

## Conditions for insensitivity of the microscopic-scale dielectric response to structural details of dipolar liquids

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Details of condensed matter structure can alter microscopic-scale response to electric fields by orders of magnitude. It is shown that dipolar liquids near boundaries is an exception where the response can be virtually insensitive to such details and can sense mainly the macroscopic dielectric permittivity. This insensitivity is due to fluidity, symmetry properties, and location of the fields' charges outside the liquid or inside impermeable solute cavities, which is the ubiquitous location in molecular scale phenomena.

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Electric fields are nonuniform at the molecular scale in many phenomena involving electrostatic interactions with and through dipolar liquids. Such interactions are determined by spatial correlations of the molecular charges and dipoles of the liquid. Patterns of the correlated charges have been demonstrated in most infinite and confined dipolar liquids by analytic theories [1–6], molecular simulations [7–9], and neutron scattering [9,10]. Due to spatial resonance of non-uniform fields with the patterns of infinite liquids, the interaction free energies can exceed the predictions of macroscopic electrostatics by 1–2 orders of magnitude[11–13].

In practice, measured interaction free energies agree to within a factor rarely exceeding two with the macroscopic dielectric continuum model assuming the absence of the microscopic structure. This model became one of the most widely used in physics, chemistry, and biology [14]. Its success is difficult to explain by compensation of errors, by uncertainties in liquid structure and in molecular-scale electric fields, or by “chemistry” of molecular systems, because the microscopic structure, the amplitudes and the characteristic lengths of the resonating patterns are very different for different liquids [12,13,15]. This paradox between the incorrect assumption of the macroscopic electrostatics and the quality of its prediction indicates the poorly understood physics of interactions between electrostatic fields and dipolar liquids.

This Brief Report explains the paradox by different mechanisms of interaction between the microscopic structure of dipolar liquids and electric fields with two different topologies distinguished by the presence of the boundary. Namely, fields produced by charges located outside the liquid are not directly coupled to the structural patterns due to fluidity and symmetry properties of the dipolar correlations. The coupling occurs via the perturbation that the boundary imposes on the short-range energy cost of polarization. This perturbation and the related deviation of the interaction free energy and polarization from their macroscopic predictions can be small, because the short-range energy remains small compared to the total energy cost of polarization down to short characteristic lengths. Fields produced by inside

charges are directly coupled and, thus, very sensitive to the structural patterns.

A rigorous relationship between liquid structure and electrostatics follows from the linear response theory [4,16,17]. The microscopic polarization  $\mathbf{P}(\mathbf{r})$  induced in the dipolar liquid by the applied “vacuum” electric field  $\mathcal{E}(\mathbf{r})$  is determined by the susceptibility tensor  $\gamma_{\alpha\beta}(\mathbf{r},\mathbf{r}')$ ,  $4\pi P_{\alpha}(\mathbf{r}) = \int \Sigma_{\beta} \gamma_{\alpha\beta}(\mathbf{r},\mathbf{r}') \mathcal{E}_{\beta}(\mathbf{r}') d\mathbf{r}'$ . The tensor  $\gamma$  is associated in the classical limit with the spatial correlator of liquid molecules approximated here by point dipoles,

$$\gamma_{\alpha\beta}(\mathbf{r},\mathbf{r}') = 2\pi T^{-1} \langle \delta p_{\alpha}(\mathbf{r}) \delta p_{\beta}(\mathbf{r}') \rangle_0, \quad (1)$$

where  $T$  is temperature in energy units;  $\alpha, \beta = x, y, z$  are indexes of the Cartesian coordinates,  $\langle \cdots \rangle_0$  denotes statistical averaging in the absence of the applied field,  $\mathcal{E} = 0$ ,  $\delta \mathbf{p}(\mathbf{r}) = \mathbf{p}(\mathbf{r}) - \langle \mathbf{p}(\mathbf{r}) \rangle_0$ , and  $\mathbf{p}(\mathbf{r}) = \Sigma_i \boldsymbol{\mu}_i \delta(\mathbf{r} - \mathbf{r}_i)$  is the instantaneous polarization of the liquid;  $\boldsymbol{\mu}_i$  is the permanent dipole moment situated at the center of molecule  $i$ .

In the presence of boundaries, the forms of the dipolar correlations (1) are poorly explored. These forms are restricted by fluidity and by symmetry properties. The restrictions can be accounted for via relationships between the induced polarization  $\mathbf{P}$  and the system's energetics following from the linear response theory. Namely, the microscopic polarization induced in a stable, ergodic system by a weak field  $\mathcal{E}$  minimizes the polarization free energy functional  $F$  [4–6,17,18],

$$\begin{aligned} F &= \sum_{\alpha,\beta} \int_V -P_{\alpha}(\mathbf{r}) \mathcal{E}_{\alpha}(\mathbf{r}) + 2\pi \int_V P_{\alpha}(\mathbf{r}) \gamma_{\alpha\beta}^{-1}(\mathbf{r},\mathbf{r}') P_{\beta}(\mathbf{r}') d\mathbf{r}' d\mathbf{r} \\ &= -\mathcal{E}\mathbf{P} + 2\pi\mathbf{P}\boldsymbol{\gamma}^{-1}\mathbf{P}, \end{aligned} \quad (2)$$

$F$  is the sum of the electrostatic interaction energy with the applied field  $\mathcal{E}$  and of the “self”-energy of nonequilibrium polarization  $\mathbf{P}$  created by another weak field. The self-energy is related to the dipolar correlator (1) via the inverse susceptibility tensor  $\boldsymbol{\gamma}^{-1}$  by the system of integral equations,  $\boldsymbol{\gamma}^{-1}\boldsymbol{\gamma} = \mathbf{I}$ , where  $\mathbf{I} = \delta_{\alpha\beta} \delta(\mathbf{r} - \mathbf{r}')$ ;  $\delta_{\alpha\beta}$  and  $\delta(\mathbf{r} - \mathbf{r}')$  are the Kronecker symbol and Dirac delta function. Hereafter, the product of bold symbols denotes the convolution over repeating indexes and integration over domain  $V$  accessible to the liquid molecules.

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Due to fluidity, the molecules sample every point in the accessible domain in response to static, weak and, therefore, piecewise continuous electric fields. Consequently, all induced polarizations and polarizations appearing in the functional (2) are continuous even at subatomic distances. I will show elsewhere that electric fields of such polarizations averaged over infinitesimal volume elements and then statistically averaged are continuous also. Then, the electrostatic relationships for structured continuous dielectrics follow from linear response theory. In particular, the free energy (2) of continuous microscopic polarizations can be separated into long-range  $F_L$  and short-range  $F_S$  components [4,6,19],

$$F = -\mathcal{E}\mathbf{P} - \underbrace{\frac{1}{2}\mathbf{P}\mathbf{T}\mathbf{P}}_{F_L} + \underbrace{2\pi\mathbf{P}\boldsymbol{\kappa}^{-1}\mathbf{P}}_{F_S}. \quad (3)$$

The long-range polarization energy  $F_L$  is the electrostatic energy of electric field  $\mathbf{E}^{\mathbf{P}} = \mathbf{T}\mathbf{P}$  produced by continuous polarization  $\mathbf{P}$ , where  $\mathbf{T}(\mathbf{r} - \mathbf{r}')$  stands for the electric field produced by a uniformly polarized cubic volume  $d\mathbf{r}'$  centered at  $\mathbf{r}'$ ,  $T_{\alpha\beta}(\mathbf{r}) = 3r_{\alpha}r_{\beta}r^{-5} - \delta_{\alpha\beta}r^{-3}$  at  $r > 0$  [19–21]. The effective short-range energy  $F_S$  of the fluctuating polarization is determined by the inverse polarizability tensor  $\boldsymbol{\kappa}^{-1}$  relating the total electric field  $\mathbf{E} = \mathbf{E}^{\mathbf{P}} + \mathcal{E}$  and the induced polarization,  $\mathbf{E} = 4\pi\boldsymbol{\kappa}^{-1}\mathbf{P}$ . Related to the dipolar correlator  $\boldsymbol{\gamma}$ , tensor  $\boldsymbol{\kappa}^{-1} = \boldsymbol{\gamma}^{-1} + (4\pi)^{-1}\mathbf{T}$  contains pertinent information about liquid structure and its perturbation by the boundary.

The fluctuating liquid structure is perturbed by the boundary in two ways. First, there is the lack of electrostatic interactions between the accessible and excluded domains. It is accounted for via integration over the accessible domain  $V$  of the long-range polarization energy  $F_L$  (3). Second, there may be a perturbation of the short-range polarization energy. To track this effect I write the short-range polarization energy  $F_S$  as the sum of the energy that the polarization would have had in the bulk and its perturbation by the boundary. The inverse polarizability tensor is split thereby onto the bulk  $\boldsymbol{\kappa}_u^{-1}$  and boundary  $\boldsymbol{\kappa}_b^{-1}$  components,

$$\boldsymbol{\kappa}^{-1} = \boldsymbol{\kappa}_u^{-1} + \boldsymbol{\kappa}_b^{-1}. \quad (4)$$

As these tensors determine energy, their forms are restricted by symmetries of the system. To account for isotropic properties of liquid bulk, I write the bulk short-range energy in terms of spatial derivatives of the polarization,

$$\mathbf{P}\boldsymbol{\kappa}_u^{-1}\mathbf{P} = \int_V (\varepsilon - 1)^{-1} |\mathbf{P}|^2 + \sum_{i=1}^{\infty} a_i^L [(\nabla \cdot)^i \mathbf{P}]^2 + a_i^T [(\nabla \times)^i \mathbf{P}]^2 d\mathbf{r}. \quad (5)$$

The expansion coefficients  $a_i^{L,T}$  and the dielectric permittivity  $\varepsilon$  are related to the Fourier components  $\boldsymbol{\gamma}^{L,T}(k) = [\mathcal{S}^{L,T} + (\varepsilon - 1)^{-1} + \sum_{i=1}^{\infty} a_i^{L,T} k^{2i}]^{-1}$  of the dipolar correlator (1) in the infinite liquid and incorporate, respectively, microscopic and macroscopic characteristics of bulk liquid structure ( $\mathcal{S}^L = 1$ ,  $\mathcal{S}^T = 0$ ). The derivatives take the forms of divergences/gradients  $(\nabla \cdot)^i$  and curls  $(\nabla \times)^i$  which are the only invariant differential operators with isotropic symmetry. They account for longitudinal and transversal polarizations that can emerge due to their entanglement near the boundary. Analogous ex-

pansions are used in the elastic and liquid crystal theories [22], but are limited to first order derivatives and weakly nonuniform displacements. This limitation can be lifted for continuous polarizations because the inverse polarizability tensor  $\boldsymbol{\kappa}^{-1}$  is believed to be short-range in dipolar liquids far from the critical point [20].

For electric fields produced by charges located *outside* the dielectric,  $\rho(\mathbf{r} \in V) = 0$ , minimization [23] of the functional  $F$  (3)–(5) results in relationship

$$\mathbf{P} = \mathbf{P}_M - \boldsymbol{\eta}\mathbf{P}_M, \quad \boldsymbol{\eta} = \boldsymbol{\gamma}\boldsymbol{\kappa}_b^{-1} \quad (6)$$

between the induced  $\mathbf{P}$  and the macroscopic  $\mathbf{P}_M$  polarizations. The latter is determined by equation  $4\pi(\varepsilon - 1)^{-1}\mathbf{P}_M = \mathcal{E} + \mathbf{T}\mathbf{P}_M = \mathbf{E}$  equivalent to the Poisson equation  $\nabla \cdot \mathbf{E} = \varepsilon^{-1}\nabla \cdot \mathcal{E}$  [19,24].

The deviation from the macroscopic polarization will be small if the parameter  $\boldsymbol{\eta}$  is small. This is the case even if the fluctuating liquid structure and the dipolar correlator  $\boldsymbol{\gamma}$  have features at the characteristic length of the applied field and exhibit the boundary perturbation due to the lack of electrostatic interactions between the accessible and excluded domains.

The physical meaning of this parameter can be clarified by comparing the response energy  $W = \frac{1}{2}\mathcal{E}\mathbf{P}$  related here to the equilibrium free energy (3),  $W = -F$ , with its macroscopic prediction  $W_M = \frac{1}{2}\mathcal{E}\mathbf{P}_M$ . The deviation  $\Delta W_b = W - W_M$  from the prediction,

$$\Delta W_b = -2\pi\mathbf{P}_M\boldsymbol{\kappa}_b^{-1}(\mathbf{I} - \boldsymbol{\eta})\mathbf{P}_M, \quad (7)$$

is small,  $|\Delta W_b| \ll W_M$ , if the boundary perturbation of the short-range energy of the macroscopic polarization  $\mathbf{P}_M$  is small compared to the total energy of  $\mathbf{P}_M$ ,  $|\mathbf{P}_M\boldsymbol{\kappa}_b^{-1}\mathbf{P}_M| \ll \mathbf{P}_M\boldsymbol{\gamma}^{-1}\mathbf{P}_M$ .

Let us illustrate this result using a simple model of a Born ion, a spherical layer of charge density  $e(4\pi r_B^2)^{-1}\delta(r - r_B)$ , in the spherical cavity of radius  $R \geq r_B$ . In the limit of weak nonuniformity of the ion's field we can omit the second and higher order derivatives in Eq. (5) and find the induced polarization  $\mathbf{P} = P(r)\mathbf{r}/r$ ,

$$P(r) = P_M \left[ 1 - \frac{b(r + \lambda)}{\lambda R \varepsilon / (\varepsilon - 1) + b(R + \lambda)} e^{(r-R)/\lambda} \right]. \quad (8)$$

I assumed for simplicity that the characteristic lengths of the short-range boundary component  $\boldsymbol{\kappa}_b^{-1}$  are shorter than the correlation length  $\lambda = \sqrt{a_1^L(1 - \varepsilon^{-1})}$  in this model,  $\boldsymbol{\kappa}_b^{-1} \rightarrow b\delta(r - R)\mathbf{I}$ . If  $b$  is small, the polarization coincides with the macroscopic prediction  $4\pi P_M = e(1 - \varepsilon^{-1})r^{-2}$ , even though the correlation length  $\lambda$  is comparable with the cavity radius: see Fig. 1.

If the applied charges are located *inside* the dielectric,  $\rho(\mathbf{r} \in V) \neq 0$ , the polarization may not approach the macroscopic polarization when the characteristic lengths of the applied field and of the dielectric are comparable; see Fig. 1. For the Born ion embedded in an infinite dielectric modeled above these lengths are  $\lambda$  and the cavity radius  $r_B$  [ $\theta(r > 0) = 1$ ,  $\theta(r \leq 0) = 0$ ],

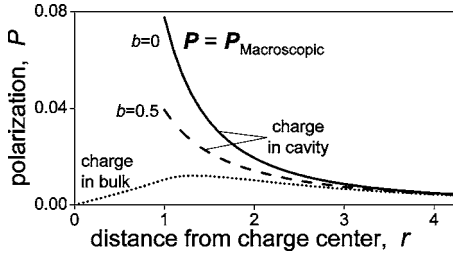


FIG. 1. Polarizations induced by a spherical charged layer embedded in the bulk and in the spherical cavity of the structured dielectric (8).  $e=1$ ,  $\lambda=1$ ,  $R=1$ ,  $\varepsilon=40$ , and  $b=0,0.5$ .

$$P(r) = P_M \left[ \theta(r - r_B) - \frac{\text{sgn}(r - r_B)r + \lambda}{2r_B} e^{-|r - r_B|/\lambda} + \frac{r + \lambda}{2r_B} e^{(r + r_B)/\lambda} \right].$$

The deviation of the induced polarization (6) from the macroscopic prediction  $\mathbf{P}_M$  is now determined by the nonlocal part of  $\boldsymbol{\kappa}^{-1}$  and its details of liquid structure,

$$\boldsymbol{\eta} = \boldsymbol{\gamma}(\boldsymbol{\kappa}^{-1} - (\varepsilon - 1)^{-1}\mathbf{I}).$$

These results can be interpreted in terms of a balance between electrostatic and effective short-range interactions. The electrostatic interactions tend to align molecular dipoles to maximize screening of the applied field. Such polarization cannot follow the rapid spatial variation of the applied field because the “nonuniformity” of polarization has finite energy cost associated with short-range spatial correlations of the dipoles. The surface charge of the macroscopic polarization  $\mathbf{P}_M$  can efficiently screen the field of outside charges. Yet the nonuniformity cost of this polarization is zero in the absence of the boundary perturbation of this cost. Indeed, by symmetry, the bulk short-range cost may depend only on divergence  $\nabla \cdot \mathbf{P}$  and curl  $\nabla \times \mathbf{P}$  (5) in isotropic materials with the vector order parameter  $\mathbf{P}$ , whereas the macroscopic polarization by the outside charges is divergence- and curl-free ( $\nabla \cdot \mathbf{P}_M = |\nabla \times \mathbf{P}_M| = 0$ ). A divergence or curl of the polarization and, hence, “nonmacroscopic” polarization modes with  $\nabla \cdot \mathbf{P} \neq 0$  or  $|\nabla \times \mathbf{P}| \neq 0$  will not emerge because their nonuniformity cost increases the total energy without enhancing the screening (the bulk polarization charge  $-\nabla \cdot \mathbf{P}$  is farther from the outside charges than the surface polarization charge). This means that the “nonmacroscopic” normal modes of polarization do not interact with the outside charges and do not produce an electric field outside the material with nonspecific boundary (with  $\boldsymbol{\kappa}_b^{-1} = 0$ ).

However, the nonmacroscopic modes can produce an electric field inside the material and can interact and respond to inside charges. The macroscopic polarization may not optimally screen the inside charges due to the substantial bulk cost of nonuniformity ( $\nabla \cdot \mathbf{P}_M \neq 0$ ). Therefore, the microscopic and macroscopic polarizations by the inside charges will differ.

Molecular simulations of a model dipolar fluid and water indicate modest deviations from the macroscopic polarization by outside charges, unless the molecules and the boundary are idealized by spheres and smooth extended surfaces [25]. Such idealizations may incur large deviations due to highly regular packing of several molecular layers near the boundary that are rarely observed in reality. Relevant examples are few because most simulations focus on structural features other than the induced polarization, inverse polarizability  $\boldsymbol{\kappa}^{-1}$  or susceptibility  $\boldsymbol{\gamma}$  tensors. The presence of structure and its perturbation by the boundary do not necessarily cause deviations from the macroscopic predictions.

Dipolar correlations in bulk liquids may indicate systems with boundaries where small deviations can be expected at rather short characteristic lengths of the fields of outside charges. For example, in simulated bulk water the short-range energy of polarization remains the smaller fraction of the total energy at  $\pi/k \geq 3$  Å lengths. This fraction is of the order of  $[|\boldsymbol{\gamma}^L(k)^{-1} - 1| + \boldsymbol{\gamma}^T(k)^{-1}] / [\boldsymbol{\gamma}^L(k)^{-1} + \boldsymbol{\gamma}^T(k)^{-1}] \sim 1 - \boldsymbol{\gamma}(k)^L$ , where the Fourier components of the dipolar correlator (1) are in the ranges of  $0.013 > 1 - \boldsymbol{\gamma}(k) > -0.5$  and  $0.013 < \boldsymbol{\gamma}^T(k)^{-1} < 0.07$  [26]. Therefore, the ratio of the boundary perturbation of the short-range energy to the total energy and the deviation  $\Delta W_b$  (7), can be relatively small,  $|\Delta W_b| / W_M \sim |1 - \boldsymbol{\gamma}(k)^L| < 0.5$ , unless other deviations are strong.

Hydrogen bonds and other strong interactions with the boundary that affect rotational and translational mobility of the molecules can substantially perturb the short-range energy cost of polarization. If the net interaction energy per molecule in a boundary layer with thickness similar to the applied field length exceeds the thermal energy, significant deviations from the macroscopic response can be expected.

Fields of outside charges may have minor components at shorter characteristic lengths where the resonant peaks in the dipolar correlators and the short-range energy of polarization become large [in simulated water  $\boldsymbol{\gamma}(k)^L \sim 10^2$  at  $\pi/k \approx 1$  Å [26]]. The contribution of such components to the response energy  $W$  should be small,  $\sim \boldsymbol{\gamma}(k)^L e^{-2k\xi} \sim 10^{-6}$ , because their field decays exponentially with the distance  $\xi$  between the charge and the boundary and  $\xi \geq 3$  Å in typical molecular systems.

Deviations caused by the nondipolar components of the liquid intramolecular charge density and by the gradual onset of the liquid density and polarization at the boundary were neglected above and should also be small. Using the macroscopic polarization as the zeroth approximation, one can expand the induced polarization and the response energy in terms of such deviations. These deviations are independent to the first approximation,  $W \approx W_M + \Delta W_b + \Delta W_{dp} + \Delta W_{sh}$ .  $\Delta W_{dp} / W_M \propto l^2 / \xi^2$  and  $\Delta W_{sh} / W_M \propto w / \xi$  scale with the characteristic size  $l$  of the liquid intramolecular charge density, the characteristic length  $\xi$  of the solute’s electric field, and the half-width of the onset layer  $w$ . These relative deviations should not exceed 0.05–0.2 for typical ionic and dipolar solutes in water [27].

Response to fields produced by inside charges is very sensitive to inter- and intra-molecular liquid structure because the charges are permeated by liquid molecules [12,13,26,28].

Due to large compensations of multipolar contributions, the response energy strongly depends on approximations of the intramolecular charge [26]. If continuous rather than point approximations of the electron density are used, the deviations from the macroscopic prediction become large already at characteristic lengths of  $\pi/k \geq 14 \text{ \AA}$ ,  $\Delta W/W_M \sim [\varepsilon^{-1} - \varepsilon(k)^{-1}]/(1 - \varepsilon^{-1}) = 1 - 75$ , where  $\varepsilon(k)$  is the permittivity obtained from a continuous charge correlations in simulated water [28]. This and similar conditions are not necessary for the fields of outside charges, but were used to claim that

quasimacroscopic response is impossible at the molecular scale.

Interacting charges are usually located outside dipolar liquids with boundaries or inside impermeable cavities formed by solute molecules carrying the charges. Weak, indirect coupling of such charges to the microscopic details of liquid structure can explain surprisingly low sensitivity of many molecular-scale phenomena to the details. Such coupling can also provide means of modeling and physical rationale for the residual sensitivity to the microscopic liquid structure.

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