

Computing the Kirkwood g -Factor by Combining Constant Maxwell Electric Field and Electric Displacement Simulations: Application to the Dielectric Constant of Liquid Water

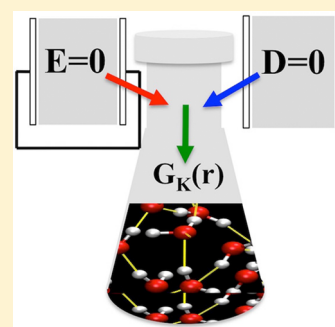
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S Supporting Information

ABSTRACT: In his classic 1939 paper, Kirkwood linked the macroscopic dielectric constant of polar liquids to the local orientational order as measured by the g -factor (later named after him) and suggested that the corresponding dielectric constant at short-range is effectively equal to the macroscopic value just after “a distance of molecular magnitude” [Kirkwood, *J. Chem. Phys.*, **1939**, 7, 911]. Here, we show a simple approach to extract the short-ranged Kirkwood g -factor from molecular dynamics (MD) simulation by superposing the outcomes of constant electric field E and constant electric displacement D simulations [Zhang and Sprik, *Phys. Rev. B: Condens. Matter Mater. Phys.*, **2016**, 93, 144201]. Rather than from the notoriously slow fluctuations of the dipole moment of the full MD cell, the dielectric constant can now be estimated from dipole fluctuations at short-range, accelerating the convergence. Exploiting this feature, we computed the bulk dielectric constant of liquid water modeled in the generalized gradient approximation (PBE) to density functional theory and found it to be at least 40% larger than the experimental value.



The static dielectric constant, ϵ , of a polar liquid is related to the thermal equilibrium fluctuations of the polarization at zero field.¹ Polarization fluctuations are long-range and vary with the shape of the dielectric body. ϵ , on the other hand, is an intrinsic response coefficient independent of geometry. This led Kirkwood to postulate that it should be possible to express ϵ in terms of a short-range orientational correlation function.² Extending Onsager’s local field approach,³ Kirkwood derived the relation

$$\frac{4\pi\beta N\mu^2 g_K}{\Omega} = \frac{(\epsilon - 1)(2\epsilon + 1)}{\epsilon} \quad (1)$$

N is the number of polar molecules in a system of volume Ω . μ is the value of the dipole of a molecule in the liquid. β , as usual, denotes the inverse temperature. The orientational correlations are contained in a single number, the Kirkwood g -factor, g_K .

Setting $g_K = 1$ in eq 1 recovers Onsager’s mean field approximation.³ For correlated polar liquids, g_K is obtained as the asymptotic value of the r -dependent Kirkwood g -factor

$$G_K(r) = \langle \mu_1 \cdot \mathbf{M}_1(r) \rangle / \mu^2 \quad (2)$$

where μ_1 is the dipole of a reference molecule, 1, at the center of a sphere of radius r . $\mathbf{M}_1(r)$ is the sum total of dipoles μ_i in the sphere (including the dipole of molecule 1). Local orientational correlations are averaged out by thermal motion after the first few coordination shells. Hence, Kirkwood argued that $G_K(r)$ should approach a constant g_K beyond a certain distance r_K (the Kirkwood correlation length); therefore, $g_K = G_K(r)|_{r \geq r_K}$. As he commented in the original 1939 paper, “ r_K is a

distance of molecular magnitude beyond which the local dielectric constant in the neighborhood of an arbitrary molecule is effectively equal to the macroscopic dielectric constant”.² The short-range character of $G_K(r)$ was demonstrated by integral equation theory for the simplest of models for dipolar fluids: hard spheres with a point dipole fixed at the center.^{4–7} This relation can be shown to hold for any point dipole system assuming that the dielectric constant is local.⁸

The practice of dielectric constant calculation in computer simulation is however very different. Rather than determining the asymptotic value of the r -dependent Kirkwood function (eq 2), ϵ is estimated from the fluctuations of the volume dipole \mathbf{M} , i.e., the dipole moment of the entire periodic model system cell. This is a crucial distinction, and it took some time before the question of the relation between the fluctuations of \mathbf{M} and ϵ was settled.^{9–11} The procedure depends on the scheme that is used for the evaluation of the long-range electrostatic interactions. The appropriate equation for the commonly used Ewald summation method is

$$\frac{4\pi\beta}{3\Omega} (\langle \mathbf{M}^2 \rangle_{E=0} - \langle \mathbf{M} \rangle_{E=0}^2) = \epsilon - 1 \quad (3)$$

where $\Omega = L^3$ is the volume of the cubic cell of length L . Analysis of the conditional convergence of Ewald summation also established that the effective electrostatic boundary

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conditions for the bare Ewald sum (no surface term) are equivalent to setting the $\mathbf{k} = 0$ component of the macroscopic electric field \mathbf{E} to zero, as indicated in eq 3 by the subscript $\mathbf{E} = 0$. These boundary conditions are often interpreted as wrapping the dielectric body in metal foil.^{9–11} This is a key difference with eq 1 which applies to an infinite system without boundaries which can be formally compared to a system under zero external electric field, $\mathbf{E}_0 = 0$.^{8,12}

The thermodynamic conjugate of the macroscopic electric field \mathbf{E} is not the external field \mathbf{E}_0 but the dielectric displacement field \mathbf{D} .¹³ $\mathbf{D} = 0$ constraints generate therefore a third electrostatic ensemble in addition to the $\mathbf{E} = 0$ and $\mathbf{E}_0 = 0$ ensembles. Polarization fluctuations can be expected to be different again.

Indeed, the counterpart to eq 3 is

$$\frac{4\pi\beta}{3\Omega}(\langle \mathbf{M}^2 \rangle_{\mathbf{D}=0} - \langle \mathbf{M} \rangle_{\mathbf{D}=0}^2) = \frac{\epsilon - 1}{\epsilon} \quad (4)$$

The fluctuation expression eq 4 was derived in a previous publication¹⁴ applying linear response theory to the constant \mathbf{D} Hamiltonian proposed by Stengel, Spaldin, and Vanderbilt (SSV).¹⁵ We verified that the polarization fluctuations obtained from a $\mathbf{D} = 0$ simulation, when substituted in eq 4, yield a static dielectric constant of SPC/E in good agreement with the estimate obtained from eq 3.¹⁴

Convergence of the $\mathbf{E} = 0$ fluctuation $\langle (\Delta \mathbf{M})^2 \rangle$ in eq 3 is notoriously slow. Computation of ϵ of liquid water requires MD runs on the nanosecond time scale. Reducing these computational costs was part of the motivation for studying $\mathbf{D} = 0$ liquid water in ref 14. We argued that the relaxation time of the $\mathbf{D} = 0$ fluctuations, corresponding to longitudinal polarization modes, can be expected to be a factor ϵ faster compared to the relaxation time of $\mathbf{E} = 0$ fluctuations which have transverse character. This was born out by the calculations.¹⁴ However, the computational effort for the determination of ϵ essentially remained the same. The reason is that the statistical accuracy in $\langle (\Delta \mathbf{M})^2 \rangle$ in eq 4 must be proportionally higher, which cancels the gain in relaxation time.

The slow relaxation times of polarization fluctuations are generally attributed to the long-range character of dipole–dipole interactions.^{7,8} However, the long-range component has been eliminated in the distance-dependent Kirkwood factor $G_K(r)$ of eq 2, which is short-range. This observation suggests that this property can possibly be exploited in an efficient scheme for computing ϵ . Unfortunately, $G_K(r)$ is only short-range in the infinite system. The boundary conditions applied in simulation reintroduce long-range effects, as has been demonstrated in a number of studies.^{16–20} The results for SPC/E water shown in Figure 1 are typical of this behavior. Neither the $\mathbf{E} = 0$ or $\mathbf{D} = 0$ curves reach a plateau value at molecular distances.

The divergence between the $\mathbf{E} = 0$ and $\mathbf{D} = 0$ Kirkwood factor with distance (Figure 1) was explained by Caillol, who derived an analytical expression for the long-range component in $G_K(r)$.²¹ The effect of a change of boundary conditions was treated in the formalism of De Leeuw, Perram, and Smith⁹ (LPS). Electrostatic boundary conditions are imposed by embedding a large spherical cluster of identical cells in a continuum of dielectric constant ϵ' . The expression obtained by Caillol is valid for distance $r > r_K$ (the Kirkwood correlation length) and can be written as

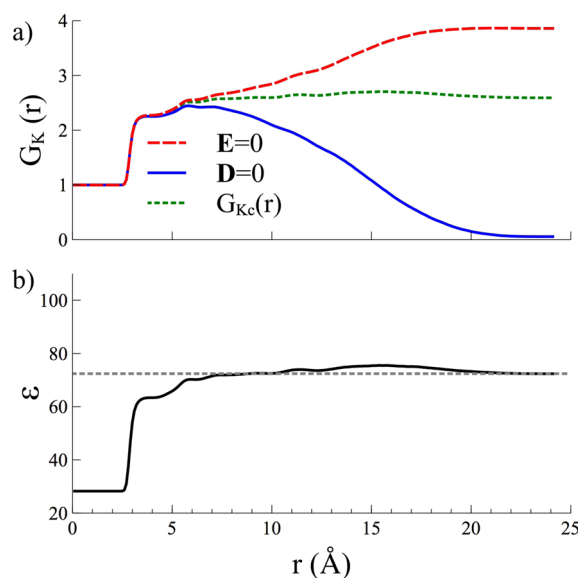


Figure 1. (a) r -dependent composite Kirkwood g -factor, $G_K(r)$, of SPC/E water (green curve) calculated by combining $\mathbf{E} = 0$ (red curve) and $\mathbf{D} = 0$ (blue curve) calculations according to eq 8. (b) The effective r -dependent dielectric constant obtained from $G_K(r)$ using eq 1 (solid curve) compared to ϵ estimated from the volume dipole fluctuation at $\mathbf{E} = 0$ using eq 3 (dashed line). The box length is 27.7 Å.

$$\frac{4\pi\beta N\mu^2 G_K(r)}{\Omega} = \frac{(\epsilon - 1)(2\epsilon + 1)}{\epsilon} + \frac{(\epsilon - 1)^2}{\epsilon} \frac{2(\epsilon' - \epsilon)}{2\epsilon' + \epsilon} \frac{\nu(r)}{\Omega} \quad (5)$$

$\nu(r)$ is the volume of the sphere defining $\mathbf{M}_1(r)$ in eq 2. For $\epsilon' = \epsilon$, the r -dependent term in eq 5 vanishes and the Kirkwood–Onsager formula is recovered ($G_K(r) = g_K$). For $\epsilon' > \epsilon$, the long-range interaction adds a positive bias unless the cell size is sufficiently large so that $G_K(r)$ reaches the asymptotic limit well before the bias sets in ($\nu(r_K) \ll \Omega$). The bias turns negative for $\epsilon' < \epsilon$. This effect has been actually observed for the Stockmayer fluid for which ϵ can be computed to high accuracy.¹¹ $G_K(r)$ is virtually constant after three neighboring shells. The dielectric constant can therefore in principle be estimated by iterating in ϵ' . However, this procedure is feasible only for simple models such as the Stockmayer fluid.¹¹

The validity of eq 5 is not restricted to spherical volumes $\nu(r)$ but also applies when the integration defining $\mathbf{M}_1(r)$ in eq 2 is extended beyond $r = L/2$. In that case, only the volume of the intersection of the sphere and cubic cell is included.²¹ The maximum value of r is therefore $\sqrt{3}L/2$ when integration is over the entire box. In this limit, $\mathbf{M}_1(r) = \mathbf{M}$ and $\nu(r)/\Omega = 1$.

Ultimately, eq 5 is based on the LPS Hamiltonian which is of the form^{9,21,22}

$$\mathcal{H} = \mathcal{H}_{\text{PBC}} - \frac{\Omega}{2} \mathbf{E}_p \cdot \mathbf{P} \quad (6)$$

\mathcal{H}_{PBC} is the standard Ewald Hamiltonian. Transformed to a reciprocal space sum, the $\mathbf{k} = 0$ term is missing. The $\mathbf{k} = 0$ contribution is added in by the second term. $\mathbf{P} = \mathbf{M}/\Omega$ is the uniform polarization density. \mathbf{E}_p is the polarization field generated by \mathbf{P} modified (“screened”) by the electrostatic boundary conditions.

$$\mathbf{E}_p = -\frac{4\pi}{2\epsilon' + 1} \mathbf{P} \quad (7)$$

In the LPS view, $-\mathbf{E}_p \cdot \mathbf{P}/2$ is interpreted as a “surface” term (for the reaction field view, see ref 11). For $\epsilon' = \infty$ (metallic medium), the polarization field vanishes leaving only \mathcal{H}_{PBC} in eq 6.^{9–11} The polarization field is canceled by the charges induced in the surrounding “virtual” metal electrode at infinity.

Substituting $\epsilon' = \infty$ in eq 5 with $\nu(r) = \Omega$ yields an expression for ϵ consistent with eq 3 (provided $\langle \mathbf{M} \rangle = 0$). For a system under $\mathbf{E} = 0$ constraints, eq 5 interpolates between the short-range orientational correlations at $r = r_K$ and the fluctuations of the volume dipole \mathbf{M} . This relation also holds for a $\mathbf{D} = 0$ system if we identify zero electric displacement with an embedding medium of dielectric constant $\epsilon' = 0$. While seemingly unphysical, $\epsilon' = 0$ boundaries have been shown to be pertinent to simulation of electrolyte solution.²³ Inserting $\epsilon' = 0$ in eq 7, we obtain $\mathbf{E}_p = -4\pi\mathbf{P}$. For $\epsilon' = \infty$, depolarization is complete ($\mathbf{E}_p = 0$). For $\epsilon' = 0$, there is no depolarization at all.¹⁴ The full polarization field couples to the polarization. Inserting in eq 6 we find that the $\epsilon' = 0$ LPS Hamiltonian is identical to the $\mathbf{D} = 0$ SSV Hamiltonian. Consistent with $\epsilon' = 0 \leftrightarrow \mathbf{D} = 0$ mapping, Caillol's eq 5 is equivalent to eq 4 for $\epsilon' = 0$ and $\nu(r) = \Omega$. The thermodynamic foundation of the SSV Hamiltonians^{14,15} conveys therefore a physical significance to an $\epsilon' = 0$ environment.

We are now ready to introduce the equation used in the calculation. This is a superposition of the correlation function eq 2 evaluated under $\mathbf{E} = 0$ and $\mathbf{D} = 0$ conditions.

$$G_{\text{Kc}}(r) = \frac{1}{3}(2G_{\text{K}}(r)_{\mathbf{E}=0} + G_{\text{K}}(r)_{\mathbf{D}=0}) \quad (8)$$

With $\epsilon' = \infty \leftrightarrow \mathbf{E} = 0$ and $\epsilon' = 0 \leftrightarrow \mathbf{D} = 0$ mapping, it can be inferred from eq 5 that long-range contributions cancel in the composite Kirkwood factor $G_{\text{Kc}}(r)$ of eq 8. $G_{\text{Kc}}(r)$ should level off to an r -independent constant at distances comparable to molecular length scales. Equation 8 gives us therefore computational access to the short-ranged Kirkwood g -factor without the need for prior knowledge of ϵ .

To validate this prediction, we performed MD simulations of liquid water at ambient conditions for the SPC/E water model²⁴ using a modified version of GROMACS 4 package.²⁵ Technical settings are as described in our previous work.¹⁴ As shown in Figure 1a, $G_{\text{Kc}}(r)$ obtained according to eq 8 is indeed short-ranged. It is effectively constant beyond $r = 6$ Å. This distance corresponds to the second minimum of the oxygen–oxygen radial distribution function of SPC/E water. The $G_{\text{Kc}}(r)$ plot can be represented as an effective r -dependent dielectric constant by inverting eq 1. The result is shown in Figure 1b. For comparison, the estimate obtained from the fluctuations of the volume dipole \mathbf{M} at $\mathbf{E} = 0$ (eq 3) is also given. These two estimates should coincide at $r = \sqrt{3}L/2 = 24.0$ Å where $\mathbf{M}_1(r) = \mathbf{M}$. The r -dependent ϵ reaches its bulk value already after the second coordination shell. Our results conform therefore to Kirkwood's rule that the dielectric constant is determined by short-range orientational correlations.

For further confirmation, the calculations were extended to a variety of nonpolarizable and polarizable water models, including SPC,²⁶ TIP3P,²⁷ TIP4P,²⁷ and SWM4-DP.²⁸ The appropriate generalizations of eqs 2–4 for polarizable models can be found in the Supporting Information. The simulations were carried out at the same conditions as for SPC/E water, in particular density and box size. The general trend is similar to what is shown in Figure 1 (see Figures S1–S4 in the Supporting Information). $G_{\text{Kc}}(r)$ is effectively constant beyond a molecular length with the corresponding r -dependent

dielectric constant equal to the bulk value. The mean absolute error of the dielectric constant calculated from $G_{\text{Kc}}(r)$ (eq 1) at $r = 6$ Å relative to the one calculated from volume dipole fluctuation (eq 3) is about 2.6, as shown in Figure 2. A better

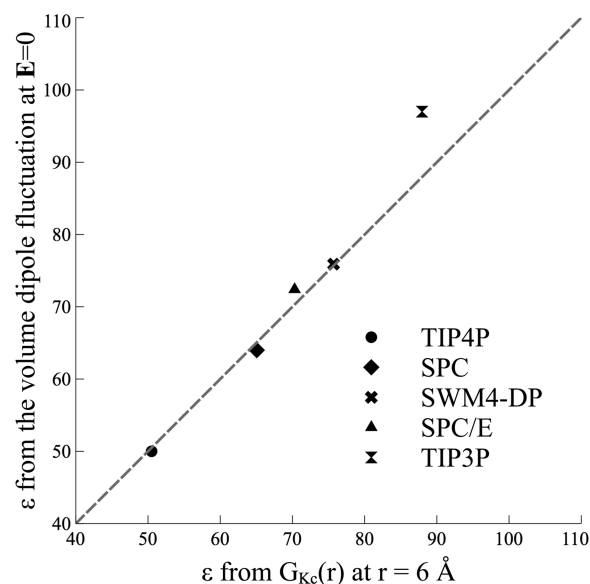


Figure 2. Correlation between the bulk dielectric constant, ϵ , calculated from volume dipole fluctuations at $\mathbf{E} = 0$ (eq 3) and the local dielectric constant calculated from the Kirkwood–Onsager formula (eq 1) using the value of the r -dependent composite Kirkwood g -factor, $G_{\text{Kc}}(r)$, of eq 8 at a distance of $r = 6$ Å. This distance corresponds to the second minimum in the oxygen–oxygen radial distribution function of SPC/E liquid water.

agreement can be obtained if one includes more neighboring molecules by increasing r further. However, the argument in favor of a minimal value is that this value can be regarded as a measure for the Kirkwood correlation length, r_K , and has therefore physical meaning.

The convergence in the distance-dependent Kirkwood factor computed using eq 8 depends on adequate sampling of $G_{\text{K}}(r)$ at $\mathbf{E} = 0$ and $\mathbf{D} = 0$. Because of the much faster relaxation of longitudinal polarization compared to transverse polarization,¹⁴ $G_{\text{K}}(r)_{\mathbf{D}=0}$ converges more rapidly than $G_{\text{K}}(r)_{\mathbf{E}=0}$ (see Figure 5 in ref 14.). Therefore, the convergence in the composite function $G_{\text{Kc}}(r)$ is dominated by the constant $\mathbf{E} = 0$ average. It varies with distance, as shown in Figure 3. The dielectric constant $\epsilon(r)$ computed from $G_{\text{Kc}}(r)$ at larger r values shows the poor convergence familiar from the computation of ϵ from fluctuations of volume dipole (eq 3). In contrast, for distances smaller than the Kirkwood correlation length, $\epsilon(r)$ is to a good approximation stationary on the 0.1 ns time scale. A technical comment regarding the way Figure 3 was constructed is in order. $\langle \mathbf{M}_1(r) \rangle$ is assumed to be zero in Kirkwood–Onsager theory (eqs 1 and 2). The average cell dipole moment $\langle \mathbf{M} \rangle$, however, explicitly appears in eqs 3 and 4 affecting the time convergence of the fluctuation. Therefore, for reasons of a consistent comparison, a term $\langle \mathbf{M}_1(r) \rangle^2 / (\mu^2 N(r))$ has been subtracted from eq 2 in the calculation of $\epsilon(r)$ in Figure 3 ($N(r)$ is the number of polar molecules in a sphere of radius r).

From an applications perspective, the big question is of course whether calculation of the short-range Kirkwood g -factor will enable us to compute the dielectric constant when MD trajectories are too short to obtain a reliable estimate from

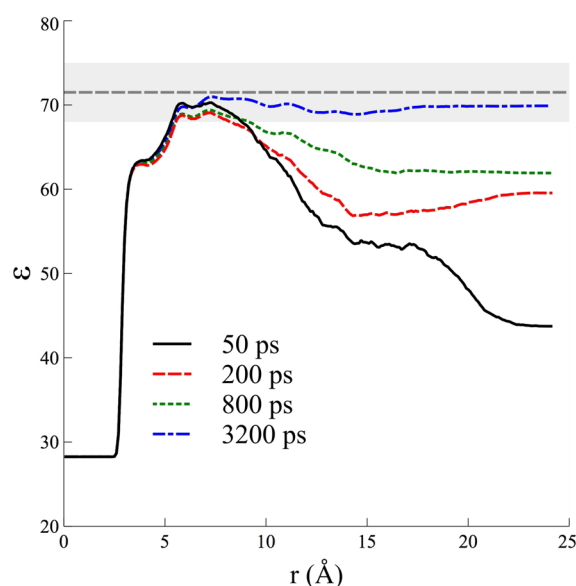


Figure 3. Convergence with MD run time of the r -dependent dielectric constant ϵ of SPC/E water computed from the Kirkwood–Onsager formula using $G_{\text{Kc}}(r)$ (eqs 8 and 1). This estimate is compared to ϵ calculated from $E = 0$ volume dipole fluctuations using eq 3 (dashed line). The shaded area is the margin for 5% deviation. The local dielectric constant converges within 100 ps. At this time scale, the volume dipole moment based estimate (the value at maximum r) has still a long way to go.

volume dipole fluctuations. Density functional theory (DFT)-based MD simulation of polar fluids is an example.^{29–31} While sampling of volume dipole fluctuation has proved feasible in some cases,^{29,31} liquid water under ambient conditions remains a challenge.³⁰ Taking up this challenge, we have carried out DFT-based MD simulations at $E = 0$ and $D = 0$. The constant D method has recently been implemented in CP2K^{32,33} and is available in version 3.0 (see section B, Tables S1–S4 and Figures S5 and S6 in the Supporting Information).

The electronic structure of liquid water was solved applying DFT in the Perdew–Burke–Ernzerhof (PBE) approximation.³⁴ Triple- ζ basis sets with two additional polarization functions (TZV2P) and a charge density cutoff of 320 Ry were used. Core electrons were taken into account using the dual-space Goedecker–Teter–Hutter (GTH) pseudopotentials.³⁵ The model system consisted of 64 water molecules in a cubic box of length 12.432 Å. The integration time-step is 0.5 fs, and MD trajectories in the NVE ensemble were collected for about 150 ps each at $E = 0$ and $D = 0$ conditions after initial equilibration. The average temperatures were 350 ± 18 and 348 ± 18 K, respectively. The molecular dipole moments were obtained from maximally localized Wannier functions (MLWFs)^{36,37} as computed by CP2K. The centers of the MLWFs were assembled in H_2O molecules using the TRAVIS analysis code.³⁸

To compute the static dielectric constant, ϵ , of polarizable water models, such as PBE water, the fluctuation equations (eqs 3 and 4) for rigid (nonpolarizable) molecules must be adjusted for an optical dielectric constant $\epsilon_\infty \neq 1$. The generalization of eq 3 appropriate for standard Ewald summation boundary conditions has been worked out.^{39–41} The agreed on expression is

$$\frac{4\pi\beta}{3\Omega}(\langle \mathbf{M}^2 \rangle_{E=0} - \langle \mathbf{M} \rangle_{E=0}^2) = \epsilon - \epsilon_\infty \quad (9)$$

The corresponding expression under $D = 0$ constraints is

$$\frac{4\pi\beta}{3\Omega}(\langle \mathbf{M}^2 \rangle_{D=0} - \langle \mathbf{M} \rangle_{D=0}^2) = \frac{\epsilon - \epsilon_\infty}{\epsilon\epsilon_\infty} \quad (10)$$

In the Supporting Information, eqs 9 and 10 are derived applying the Hellmann–Feynman theorem to the SSV Hamiltonians. Superposition of eqs 9 and 10 recovers the correct form of the Kirkwood–Onsager formula for polarizable polar liquids, as given by Wertheim⁴² (see Supporting Information). Therefore, the procedure to extract the short-ranged Kirkwood g -factor for polarizable models is again eq 8.

The r -dependent dielectric constant calculated from $G_{\text{Kc}}(r)$ is shown in Figure 4. $G_{\text{Kc}}(r)$ in the first coordination shell is close

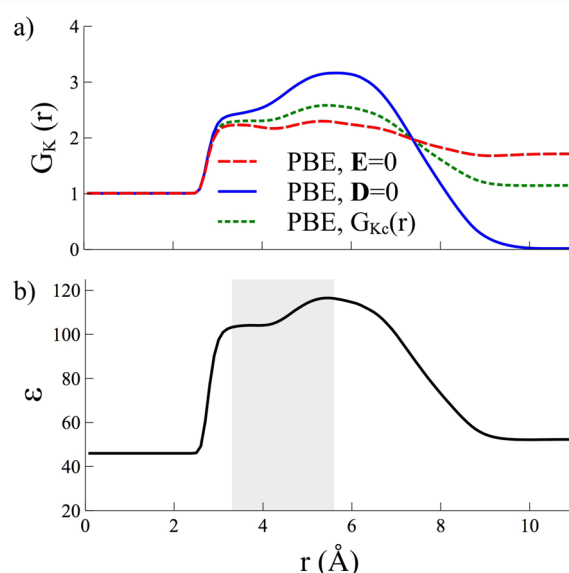


Figure 4. (a) Kirkwood g -factor $G_{\text{Kc}}(r)$ of PBE water calculated at $E = 0$ (in red) and $D = 0$ (in blue) and the resulting composite g -factor $G_{\text{Kc}}(r)$ (green) according to eq 8. (b) The corresponding r -dependent dielectric constant $\epsilon(r)$ calculated from $G_{\text{Kc}}(r)$ using the variant of eq 1 for polarizable polar model⁴² (see Supporting Information, section A). The shaded region corresponds to the interval between the first and second minimum of the oxygen–oxygen radial distribution function (3.3 and 5.5 Å, respectively). Our final estimate of the dielectric constant of PBE water ($\epsilon = 112$) is the average of $\epsilon(r)$ over this interval.

to 2.2, which is in agreement with previous DFT–MD results for PBE water.³⁰ Moreover, already after 50 ps of simulation, the overall shape of $G_{\text{Kc}}(r)$ at short-range resembles that of SPC/E water (see Figure 3). Using r values between the first and second minimum of the oxygen–oxygen radial distribution function, we arrive at a dielectric constant of PBE water of 112 ± 6 . As expected, distances approaching $r = \sqrt{3}L/2$ lead to significant underestimation of ϵ even with 150 ps simulation, which is as long as we could afford.

While our scheme for the calculation of ϵ is new, the result is not really a surprise. It is consistent with the enhancement of the average dipole moment of PBE water relative to SPC/E. We find 3.2 ± 0.3 D for PBE compared to 2.35 D for SPC/E. Scaling the bulk dielectric constant of SPC/E water (i.e., 71) by the square of this ratio puts the dielectric constant of PBE at 131, which is close to our estimates derived from the composite Kirkwood g -factor. Therefore, PBE water overestimates the dielectric constant of liquid water by at least 40%, compared

with the experimental value of 78. This finding is in accord with recent studies of the dielectric constant of ice.^{43,44}

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpclett.6b01127](https://doi.org/10.1021/acs.jpclett.6b01127). Additional data related to this publication are available at the University of Cambridge data repository, <http://dx.doi.org/10.17863/CAM.502>.

Fluctuation equations for polarizable polar models; r -dependent composite Kirkwood g -factor, $G_{Kc}(r)$, and r -dependent ϵ for SPC, TIP3P, TIP4P, and SWM4-DP water models at $E = 0$ and $D = 0$; and calculated Born charges, optical dielectric constant, and the oxygen–oxygen radial distribution function of PBE water from $E = 0$ and $D = 0$ CP2K simulations (PDF)

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Notes

The authors declare no competing financial interest.

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