\parallel}$  is the inverse of the matrix  $a_{ij} + 4\pi$ . Thus,

$$i\omega \int_0^\infty dt e^{-i\omega t} G_{\parallel}^{ij}(t) = \chi_{\parallel}^{ij} - U_{ij}^*(\omega) L_j.$$
 (D3)

Here,  $p_i^*/E_0^* = \sum_j U_{ij}^*(\omega) L_j$  from Eqs.(70), (71), and (84). Thus,  $\alpha_i^*(\omega)$  are the FL transforms of  $-dG_{i\parallel}(t)/dt$ . In the same manner,  $\epsilon_i^*(\omega)$  are the FL transforms of  $-dG_{i\perp}(t)/dt$ . The results in Sec.VII follow for  $L_2 \to \infty$ .

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