

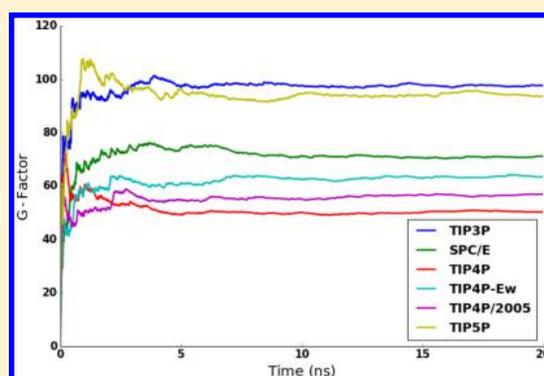
Dynamic and Electronic Polarization Corrections to the Dielectric Constant of Water

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ABSTRACT: The standard approach to calculating the dielectric constant from molecular dynamics (MD) simulations employs a variant of the Kirkwood–Fröhlich methodology. Many popular nonpolarizable models of water, such as TIPnP, give a reasonable agreement with the experimental value of 78. However, it has been argued in the literature that the dipole moments of these models are effective, being smaller than the real dipole of a liquid water molecule by about a factor of $\sqrt{\epsilon_{\text{el}}}$, or roughly $\sqrt{2}$. If the total or corrected dipole moment is used in calculations, the dielectric constant comes out nearly twice as large, i.e., in the range of 160, which is twice as high as the experimental value. Here we discuss possible reasons for such a discrepancy. One approach takes into account dynamic corrections due to the dependence of the dielectric response of the medium producing the reaction field on the time scale of dipole fluctuations computed in the Kirkwood–Fröhlich method. When dynamic corrections are incorporated into the computational scheme, a much better agreement with the experimental value of the dielectric constant is found when the corrected (real) dipole moment of liquid water is used. However, a formal analysis indicates that the static properties, such as dielectric constant, should not depend on dynamics. We discuss the resulting conundrum and related issues of simulations of electrostatic interactions using periodic boundary conditions in the context of our findings.



INTRODUCTION

In the past several decades, there has been much interest in developing methods to calculate the dielectric constant of materials, particularly water and biomolecules, from classical molecular dynamics (MD) simulations.^{1–8} Such information is critical to theoretical calculations of pKa's,⁹ solvation energy,¹⁰ and interaction potentials between the quantum mechanical and classical zones of embedded QM/MM simulations.¹¹ However, even in the case of a homogeneous, isotropic medium, calculating the dielectric properties of a material carries many subtleties. (For a recent discussion, see, e.g., ref 12.)

The original statistical dielectric response theory was developed by Kirkwood and Fröhlich^{13,14} (see the Appendix for a discussion of this theory). It considers a homogeneous medium from which a spherical sample is drawn. Fluctuations in the dipole moment of the sample can be related to the dielectric constant of the medium via the Kirkwood–Fröhlich (KF) equation

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon} = \frac{4\pi \langle \delta M^2 \rangle_{\text{KF}}}{3 V k_{\text{B}} T} \quad (1)$$

However, when calculating the dielectric constant from MD simulation, eq 1 is modified in order to account for the boundary conditions of the simulation.^{15–17} An ingenious original analysis by De Leeuw, Perram, and Smith,¹⁸ and later

Neumann and Steinhauser^{16,19} showed that if calculations are done using periodic boundary conditions (PBCs) the corresponding expression is simplified to

$$\epsilon - 1 = \frac{4\pi \langle \delta M^2 \rangle_{\text{PBC}}}{3 V k_{\text{B}} T} \quad (2)$$

This will be further elaborated upon in the theory section of this paper. This expression has become the standard method for computing dielectric constants in MD simulations. For example, to probe dielectric properties of water models, one calculates quadratic fluctuations, and because the constant is large, the right-hand side, which is sometimes called the Kirkwood factor, G , essentially gives the dielectric constant of the model. Results for typical TIPnP water models, given later in this paper (Table 2), produce results for a Kirkwood factor on the order of 70–90 (see Table 2).

We notice, however, that the model TIPnP dipole values are all in the range of 2.2–2.3 D, whereas ab initio MD calculations show that the actual average dipole moment of a liquid bulk water is around 3.0 D or even slightly higher at temperatures near 300 K.^{20–22} This difference was argued to be related to the fact that the dipole moments of models are all

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effective, being scaled by a factor of about $\sqrt{\epsilon_{\text{el}}}$ or $\sqrt{2}$ ($\epsilon_{\text{el}} \equiv \epsilon_{\infty}$ is the electronic dielectric response at high frequency) to implicitly account for the electronic screening of real charges. Therefore, if a total or corrected dipole moment of about 3.0 D were used in calculations, the Kirkwood factor in eq 2 would be twice as large, and the corresponding dielectric constant would come out roughly in the range of 160, which is twice as high as the experimental value. Here we discuss possible reasons for such a discrepancy.

The KF equation, in all of its forms, considers only the static dielectric constant and assumes, by self-consistency, that the polarization of the surrounding medium follows instantaneously the fluctuating polarization of the spherical sample. This assumption, a key subtle point of KF theory, is discussed in this paper. The discrepancy discussed above prompted us to revisit KF theory and consider again the nature of the average $\langle \delta M^2 \rangle_{\text{KF}}$ in eq 1. We show that the ambiguous nature of $\langle \delta M^2 \rangle_{\text{KF}}$ may result in a different connection of dielectric constant and dipole fluctuations simulated under PBCs than that in the usually employed eq 2. Both experiments and theory show that the dipole reorientation of water molecules has a finite time scale; therefore, the dielectric response of the medium must occur on a similar time scale.^{19,23} Here we show that a modified theory, which corrects for the finite time scale of dielectric response, gives rise to a different connection than eq 2. Our theory, inspired in part by an approach originally suggested by Neumann and Steinhauser,¹⁹ uses the frequency-dependent dielectric constant $\epsilon(\omega)$ to introduce a correction in the formula for the static dielectric constant, $\epsilon \equiv \epsilon(\omega = 0)$.

We applied our theory to study six commonly used water models: SPC/E,²⁴ TIP3P,²⁵ TIP4P,²⁶ TIP4P-Ew,²⁷ TIP4P/2005,²⁸ and TIP5P.²⁹ For the purposes of this paper, we focus our attention on PBC MD simulations using Ewald summation algorithms for the evaluation of electrostatics. We do so because, while other methods do exist, PBC MD simulations using Ewald sums have seen widespread use due to their efficiency and accuracy.

We then further analyze the obtained results within the context of KF theory of dielectric constants and in a broader context of application of Ewald summation in MD simulations and arrive at the conclusion that, while the dynamic corrections appear to help reconcile the absent electronic polarizability in nonpolarizable water models and their high dielectric constant, the problem remains open because static properties such as dielectric constant should not depend on dynamics. We discuss the resulting conundrum and related issues of simulations of electrostatic interactions using PBCs in the context of our findings. Our analysis highlights once again the difference between the artificial Ewald field and the reaction field (RF) of a real system.

THEORY

Kirkwood–Fröhlich Formalism. We begin the discussion of our theoretical model with a brief review of KF theory and its extension to PBC MD simulation using Ewald summation algorithms (including particle-mesh Ewald).⁴

Consider the thermal fluctuations in a dielectric material. Select a spherical sample from the material and assign that sample a total dipole moment M (say in direction x). Fluctuations in M are quadratic if the sample is sufficiently large, and the distribution over M is Gaussian³⁰

$$P(M) \propto e^{-M^2/2\langle M^2 \rangle} = e^{-H_{\text{eff}}(M)/k_{\text{B}}T} \quad (3)$$

where we defined the effective Hamiltonian of our system as

$$H_{\text{eff}} = \frac{M^2 (k_{\text{B}}T)}{2 \langle M^2 \rangle} \quad (4)$$

On the other hand, for polarization energy of the sample, we can write

$$H_{\text{eff}}^{(0)} = \frac{M^2}{2\alpha} \quad (5)$$

where α is polarizability of the sample. If the sample were isolated, eq 5 would be its total polarization energy. However, because the sample is actually part of the larger dielectric medium, the induced dipole M polarizes the surrounding dielectric, creating the RF, which in turn interacts with the dipole M . Thus, the effective Hamiltonian in eq 5 must be modified.

To find the RF, we make the following approximation. Assume that the dipole M is a point dipole sitting in the center of the spherical cavity occupied by the sample; alternatively, we can assume that dipole M is homogeneously distributed in the sample. In both cases, the RF of a polarized dielectric surrounding the spherical sample of radius R is

$$E_{\text{RF}} = \frac{M}{R^3} \frac{2(\epsilon - 1)}{2\epsilon + 1} = \frac{4\pi}{3} \frac{M}{V} \lambda \quad \lambda = \frac{2(\epsilon - 1)}{2\epsilon + 1} \quad (6)$$

V is the volume of the sample. This field is directed along the dipole M and “helps” to polarize the sample. The modified–reduced energy of polarization now is

$$H_{\text{eff}} = \frac{M^2}{2} \left(\frac{1}{\alpha} - \frac{4\pi}{3} \frac{\lambda}{V} \right) \quad (7)$$

The parameter λ in eqs 6 and 7 is of critical importance. It depends on the nature of the boundary conditions of the sample considered. For a sample with spherical boundary conditions, the “true” RF gives the λ_{RF} shown in eq 6. However, in the case of PBCs, as we show next, an artificial RF is produced that corresponds to a different λ . Also, if we formally assume that outside of the spherical sample the dielectric material has a different value of ϵ' , the RF will be different as well, but the form of the effective Hamiltonian will be the same, only with a different λ' that correspond to ϵ' as given by eq 6.

In PBC simulations, the simulation box is replicated in 3D space; hence, each replica box will have the same dipole M . Therefore, we can treat our system in the same manner that we would treat a homogeneously polarized dielectric of polarization density P . Because our sample was spherical, the field from the surrounding polarization was

$$E_{\text{PBC}} = \frac{4\pi}{3} P = \frac{4\pi}{3} \frac{M}{V} \quad (8)$$

Comparing this with E_{RF} , we see that the artificial field created by the image simulation boxes produces a field similar to that of the true RF E_{RF} . The only difference is that now

$$\lambda = \lambda_{\text{PBC}} = 1 \quad (9)$$

Thus, the effective Hamiltonian is the same in both PBC and RF cases and is given by eq 7. The only difference is the value of λ . From here we can derive a modified KF expression for

PBC. Rearranging terms in eq 7 using eq 4, we see that for thermal fluctuations we have

$$\langle M^2 \rangle_{\text{RF}} = \frac{k_B T}{\frac{1}{\alpha} - \frac{4\pi\lambda_{\text{RF}}}{3V}} = \frac{\langle M^2 \rangle_{\text{PBC}}}{1 + \frac{4\pi(1-\lambda_{\text{RF}})}{3Vk_B T} \langle M^2 \rangle_{\text{PBC}}} \quad (10)$$

Introducing now the Kirkwood factor G as

$$G = \frac{4\pi \langle \vec{M}^2 \rangle}{3 V k_B T} \quad (11)$$

for an isotropic dielectric, we have

$$\langle \vec{M}^2 \rangle = 3 \langle M_x^2 \rangle \equiv 3 \langle M^2 \rangle \quad (12)$$

Combining eqs 10 and 11 together with eq 6, we find

$$\frac{1}{G_{\text{RF}}} = \frac{1}{G_{\text{PBC}}} + \frac{(1-\lambda_{\text{RF}})}{3} = \frac{1}{G_{\text{PBC}}} + \frac{1}{2\epsilon + 1} \quad (13)$$

At this point, a crucial assumption is made, namely, that the Kirkwood factor calculated within a RF model (with the same ϵ outside as in the sample) G_{RF} is the same as that in eq 1 G_{KF} . The nature of this assumption is discussed in the Appendix. According to this model then

$$G_{\text{RF}} = \frac{4\pi \langle \vec{M}^2 \rangle_{\text{RF}}}{3 V k_B T} = \frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon} \quad (14)$$

By solving eq 13 for G_{PBC} , we find that

$$G_{\text{PBC}} = \frac{4\pi \langle \vec{M}^2 \rangle_{\text{PBC}}}{3 V k_B T} = \epsilon - 1 \quad (15)$$

This is the key equation that is used in computing the dielectric constant in computer simulations. This is only one specific case when the Kirkwood factor G is calculated in a model system that formally corresponds to $\lambda = 1$.

In a more general case, when the Kirkwood factor G'_{RF} is calculated for a (RF) model of a spherical sample of dielectric material ϵ , surrounded by a dielectric with different ϵ' , the connection is as follows¹⁶

$$G'_{\text{RF}} = \frac{4\pi \langle M^2 \rangle'_{\text{RF}}}{3 V k_B T} = \frac{(\epsilon - 1)(2\epsilon' + 1)}{\epsilon + 2\epsilon'} \quad (16)$$

It is seen that the above case of PBC with $\lambda = 1$ (see eq 6) indeed corresponds to formal $\epsilon' = \infty$, as was shown by the pioneers of the field using different methods.^{16,18} The above equation holds for any possible value of ϵ' , including the case of $\epsilon' = 1$ or $\epsilon' = \epsilon$. Here again the same key assumption, $G_{\text{KF}} = G_{\text{RF}}$, is made. We consider next a possibility that this key assumption is treated differently.

Frequency-Dependent Dielectric Response. In the above, we assumed that polarization of the medium instantaneously follows fluctuations of the dipole of the sample, and therefore, in the RF (eq 6), we use the same dielectric constant, ϵ , as that in the KF formula, eq 14. This is motivated by the idea of self-consistency; the dielectric constant of the spherical sample should match the dielectric constant of the surrounding material. However, this assumption can be doubted because we know that dielectric response depends on the time scale of the perturbation, $\epsilon(\omega)$. More discussion of this key point is given in the Appendix.

Suppose that actual fluctuations of the dipole occur on the time scale of ω' and the corresponding dielectric response is $\epsilon(\omega') \equiv \epsilon'$. Then, according to eq 13

$$\frac{3\epsilon}{(\epsilon - 1)(2\epsilon + 1)} = \frac{1}{G_{\text{PBC}}} + \frac{1}{2\epsilon' + 1} \quad (17)$$

This is the actual relation that can be used to calculate the static dielectric constant of the material ϵ , assuming that we know ϵ' . Consider a case when dielectric constants are large, as they are in the case of water; we then can simplify the above relation to

$$\frac{3}{2(\epsilon - 1)} \approx \frac{1}{G_{\text{PBC}}} + \frac{1}{2\epsilon'} \quad (18)$$

or

$$\epsilon - 1 \approx \frac{3\epsilon' G_{\text{PBC}}}{G_{\text{PBC}} + 2\epsilon'} \quad (19)$$

ϵ' can be obtained experimentally using dielectric spectroscopy. Figure 1 shows the dielectric response of water as a function of the driving electromagnetic field.

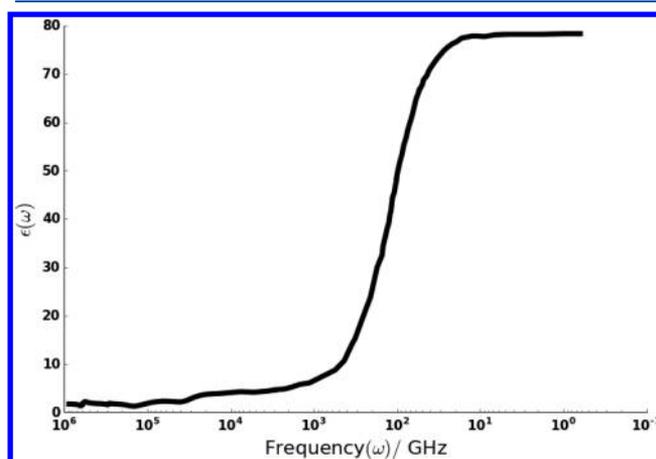


Figure 1. Dielectric response of liquid water at 300 K as a function of the frequency of the applied electric field. The data used to generate this plot was taken from Daimon et al. and Ellison et al.^{23,31}

In practice, it is difficult to assign a precise value for ω using just MD simulation. One good approximation is to use the reciprocal of the Debye relaxation time. The Debye relaxation is defined by the exponential fit to the dipole autocorrelation function

$$\Phi(t) = \frac{\langle \vec{M}(t) \cdot \vec{M}(0) \rangle}{\langle \vec{M}(0) \cdot \vec{M}(0) \rangle} = A e^{-t/\tau_D} \quad (20)$$

We will denote the special frequency corresponding the reciprocal of τ_D as ω_D .

A more theoretically accurate formula is to say that the Fourier transform of an exponential autocorrelation function is a Lorentzian probability distribution centered at around τ_D . Therefore, in order to calculate ϵ , we take the average of eq 19 using the Lorentzian weighted probability distribution

$$\epsilon = \int_0^\infty \left(1 + \frac{3\epsilon(\omega) G_{\text{PBC}}}{G_{\text{PBC}} + 2\epsilon(\omega)} \right) \cdot \frac{2}{\pi} \frac{\omega_D}{\omega_D^2 + \omega^2} d\omega \quad (21)$$

In the subsequent analysis of nonpolarizable water models with MD simulations, eq 21 was used to calculate the dynamically corrected dielectric constant. These calculations provide data for probing quantitatively the general effect of frequency-dependent response of the medium.

METHODS

For each separate water model, a 20 ns simulation was performed in an *NVT* ensemble using Langevin dynamics and a temperature of 300 K. This is in accordance with many studies that have shown that simulations in excess of 10 ns are required in order for dielectric properties to converge.^{7,32} Simulations were performed using PBCs with the particle-mesh Ewald algorithm for the evaluation of long-range electrostatics. A cutoff distance of 12 Å was employed. Each simulation box was of size 30 Å × 30 Å × 30 Å and consisted of 895 separate water molecules; this corresponds to a number density of 0.033 waters per cubic Å or alternatively 33 waters per cubic nanometer.

RESULTS

Table 1 compares the standard KF approach to calculating the dielectric constant to our dynamically corrected approach.

Table 1. Dielectric Properties and the Dynamically Corrected Dielectric Constant for All Water Models Studied^a

| water model | G_{PBC} | τ_{D} (ps) | ϵ (KF) | ϵ (dynamically corrected) |
|-------------|------------------|------------------------|-----------------|------------------------------------|
| TIP3P | 97.7 ± 1.1 | 9.4 | 98.7 | 64.52 |
| SPC/E | 71.3 ± 1.2 | 16.8 | 72.3 | 61.18 |
| TIP4P | 50.3 ± 0.8 | 9.6 | 51.3 | 44.78 |
| TIP4P-Ew | 63.4 ± 0.9 | 16.1 | 64.4 | 56.60 |
| TIP4P/2005 | 57.0 ± 0.4 | 17.3 | 58.0 | 53.44 |
| TIP5P | 93.7 ± 1.0 | 19.8 | 94.7 | 73.42 |

^aThe errors shown in G_{PBC} were estimated using the method described in Straatsma et al.³³

Note that the values presented for G_{PBC} and τ_{D} generally correspond to values found in other studies^{4,7,24–29,32} and that G_{PBC} converges well over the course of the 20 ns simulations (Figure 2). In all cases, our results show that accounting for the frequency of dielectric response significantly reduces the overall static dielectric constant.

Results of Table 1 show the substantial quantitative difference between the static and dynamic response of the medium in computing dipole fluctuations of a sample by MD simulations; the latter of course is much closer to reality than the assumed instantaneous response with a static dielectric constant. (This seemingly obvious and intuitive point will be discussed further later in the paper.) With the dynamically corrected values of the Kirkwood factor and corresponding dielectric values given in Table 1, we can now return to the question of missing electronic polarizability in water models used in our calculations as calculated values of static dielectric constant are mostly well below the experimental value of 78. This is done next.

We first recall the following. All nonpolarizable water models, including the ones used in this study, are reported to have significantly lower dipole moments (Table 2) than what is measured in experimental and ab initio studies, where the dipole moment of water is reported to be around 3.0 D.³⁴ Previous work by Leontyev and Stuchebrukhov^{35–37} has

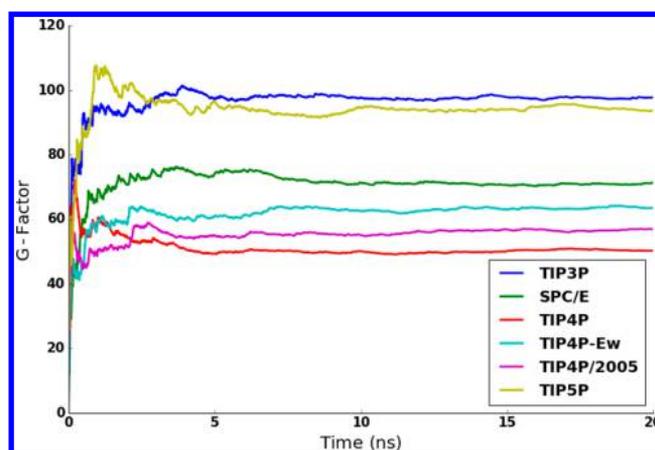


Figure 2. Convergence of G_{PBC} for simulations of all water models studied.

Table 2. Dipole Moments of Water Models and Results of Scaling G_{PBC} by $\epsilon_{\text{el}} = 1.78$ in Accordance with the Missing Electronic Polarizability of Water Models^a

| water model | μ^{eff} (D) | G_{PBC} | $G_{\text{PBC}}^{\text{scaled}}$ | ϵ | ϵ scaled |
|-------------|------------------------|------------------|----------------------------------|------------|-------------------|
| TIP3P | 2.35 | 97.7 | 173.9 | 64.52 | 82.68 |
| SPC/E | 2.35 | 71.3 | 126.8 | 61.18 | 83.42 |
| TIP4P | 2.18 | 50.3 | 89.6 | 44.78 | 62.06 |
| TIP4P-Ew | 2.32 | 63.4 | 112.9 | 56.60 | 78.14 |
| TIP4P/2005 | 2.31 | 57.0 | 101.5 | 53.44 | 74.93 |
| TIP5P | 2.29 | 93.7 | 166.8 | 73.42 | 97.20 |

^aThe ϵ scaled column corresponds to results of using G_{PBC} scaled in eq 19.

shown that the dipole moment of water models can be thought of as an effective value, $\mu^{\text{eff}} = \mu_1 / \sqrt{\epsilon_{\text{el}}}$, where μ_1 is the true dipole moment of liquid water and $\epsilon_{\text{el}} = 1.78 \approx \sqrt{2}$ is the electronic, high-frequency dielectric constant of water. (The exact scaling factor is difficult to pinpoint as it depends on the model of interaction of the dipole moment with the polarizable electronic continuum.³⁶)

Because the effective dipole moment of water in MD models is indeed significantly lower than the experimental dipole moment, one would expect that the dielectric constant should be lower as well. While the standard KF formalism does not give such results, taking into account dielectric response time with dynamic corrections does.

It is noteworthy that the dependence of dielectric constant on the Kirkwood factor in the dynamically corrected eq 19, unlike eq 15, is sublinear, which means that if one simply scales G_{PBC} by a factor of $\epsilon_{\text{el}} = 1.78$ this does not scale the dielectric constant in eq 19 by the same value. Indeed, Table 2 demonstrates this sublinear dependence. Now, as we correct (scale) the Kirkwood factor by the value of electronic polarizability $\epsilon_{\text{el}} = 1.78$, the resulting dielectric constant is in much better agreement with the experimental value. Thus, it appears that the dynamic corrections provide a solution to the problem of accounting for the missing electronic polarizability in dielectric constant calculations using nonpolarizable water models.

DISCUSSION

Dynamics Correction. Our computational results demonstrate several important points. First, the simulations with

PBCs and Ewald treatment of electrostatic interactions produce fluctuations of the dipole moment of the sample $\langle \delta M^2 \rangle_{\text{PBC}}$, measured here as the Kirkwood factor G_{PBC} , that are quite different from the “real” fluctuations, G_{KF} , which are physically related to those evaluated with the RF model, G_{RF} . The difference is due to the artificial character of the Ewald field acting on a sample, which is similar to the RF, but corresponds to the environment with dielectric constant $\epsilon' = \infty$; see eq 16 and related comments. Numerically the difference for water is a factor of about 3/2, as seen in comparison of eqs 1 and 2. Indeed, if both equations are correct, the PBC Kirkwood factor G_{PBC} (see Table 2) and the “real” G_{KF} are different by a factor of about 3/2.

For quadratic fluctuations of the dipole moment, theory provides a simple relation between G_{PBC} and G_{RF} , which allows connection to the artificial fluctuations G_{PBC} and the real dielectric constant, expressed by eq 2. In this connection, however, we make a subtle assumption that the real fluctuations G_{KF} are the same as those calculated with the instantaneous RF of the static dielectric constant ($\epsilon' = \epsilon$ in eq 16). This instantaneous character of the response, in general, is also questionable because the response of the medium is obviously time-dependent.

Second, our calculations in the previous section clearly demonstrate the substantial difference for water between the static and time-dependent response. The latter is obviously more closely related physically to a typical real system of interest: a sample surrounded by the material, of which dielectric response depends on the time scale of perturbation. Yet, for specific calculations of the static dielectric constant, the role of dynamics is not at all clear as we specifically evaluate response to an infinitely slow (i.e. static) perturbation. Although we run MD for calculation of the average quadratic fluctuations and dynamics does depend on the type of response of the surrounding medium to our sample, the question still remains as to whether it is what we need to calculate for this specific problem. The problem is not at all straightforward and requires detailed analysis of what we are actually evaluating. This analysis for clarity purpose is given separately in the Appendix (which is in fact an essential part of this paper). The conclusion of this analysis is as follows.

Although our dynamic corrections do help to incorporate the missing electronic polarizability into nonpolarizable models and achieve agreement with experiment, the analysis shows that formally the static dielectric response cannot depend on the time scales of the system and hence on its dynamics (therefore, e.g., Monte Carlo simulations can be used and indeed are preferred in this case). One can argue that the static response should not depend on the masses of the medium particles, which define the time scales of the dynamics. This puts into question the approach with dynamic corrections that provided so nicely the sought agreement between the experimental value of the total static dielectric constant that includes electronic polarization of the medium and non-polarizable models, which are lacking this important polarization component. It appears therefore that the agreement with experiment achieved in the dynamically corrected model is fortuitous. Although the need to include the time-dependent nature of the response of the medium surrounding the simulated sample seems to be obvious and natural for most simulations, for static properties this is not the case. If so, our attempt to incorporate the missing electronic polarizability into dielectric constant calculations using nonpolarizable models

cannot be considered satisfactory, and the problem appears to be still open.

Electronic Polarization Correction. It is interesting to mention that exactly the same problem of incorporating electronic polarizability within a continuum approach was already considered by Fröhlich in his classic “Theory of Dielectrics”.³⁸ One modification of eq 1 is eq 7.38 of his text, reproduced in our Appendix. We then ask how the connection with PBC should look if modified eq 1 is used. We address this next.

If we assume that the dipoles (these are real average dipoles of the molecule, not scaled ones as in TIPnP models) are moving in an electronic continuum with dielectric constant ϵ_{el} , as was shown by Fröhlich³⁶, electronic polarizability modifies eq 1 to become

$$\frac{(\epsilon_0 - \epsilon_{\text{el}})(2\epsilon_0 + \epsilon_{\text{el}})}{3\epsilon_0} = \frac{4\pi}{3Vk_{\text{B}}T} \left\langle \left(\sum \vec{p}_i \right)^2 \right\rangle_0 \quad (22)$$

It is noticed that when the total dielectric constant ϵ_0 is large the difference between this and the original eq 1 equation is not substantial. However, let us now see how the same electronic polarization effects modify eq 2.

In the analysis, we need now to assume that the RF of eq 6 is calculated in a model of a spherical cavity with the total static dielectric constant outside and electronic ϵ_{el} inside. In this case, the RF modifies to give parameter $\lambda_{\text{RF}}^{\text{pol}}$ instead of eq 6

$$\lambda_{\text{RF}}^{\text{pol}} = \frac{2(\epsilon_0 - \epsilon_{\text{el}})}{2\epsilon_0 + \epsilon_{\text{el}}} \frac{1}{\epsilon_{\text{el}}} \quad (23)$$

and the corresponding relation between G_{PBC} and G_{RF} , replacing eq 13, turns out to be as follows

$$\frac{1}{G_{\text{RF}}} = \frac{1}{G_{\text{PBC}}} + \frac{1}{2\epsilon_0 + \epsilon_{\text{el}}} \quad (24)$$

After substitution into the above relation for the corrected expression for G_{RF} , we arrive at the following connection between G_{PBC} and dielectric constants

$$(\epsilon_0 - \epsilon_{\text{el}}) = G_{\text{PBC}} = \frac{4\pi}{3Vk_{\text{B}}T} \left\langle \left(\sum \vec{p}_i \right)^2 \right\rangle_{\text{PBC}} \quad (25)$$

Thus, the only difference compared with eq 2 is that electronic contribution is present explicitly. The above equation provides the link between the polarizable and non-polarizable models. Namely, if electronic polarization in eq 2 is formally treated as an independent high-frequency oscillator, then the fluctuations of this collective electronic polarizability mode give an additive contribution to the total G -factor, which is obviously equal to ϵ_{el} . The remaining “nuclear” G -factor is present explicitly in eq 25.

From the derivation, it follows that the dipoles in the G factor here are actual unscaled full dipoles. Again, these dipoles (the average dipoles in the system) are presumably higher than the effective TIPnP dipoles; therefore, the problem remains still open, as the G factor calculated with the effective dipoles for most of the models is already sufficiently high and does not permit any further up-scaling.

To elaborate eq 25 a bit further, we note again that in the above equation the fluctuations of “real” unscaled dipoles are described; however, their dynamics is calculated in the presence of an electronic continuum, as follows from the model. If we assume now that scaling of individual dipoles is

given by factor of $\sqrt{\epsilon_{\text{cl}}}$, the G factor of scaled effective dipoles, i.e., that of dipoles that actually participate in MD calculations (i.e., the actual dipoles of TIPnP models) \tilde{G}_{MD} , is different from that in eq 25 by a factor of ϵ_{cl} . Therefore, in terms of scaled dipoles, the expression for the dielectric constant assumes the following form (PBCs are assumed)

$$\begin{aligned}\epsilon_0 &= \epsilon_{\text{cl}} \tilde{\epsilon}_{\text{MD}}, \\ \tilde{\epsilon}_{\text{MD}} &= 1 + \tilde{G}_{\text{MD}}\end{aligned}\quad (26)$$

As we saw above, the TIPnP models produce directly \tilde{G}_{MD} in the range of 80–90; therefore, the additional scaling by a factor of ϵ_{cl} , as the above expression suggests, brings the actual dielectric constant much above the experimental value.

CONCLUSIONS

Following an approach originally suggested by Neumann and Steinhäuser,¹⁹ we modified the traditional KF dielectric theory to account for the time scale τ_{D} of dielectric response between the spherical sample and the surrounding medium. Doing so gives us an equation that corresponds to the original KF equation in the limit where the dielectric relaxation time τ_{D} is sufficiently slow but can differ drastically when τ_{D} is sufficiently fast. Applying this modified theory to several of the most commonly used water models gives a calculated dielectric constant lower than what is experimentally measured. The lower dielectric constant would be in accordance with the fact that nonpolarizable models leave out electronic polarizability, which scales the square dipole moment of the water model by approximately a factor of $\epsilon_{\text{cl}} = 1.78$, and thus increase overall dielectric constant of a model.

However, despite the success of improved theory with regard to accounting for the missing electronic polarizability in nonpolarizable models, the key assumption of the theory about the nature of the RF acting in the sample is admittedly difficult to rationalize without more detailed theory. Here we made a natural intuitive assumption that the time-dependent response of the medium should be included, which helps to resolve the electronic polarizability issue; however, theoretically, the standard assumption of static response appears to be the only valid approach, but it results in a grossly overestimated dielectric constant when electronic polarizability is taken into account.

We then considered a modification of the theory that includes electronic polarizability explicitly, although we treated it only within a continuum phenomenological model. This model does not appear to provide explanation for the scaling nature of the effective dipoles of TIPnP models.

That the effective water models fit the experimental dielectric constant directly appears intuitively attractive and practical; however, one needs to remember that the charges of the effective models are different from the actual (average) charges of the molecules in liquids; thus Coulombic interactions with other charges, such as Na^+ or Cl^- , which are usually described with their true $+/-$ unit charges, are set incorrectly. Obviously, one cannot fit both correct charges and the dielectric constant within the same fixed-charge model, unless a more elaborate charge-scaling scheme, i.e., eq 26, is used. However, it appears that this is not the case for TIPnP models. We therefore conclude that to finally resolve these issues more studies of nonpolarizable fixed-charge models are still needed.

An alternative approach, of course, is to use polarizable modes, where the problem does not seem to appear.

APPENDIX

Fröhlich's Derivation. A Discussion

Fröhlich's argument is as follows. Suppose in a homogeneous dielectric medium that the total (microscopically averaged) electric field is E ; then the microscopically averaged polarization of a unit volume is

$$P = \frac{\epsilon - 1}{4\pi} E = \frac{1}{Z} \int \left(\sum \vec{p}_i \right) \exp \left(- \frac{H_0 - (\vec{G} \cdot \sum \vec{p}_i)}{k_{\text{B}} T} \right) d\Gamma \quad (27)$$

where we imagine a unit volume sample, dipoles in the sample are \vec{p}_i , and the averaging on the right-hand side is over phase-space configurations (Γ) whose energies are described by Hamiltonian H_0 and by interaction of the dipoles with the electric "cavity" field \vec{G} , which is not the same as the total electric field \vec{E} as total electric field already includes that of the polarized dipoles of the sample \vec{p}_i . Thus, we need to establish the relation between \vec{G} and \vec{E} . In a linear approximation (weak fields), obviously, \vec{G} and \vec{E} are linearly related, i.e.

$$G = \kappa E \quad (28)$$

so that the following expansion of the Boltzmann's exponent in small G , assuming no polarization in the absence of the field, gives the right-hand side linearly proportional to E , and after cancellation of E on both sides, one obtains the relation between the dielectric constant and the quadratic fluctuation of the total dipole moment of the sample

$$\frac{\epsilon - 1}{\kappa} = \frac{4\pi}{3Vk_{\text{B}}T} \left\langle \left(\sum \vec{p}_i \right)^2 \right\rangle_0 \quad (29)$$

where the averaging on the right-hand side is over Hamiltonian H_0 of the dipoles of the sample, now of volume V ; the factor of 3 is due to dimensionality (3D) of averaging, and the factor of κ is from the above relation between G and E .

The factor of κ is determined as follows. The total electric field E in the sample consists of the following contributions: (1) "cavity" field G , (2) the field of the polarized dipoles of the sample, and (3) RF of the polarized dielectric around the sample by the dipole of the sample. If we imagine that the sample is spherical, then the last two contributions are easy to evaluate, and one finds that

$$G = E + \frac{4\pi}{3} P - \frac{4\pi}{3} \frac{2(\epsilon - 1)}{2\epsilon + 1} P = \frac{3\epsilon}{2\epsilon + 1} E \quad (30)$$

The first term on the right-hand side that modifies E is the field of the homogeneously polarized sphere (inside of the sphere; it is directed opposite of E ; thus we add it to get G), and the second term is the RF inside of the sample of the polarized dielectric around the spherical sample (it is directed along E ; thus we subtract it). Thus, the factor is $\kappa = 3\epsilon/2\epsilon + 1$, and we find the Fröhlich relation

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon} = \frac{4\pi}{3Vk_{\text{B}}T} \left\langle \left(\sum \vec{p}_i \right)^2 \right\rangle_0 \quad (31)$$

which connects quadratic fluctuations of the dipole moment of the sample to the dielectric constant of the material.

As was shown by Fröhlich in his classic text “Theory of Dielectrics”³⁶, electronic polarizability modifies the above expression to become

$$\frac{(\varepsilon - \varepsilon_{\text{el}})(2\varepsilon + \varepsilon_{\text{el}})}{3\varepsilon} = \frac{4\pi}{3Vk_{\text{B}}T} \left\langle \left(\sum \vec{p}_i \right)^2 \right\rangle_0 \quad (32)$$

It is noticed that when the dielectric constant is large the difference between this and the previous equation is not that important.

Computer simulations can now be used to find the latter, and thus, the dielectric constant can be determined. As the dielectric constant of the isotropic material cannot depend on the sample shape, provided that it is large enough, in simulations one can use an arbitrary shaped sample, although the derivation above is based on the spherical assumption.

However, there still remains one subtle and crucial point in the above expression that needs to be clarified. Namely, what actually is H_0 over which we are averaging the dipole fluctuations of the sample? H_0 determines the dynamics of the dipoles and thus is crucial for simulations.

According to the construct of the method, the sample is part of the infinite homogeneous material; thus, the molecules and dipoles of the sample interact not only between themselves but also with the surrounding medium, which is not simulated explicitly. This is a crucial point of the method as the interaction of the sample with the rest of the medium is not small and is in fact of the same order as interactions between the molecules within the sample. Qualitatively, the interaction of the sample with the medium is divided into two parts; first, there is a boundary effect, which involves short-range interactions and that can be neglected if sample is big enough, and second, there is polarization of the medium outside of the sample, which produces RF with which the dipoles of the sample interact. The surrounding medium effect therefore should be implicitly included in H_0 . This is a fundamental feature of the model as we are trying to write the Hamiltonian of the sample that is not isolated but part of the infinite medium with strong long-range electrostatic interaction. We focus now on this second polarization interaction, neglecting other boundary effects, assuming that they are small.

The polarization interaction of the sample dipoles with the surrounding medium is subtle as the medium has the same unknown dielectric constant that we are trying to determine; thus, the procedure should be self-consistent. Moreover, the dielectric response depends on the time scale of the perturbation: for high frequencies and short time scales, the dielectric response of the medium is only due to electronic polarization, which corresponds to the dielectric constant at high frequencies, $\varepsilon_{\infty} \equiv \varepsilon_{\text{el}}$; for the long-time scale, the static dielectric response occurs with static dielectric constant ε_0 . Thus, the time scale of dipole fluctuations of the sample will determine the response of the surrounding medium. This of course only means that the dielectric constant of the sample is frequency-dependent $\varepsilon(\omega)$ and in a rigorous procedure should be self-consistently determined as such.¹⁹

On the other hand, one can argue that because the static dielectric constant is evaluated, the mean polarization of the medium should occur infinitely slowly; thus, the external medium would respond with the static dielectric constant ε_0 , and thus, the external dielectric ε_0 should be assumed for the medium surrounding the sample. It appears that qualitatively and intuitively one can argue both ways.

All of these uncertainties are due to the fact that we are trying to describe dynamics of a sample that is *strongly* coupled to the external medium; naturally, this cannot be done exactly, and therefore, some model assumptions have to be introduced. The idea of self-consistency is natural and simple and stems from the fact that the medium is homogeneous and that our sample is the same as the surrounding medium. However, the nature of the *effective* Hamiltonian of the sample H_0 is not that clear and thus is a subject of approximations, which in turn depend on the nature of the question that we ask.

It is appropriate therefore to call the effective Hamiltonian of the sample H_0 the Kirkwood–Fröhlich (KF) Hamiltonian, H_{KF} , and write for corresponding averaging $\langle \dots \rangle_{\text{KF}}$, as we did in the main text.

It appears that, at least in linear approximation, the average of the square of the dipole moment is calculated with the Hamiltonian H_0 that is not restricted by the nature of the external perturbation but rather by the dynamical nature of the sample itself; naturally, the dynamics of the sample, not the time scale of external perturbation, will determine the effective interaction with the surrounding medium. Thus, it is natural to think that the response should depend on the time scale of the dynamics of the sample dipoles.

On the other hand, formally, one can argue that the corresponding conjugated momenta of the dipoles in the integral (eq 27) (where $d\Gamma$ involves both dipoles, i.e., generalized coordinates, and their conjugated momenta) will be integrated out, and after that, only configurations of dipoles with their energies will remain. In this case, we tacitly assume a formal infinite lifetime of the configurations or infinite time scale of external perturbation, and therefore, the static dielectric response of the surrounding medium will determine the energy of configurations over which we average dipoles of the sample. However, this is only when we assume that the surrounding medium effect does not depend on the conjugated momenta of the sample dipoles, which is obviously not true as the medium response depends on the time scale of motion of the sample dipoles. Formally, it means that the effective interaction of the dipoles in the sample depends on their conjugated momenta, and the seemingly simple “integrating out” is not possible. On the other hand, one can assume that the integration out of the conjugated momenta is done *before* the separation of the sample and the rest of the medium is done. Formally, it is not clear which procedure actually should be employed. However, it is clear from more general considerations that the static properties of the system, such as the static dielectric constant, should not depend on dynamics.

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