

Nonlocal Dielectric Saturation in Liquid Water

Alexei A. Kornyshev* and Godehard Sutmann†

Institut für Energieverfahrenstechnik, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

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The linear and nonlinear dielectric response of water to spatially varying electric fields of different wavelength and field strengths is calculated by means of molecular dynamics computer simulation for a central force model of water. We find that nonlinear effects are strongest at $k \approx 3 \text{ \AA}^{-1}$, where the linear response function $\chi(k) = 1 - 1/\epsilon(k)$ has its main maximum. For small k the response is linear up to field strengths of $E_0 \approx 1 \text{ V/\AA}$. A phenomenological theory is discussed which reproduces the main nonlinear effects found in the simulation. [S0031-9007(97)04236-1]

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The wave vector dependent dielectric tensor $\epsilon_{\alpha\beta}(\mathbf{k})$ determines the response of a polar liquid to an embedded microscopic charge distribution at distances of the characteristic liquid structure. It appears in the thermodynamic description of electrolytes, charge transfer kinetics, electrochemistry, adsorption and interaction of biological membranes and macromolecules. For the case when the response is linear, it is only the longitudinal component $\epsilon(k) = k_\alpha k_\beta \epsilon_{\alpha\beta} / k^2$ that appears in electrostatics. Under this assumption a variety of solvation determined phenomena were described, but it was never checked whether the linear response assumption holds for water. At least one would expect nonlinear behavior when the interaction energy between the water dipoles and the external field becomes so large that the hydrogen bonds are broken ($\mu E_0 > 0.25 \text{ eV}$).

The linear dielectric response function $\chi(k) = 1 - 1/\epsilon(k)$ is related to the correlation function of equilibrium bound charge density fluctuations via the fluctuation dissipation theorem (FDT). A number of works were devoted to the calculation of $\epsilon(k)$ of polar liquids by using computer simulations or different statistical mechanical schemes [1]. In a recent work we have calculated the linear response function for water by means of molecular dynamics computer simulation and compared it to the available experimental data [2]. The main features found for $\epsilon(k)$ were (i) a decrease from the macroscopic value ($\epsilon = 80$) to a value near 15 at small k from where it increases to a divergence point at $k \approx 1 \text{ \AA}^{-1}$, (ii) a negative region in an intermediate k range, and, after crossing a second divergence point at $k \approx 12.5 \text{ \AA}^{-1}$, (iii) a monotonic decrease to the high frequency limit $\epsilon(k \rightarrow \infty) = 1$. The corresponding response function $\chi(k)$, which reflects the spatial distribution of the bound charge density pattern, showed a high peak at $k \approx 3 \text{ \AA}^{-1}$ and a satellite maximum at $k \approx 5 \text{ \AA}^{-1}$ (see Fig. 1).

The present work is to be understood as a first step towards building a bridge between the nonlinear and the nonlocal effects. Our goal will be to answer the following questions: At which electric field strengths does the linear response assumption break down and for which wave

number k are the nonlinear effects the strongest? For this we have performed a series of molecular dynamics computer simulations for a flexible water model in static external electric fields and have calculated the longitudinal polarization as a function of the field amplitude and its wavelength.

The description of the nonlocal medium polarization becomes a difficult task when the response is not linear. There is no closed-form FDT, no superposition of different \mathbf{k} modes, and there are off-diagonal elements in the response tensor. The constitutive relation between polarization $\mathbf{P}(\mathbf{k})$ and external field $\mathbf{E}^{(0)}(\mathbf{k})$ then reads [4]

$$P_\alpha(\mathbf{k}) = \chi_{\alpha\beta}^{(0)}(\mathbf{k})E_\beta^{(0)}(\mathbf{k}) + \int d\mathbf{k}' d\mathbf{k}'' \delta(\mathbf{k} - \mathbf{k}' - \mathbf{k}'') \times \chi_{\alpha\beta\gamma}^{(1)}(\mathbf{k}', \mathbf{k}'')E_\beta^{(0)}(\mathbf{k}')E_\gamma^{(0)}(\mathbf{k}'') + \dots, \quad (1)$$

where (...) denotes integrals of higher powers in $\mathbf{E}^{(0)}$, which contain response tensors of increasing rank. In

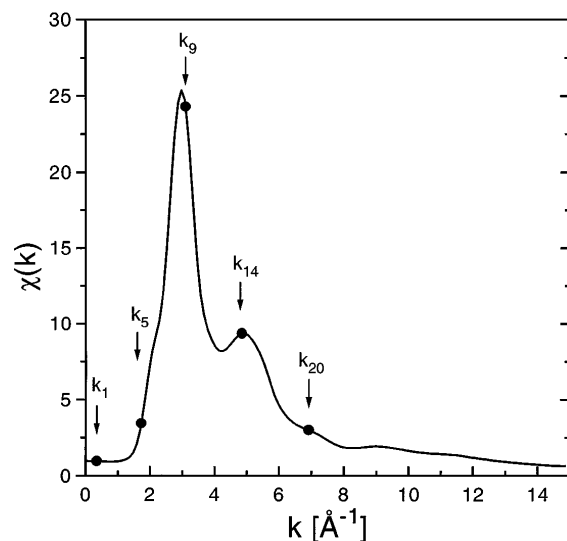


FIG. 1. The dielectric response function $\chi(k)$ as obtained from an equilibrium computer simulation with the help of the classical fluctuation dissipation theorem [2]. The indicated points mark the k values for which we perform the external electric field simulations.

the linear response limit, the right-hand side of Eq. (1) reduces to the longitudinal component of the first item. While it is a hard task to evaluate the off-diagonal components and the higher rank tensors of the response, it is possible to reveal the limits of the linear response assumption by studying each k component of the polarization separately. Creating in the computer simulation an external field of the form $\mathbf{E}^{(0)}(\hat{\mathbf{k}}) = \hat{\mathbf{k}}E_0 \cos \mathbf{k}\mathbf{r}$ ($\hat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|$) and calculating the polarization as a function of the amplitude E_0 and wave vector \mathbf{k} , we may follow the transition from the linear to nonlinear response. In the linear regime this *direct method* of calculating the response function provides also an independent verification of the previously obtained results [2,3], based on the FDT.

We consider a system of 200 water molecules in a cubic box with periodic boundary conditions. The side length of the box is $L = 18.1 \text{ \AA}$, which leads to a mass density of $\rho = 0.999 \text{ g/cm}^3$. We used the Bopp-Janáso-Heinzinger (BJH) water model [5] (the same as in Refs. [2,3]) which allows the molecules to vibrate, but which has no electronic polarizability. The computer simulations were performed for a temperature of 300 K. The time step of integration was $\Delta t = 0.25 \text{ fs}$ and the total trajectory length differed between 100 and 500 ps, depending on the convergence of the mean value of polarization. To speed up the computer simulation time, we used as a boundary condition a shifted force potential to truncate long range interactions beyond the cutoff radius $R_c = 8.85 \text{ \AA}$ [6]. Furthermore, we applied a multiple time step method where, around each molecule, regions of fast and slow fluctuating forces are separated [7]. Fast components are calculated explicitly at every time step. The slow components are Taylor expanded in time up to the linear term and are extrapolated over a time step interval at the beginning of which they are explicitly calculated. This procedure allows the simulation to speed up ≈ 8 times with respect to a conventional Ewald summation method which was used in our previous studies [2,3].

For the case of the field-free simulations using FDT one may calculate the whole k spectrum of the linear response function from one simulation run. In the direct method, one has to perform a separate simulation for every k point and every field strength E_0 . We, therefore, focused on five representative k points of the linear response spectrum (see Fig. 1). From the periodicity of the simulation cell the k values are limited to $k_n = 2\pi n/L$. For our calculations we choose $k_1 = 0.34 \text{ \AA}^{-1}$ (the smallest k value accessible in the simulation), $k_5 = 1.73 \text{ \AA}^{-1}$, $k_9 = 3.11 \text{ \AA}^{-1}$ (the main maximum position), $k_{14} = 4.84 \text{ \AA}^{-1}$ (the satellite maximum position), and $k_{20} = 6.92 \text{ \AA}^{-1}$. For each k point, we applied between eight to ten different electric field strengths within the interval $0.005 < E_0 < 5 \text{ V/\AA}$, corresponding to $E_0 \in [0.08; 80]k_B T/\mu$, where $\mu = 1.97D$ is the average dipole moment of a water molecule. From simulation data, we then calculated the k dependent bound charge density pattern $\rho_b(k) = 1/\sqrt{N} \sum_{\alpha j} q_{\alpha} \exp\{i\mathbf{k}\mathbf{r}_{\alpha j}\}$ ($j = 1, \dots, N$, where N is the

number of molecules and q_{α} is the partial charge of site α of the molecule j), which is related to the longitudinal part of polarization via $\hat{\mathbf{k}}\mathbf{P}(\mathbf{k}) = \rho_b(\mathbf{k})/ik$ [since $4\pi\hat{\mathbf{k}}\mathbf{P} = \chi(k)\hat{\mathbf{k}}\mathbf{E}^{(0)}$, the external field and the bound charge density pattern exhibit a phase shift of 90°].

To check our computational approach, we first compared our results for the selected k values with previous results which were based on the linear FDT [8]. We found a nearly perfect agreement within the error bars [9]. Figure 2 shows the dependence of the Fourier amplitude of the bound charge density $\rho_b(k)$ on the external field strength E_0 . This dependence is well fitted by a Langevin function

$$\rho_b(k) = A_k \left[\coth(B_k E_0) - \frac{1}{B_k E_0} \right], \quad (2)$$

where A_k and B_k are the fitting parameters, which are shown in Table I. For small values of the external field, all k components of polarization respond linearly, as expected. The deviation from a straight line starts at different field strengths for the different k . This deviation is the signature of nonlinearity and it is characterized through the parameter B_k in Eq. (2): the larger B_k , the earlier the appearance of nonlinear behavior. From Table I we find a pronounced k dependence of B_k which resembles the shape of the linear response function. With increasing k , B_k sharply increases to a value of 20 at the main maximum position of $\chi(k)$ and then decreases with higher k . This means that the nonlinear behavior occurs first at the resonance position, where the absolute value of the response decreases with respect to the linear case; i.e., normal saturation is observed [10].

One might argue that such field dependence could be due to the specific boundary conditions which we used in

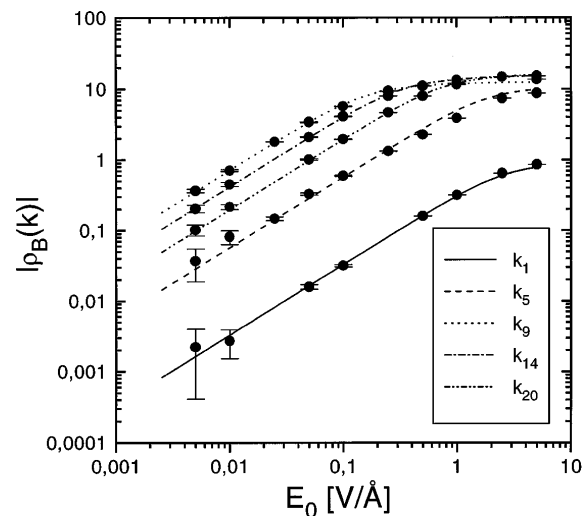


FIG. 2. The absolute value of the bound charge density $|\rho_b(k)|$ as a function of the external field strength E_0 shown for the five simulated k values (see Fig. 1). The points with error bars are the simulated values; the curves correspond to the Langevin function [see Eq. (2)]. For the parameter values see Table I.

TABLE I. Dependence of the Langevin parameters A_k and B_k on k .

| | k [\AA^{-1}] | A_k [e] | B_k [$\text{\AA}/\text{V}$] |
|----------|---------------------------|---------------|---------------------------------|
| k_1 | 0.35 | 0.986 | 1.0 |
| k_5 | 1.73 | 6.0 | 3.0 |
| k_9 | 3.46 | 10.8 | 20.0 |
| k_{14} | 5.19 | 15.6 | 8.0 |
| k_{20} | 6.92 | 16.8 | 3.5 |

the computer simulation. Indeed, in the limit of $k = 0$, several authors have found a strong dependence of the field strength, from which water starts to respond nonlinearly on the boundary conditions [11]. This dependence, however, should not be that strong for $k \neq 0$, since long range correlations decay with increasing k . In order to verify our approach, we made the following investigation: For the smallest k value (k_1), we performed an Ewald summation simulation for the same set of electric fields and found the same field dependence of the bound charge density.

We note that for the strongest fields which we studied, the system is completely saturated, i.e., $\cos(\hat{\mathbf{k}}\boldsymbol{\mu}) \approx 1$. This saturation is the result of a *phase transition* [12], leading to an icelike structure, which is different for the different wave numbers. For k_5 it resembles a hexagonal structure but due to the alternating orientation of the molecular dipoles it is not identical with ice I_h .

$$\mathbf{P}_2 - (\lambda_2^2 + l^2 - L^2)\nabla^2\mathbf{P}_2 + \lambda_2^2 l^2 \nabla^2(\nabla^2\mathbf{P}_2) + \frac{4\alpha}{a_2}[\mathbf{P}_2^3 - l^2\nabla^2(\mathbf{P}_2^3)] = \frac{1}{a_2}(\mathbf{D} - l^2\nabla^2\mathbf{D}), \quad (7)$$

where $L^2 = \gamma^2/a_2b$. When $\alpha = 0$, the linear response result is recovered (for details, see Ref. [13]). For $\alpha \neq 0$ there is no closed form solution of Eq. (7). Assuming small external fields of the form $\mathbf{E}^{(0)}(\mathbf{r}) = \hat{\mathbf{k}}E_0 \cos \mathbf{k}\mathbf{r} = \mathbf{D}(\mathbf{k})$ (which are equal to induction in this case) one may apply a perturbation approach to obtain a series solution in powers of the external electric field $\mathbf{P}_2 = \mathbf{P}_2^{(0)}[E_0] + \mathbf{P}_2^{(2)}[E_0^3] + \dots$

The solution shows the appearance of odd higher order k harmonics with increasing powers of E_0 , with $\mathbf{k}_n = (2n + 1)\mathbf{k}$ ($n = 0, 1, 2, \dots$). We observe the same property in the simulation results. For the first terms of the power series we get $4\pi\mathbf{P}_2^{(0)}(\mathbf{r}) = \chi(k)\hat{\mathbf{k}}E_0 \cos \mathbf{k}\mathbf{r}$, which corresponds to the linear response and $4\pi\mathbf{P}_2^{(2)}(\mathbf{r}) = \hat{\mathbf{k}}\mathcal{P}_{21} \cos \mathbf{k}\mathbf{r} + \hat{\mathbf{k}}\mathcal{P}_{23} \cos 3\mathbf{k}\mathbf{r}$, where $\mathcal{P}_{21} = -3\alpha\chi^4(k)E_0^3$ and $\mathcal{P}_{23} = -\alpha\chi^3(k)\chi(3k)E_0^3$. This shows that (i) due to the negative sign, the correction term *decreases* the response, i.e., it shows normal saturation behavior as in the simulation and (ii) since the leading term of the correction is proportional to the fourth power of χ , the effect is particularly enhanced at the resonance wave vector, where $\chi(k)$ has a sharp maximum (see Fig. 1). Thus with the increase of E_0 , the saturation will be first observed at the resonance k . From the criterion $\mathbf{P}_2^{(2)} \ll \mathbf{P}_2^{(0)}$,

In order to rationalize our findings, we extended a phenomenological theory, which was developed to reproduce the linear response results [13], to the nonlinear case. It consists of a Landau-Ginzburg Hamiltonian where two polarization modes are considered: a slow one \mathbf{P}_1 and a fast one \mathbf{P}_2 , the latter of which is coupled through a gradient term to the scalar order parameter η . For the nonlinear case the Hamiltonian reads

$$\mathcal{H} = \int (h_1 + h_2)d\mathbf{r}, \quad (3)$$

where

$$h_1 = \frac{a_1}{2}[\mathbf{P}_1^2 + \lambda_1^2(\nabla\mathbf{P}_1)^2] - \mathbf{P}_1\mathbf{D}, \quad (4)$$

$$h_2 = \frac{a_2}{2}[\mathbf{P}_2^2 + \lambda_2^2(\nabla\mathbf{P}_2)^2] + \frac{b}{2}[\eta^2 + l^2(\nabla\eta)^2] + \frac{\gamma}{2}\mathbf{P}_2\nabla\eta - \mathbf{P}_2\mathbf{D} + \alpha\mathbf{P}_2^4. \quad (5)$$

The parameters a_i , b , γ determine the weight of the contributions and λ_i , l are characteristic length scales. α describes the deviation from a harmonic fluctuation pattern. The Euler-Lagrange equations of the functional, Eq. (3), then read

$$\mathbf{P}_1 - \nabla^2\mathbf{P}_1 = \frac{1}{a_1}\mathbf{D}, \quad (6)$$

necessary for the convergence of the power series, we find $E_0 \lesssim 1/\sqrt{17.5\alpha\chi^3(k)}$. In Fig. 3 we compare the results of the mean-field theory with the simulation data for the value of the anharmonicity coefficient $\alpha = 5 \times 10^{-4} \text{\AA}^3/\text{eV}$. Here we have defined an effective response function $\chi_{\text{eff}}(k) = 4\pi|\mathbf{P}(\mathbf{k})|/|\mathbf{D}(\mathbf{k})|$. This value of α allows for a maximum field of $E_0 = 0.1 \text{ V/\AA}$ [for larger fields the higher powers of \mathbf{P} should appear in Eq. (5)].

From our simulation results we also see that within the error bars the response in the small k range is still linear at these fields. However, at the resonance position ($k = 3.11 \text{\AA}^{-1}$) it is well seen that the response becomes nonlinear already for field strengths of $E_0 = 0.05 \text{ V/\AA}$. At $E_0 = 0.1 \text{ V/\AA}$ (the maximum field in the perturbation approach) it is decreased to about 80% of the linear result. Thus, the simulated response spectrum is perfectly reproduced by the mean-field theory up to the resonance k value [14].

Are our results discouraging or not for the application of the linear response theory to the screening of ions in solution? In fact, the response depends not on the overall Coulomb field of the ion [15] but rather on the separate Fourier components of the field. Thus an important criterion for the applicability of the linear response theory to the calculation of ion hydration energy

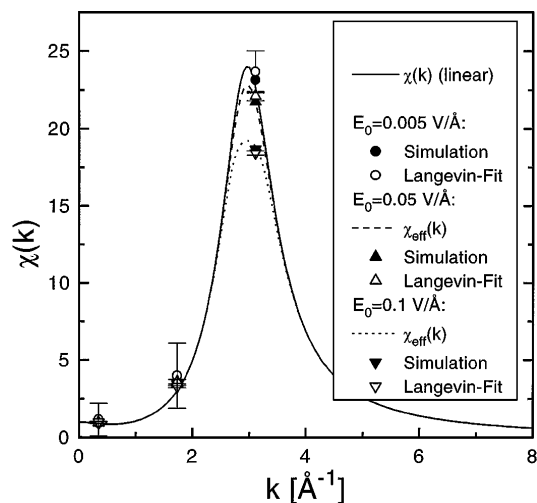


FIG. 3. Comparison of the mean-field theory result for $\chi(k)$ and the computer simulation results for a parameter $\alpha = 5 \times 10^{-4} \text{ \AA}^3/\text{eV}$. Linear response parameters are fixed as in Ref. [13].

$[E_{\text{hyd}} = -1/\pi \int_0^\infty dk \chi(k) |\rho(k)|^2]$ would be a small *overlap* of the external charge distribution $\rho(k)$ in the integrand with the resonance in $\chi(k)$; i.e., it depends on how the ion structure matches the solvent structure. If the form factor has profound contributions at the resonance k values, linear response results may become inaccurate. As was discussed in Ref. [16], the coupling between ion and solvent becomes weaker at the resonance k if the charge distribution of the ion is considered to be smeared out spatially, i.e., when it is not considered as an ideally thin charge layer (the Born sphere model [17]). Having these considerations in mind, the application of linear response may still be a good approximation in a number of situations.

In the present Letter we considered only the contribution of the diagonal elements of the response tensor. How much the off-diagonal elements will affect the so-far discussed results is still an open question. These elements will play a particularly important role, if one calculates the dielectric response for an anisotropic system, as is the case for a fixed impurity or a surface.

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*Also at The A.N. Frumkin Institute of Electrochemistry of the Academy of Sciences, 117071 Moscow, Russia. Electronic address: a.kornyshev@fz-juelich.de

†Electronic address: g.sutmann@fz-juelich.de

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