

Relative Permittivity of Polar Liquids. Comparison of Theory, Experiment, and Simulation

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A molecular-based second-order perturbation theory is applied to calculate the relative permittivity of polar liquids. Our basic model is the dipolar hard sphere fluid. The main purpose of this work is to propose various approaches to take into account the molecular polarizability. In the continuum approach, we apply the Kirkwood–Fröhlich equation and use the high-frequency relative permittivity. The Kirkwood g -factor representing molecular correlations is calculated by a perturbation theory. In the molecular approach, the molecular polarizability is built into the model on the molecular level (the polarizable dipolar hard sphere fluid). To calculate the relative permittivity of this system, an equation obtained from a renormalization procedure is used. In both approaches, we apply a series expansion for the relative permittivity and show that these series expansions give results in better agreement with simulation data than the original equations. After testing our theoretical equations against our own Monte Carlo simulation results, we compare the results obtained from our theoretical equations and simulations to experimental data for amines, ethers, and halogenated, sulfur, and hydroxy compounds. We propose a procedure to calculate potential parameters (hard sphere diameter, reduced polarizability, and reduced dipole moment) from experimental data such as the permanent dipole moment, refractive index, density, and temperature. We show that for compounds of low relative permittivity the polarizable dipolar hard sphere (PDHS) model and the continuum approach give reasonable results. For nonassociative liquids of higher relative permittivity, the PDHS model overestimates experimental data due to unsatisfactory representation of the shape of the molecules. In the case of associative liquids, the PDHS model works well, and in some cases it underestimates the experimental values due to the unsatisfactory treatment of electrostatic interactions.

1. Introduction

One of the basic properties of polar fluids is the relative permittivity, which is defined as a dielectric response to an external electric field, \mathbf{E}_0 . If we assume that the dielectric is linear, then the relation between the polarization (\mathbf{P}) and the electric field strength inside the dielectric (\mathbf{E}) is

$$4\pi\mathbf{P} = (\epsilon - 1)\mathbf{E} \quad (1)$$

where ϵ is the relative permittivity. In homogeneous, isotropic dielectrics, ϵ is a constant. Its value depends on the polarizability of the dielectric, and it is a well-defined physical property of a given substance. Although measuring the relative permittivity is straightforward, its calculation on the basis of a molecular model is a task of statistical mechanics and is quite difficult.¹ The external field does not usually agree with the average (macroscopic) field in the dielectric; their relation depends on the boundary conditions at the boundary of the dielectric sample and its environment.

Classical theories use a continuum approach; they place the molecule in a cavity surrounded by the material treated as a continuum. These approaches introduce helpful quantities such as the internal field, the directing field, the reaction field, or the cavity field and use the Boltzmann distribution to calculate the orientation polarization of the permanent dipoles. The

Clausius–Mossotti (CM) equation is valid for apolar molecules, while the Debye equation² holds approximately for gases and dilute solutions of molecules carrying a permanent dipole. The Debye equation for a spherical-shaped sample is

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3}\alpha\rho + y_0 \quad (2)$$

where α is the polarizability of the molecule, ρ is the number density, and y_0 is the dimensionless dipole strength function, $y_0 = 4\pi\rho\mu_0^2/9kT$, where μ_0 is the permanent dipole moment, k is the Boltzmann factor, and T is the temperature (for $y_0 = 0$, eq 2 yields the CM equation).

At high densities, the situation is more difficult. The molecules are close to each other, so the orientation polarization of a molecule is influenced by the surrounding dielectric. Onsager has given a more careful treatment of the continuum approach. In his model,³ a point dipole is placed in the center of a cavity of relative permittivity ϵ_∞ , and the effect of the surrounding dielectric is measured by the dielectric response of the polarization charges induced on the wall of the cavity. The resulting equation is

$$\frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} = y_0 \quad (\text{ONS}) \quad (3)$$

The high-frequency relative permittivity ϵ_∞ is commonly calculated from the Maxwell relation $\epsilon_\infty = n^2$, where n is the

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inner refractive index. Besides, the high-frequency relative permittivity can be related to the molecular polarizability via the CM equation

$$\frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} = \frac{4\pi}{3} \alpha \rho \quad (4)$$

The Onsager (ONS) equation works quite well for liquids when the dipole moment is not too high. Nevertheless, this is still a continuum theory; the correlation between the dipoles is not taken into account on the molecular level.

To consider this correlation, we need a molecular model and a statistical mechanical method to study the model. Most statistical mechanical theories operate with model potentials that are pairwise additive. Including the molecular polarizability makes the intermolecular potential nonadditive. In molecular simulations, this can be included in a self-consistent way, while theories avoid treatment of many-body correlations by using a renormalization procedure. In our previous works,^{4,5} we have proposed two possibilities to take into account the polarizability, a continuum approach,⁴ in the spirit of the ONS equation, and a renormalization theory, in which the polarizability is built into the model on the molecular level.⁵ In both cases, the basic molecular model is a point dipole embedded in a spherical core potential representing van der Waals forces (in this study, the dipolar hard sphere (DHS) potential is used), while the statistical mechanical theory that we use is a thermodynamic perturbation theory. The description of the models and the theories can be found in the subsequent sections.

In each case, an important aspect of our equations is a series expansion of the relative permittivity with respect to the dipole strength function or the density. In general, the equations that are well-known for the calculation of the relative permittivity are in the same form as those of eqs 2 or 3. A given function of ϵ stands on the left-hand side of these equations, the form of which usually depends on the boundary conditions and the shape of the sample. To obtain a direct equation for ϵ , a series expansion can be given. These series expansions, apart from the fact that they give better agreement with simulation results, have a strong theoretical basis. For instance, Jepsen^{6,7} and Rushbrooke^{8,9} have shown for the DHS fluid that the next exact term in the y_0 -expansion of the Debye equation is given as (with $\alpha = 0$)

$$\frac{\epsilon - 1}{\epsilon + 2} = y_0 - \frac{15}{16} y_0^2 \quad (5)$$

from which the following series can be derived for the relative permittivity

$$\epsilon = 1 + 3y_0 + 3y_0^2 + \frac{3}{16}y_0^3 + \dots \quad (6)$$

This equation is exact in the limit of low densities. The ONS³ and the van Vleck¹⁰ theories are valid up to the second order in y_0 . The y_0 -expansion of the relative permittivity given by Wertheim's mean spherical approximation (MSA)¹¹ yields this equation too.

At high densities, eq 6 is no longer satisfactory. The short-range correlations between dipoles are usually taken into account by the dimensionless correlation parameter, the Kirkwood g -factor¹² g_K , which is 1 in the limit of low densities when the dipoles are far from each other on average. On the basis of the Kirkwood equation,¹² Tani et al.¹³ developed a series expansion for the relative permittivity of the DHS fluid that contains an

integral in the third-order term that takes into account molecular correlations. This approach is a basic point of our investigation, and it will be discussed in detail. Our previous results^{5,14} for the polarizable Stockmayer fluid (in this model the core is the Lennard-Jones potential) and the results presented in this paper for the polarizable DHS (PDHS) fluid show that these series expansions give results that are in better agreement with simulation data.

We can represent a whole class of molecules if we use a simple model such as the DHS potential. Its other advantage is that it can be studied by all the basic statistical mechanical theoretical methods such as the MSA,¹¹ the reference hypernetted chain,¹⁵ and density functional^{16,17} theories. Another possibility is to construct detailed models for which computer simulations provide a powerful tool of study. Nevertheless, these complex models are valid only for the specific molecule that they are intended to model; general conclusions for a whole class of materials cannot be withdrawn from them.

Regarding application to real liquids, there is a gap between classical continuum theories and simulations performed for detailed molecular models. We are aware of only a series of papers by Goldman et al. dealing with the estimation of the dielectric properties of real substances on the basis of molecular-based theoretical approaches. Goldman¹⁸ applied a second-order perturbation theory (PT) to a Stockmayer fluid to obtain the relative permittivity and found reasonable agreement with simulations. This is the PT that we use in this work. Besides, Goldman and Joslin¹⁹ extended the theory to more difficult potentials with spherical cores and discrete point charge distributions. They applied the theory to study the SPC and TIP4P models of water and compared the results to simulations.¹⁹ In another publication, they calculated the relative permittivity of water at high temperature and pressures and found good agreement with the experimental data that are sparse in this regime.²⁰ Taking into account higher-order multipole moments, Goldman and Joslin²¹ have made a systematic study comparing the dielectric properties of hydrogen-bonded and dipolar aprotic liquids. They found that hydrogen-bonded liquids tend to have higher static dielectric constants than dipolar aprotic liquids.

In this paper, we estimate the relative permittivity of real polar liquids by the help of different methods. We take into account the polarizability of the molecules on various levels, while short-range correlations are treated by a second-order PT. For the PDHS fluid, which is a well-defined molecular model, we validate our theoretical approaches by comparing the theoretical results to our own Monte Carlo (MC) simulation data. Finally, after presenting a method for estimating molecular parameters from experimental data, we apply our theoretical methods for the calculation of the relative permittivity of various classes of polar liquids and compare our results to experimental and simulation data.

2. Models

In this section, we introduce the PDHS model of which the DHS fluid is a special case with $\alpha = 0$. Because the potential in the PDHS system is not pairwise additive, we have to define the total energy of the system for a complete definition of the Hamiltonian. In the case of the DHS fluid, the system can be defined merely by giving the pair potential; the total energy is the sum of the pair potentials.

The total energy of the N -particle system of the PDHS fluid can be divided into three parts

$$U = U_{\text{ref}} + U_{\text{el}} + U_{\text{ind}} \quad (7)$$

The first part, the nonelectrostatic spherical reference potential, is a sum of the pairwise additive potentials. In this study, we use the hard sphere (HS) potential

$$u_{\text{HS}}(r_{ij}) = \begin{cases} \infty & \text{if } r_{ij} < \sigma \\ 0 & \text{if } r_{ij} \geq \sigma \end{cases} \quad (8)$$

where σ is the hard sphere diameter and r_{ij} is the magnitude of the vector $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. The role of this term is to forbid the overlapping of the spheres. The electrostatic terms of the energy consist of the interaction between the permanent dipoles

$$U_{\text{el}} = -\frac{1}{2} \sum_i (\boldsymbol{\mu}_0)_i \cdot (\mathbf{E}_0)_i \quad (9)$$

and the induction energy²²

$$U_{\text{ind}} = -\frac{1}{2} \sum_i (\boldsymbol{\mu}_{\text{ind}})_i \cdot (\mathbf{E}_0)_i \quad (10)$$

where $(\boldsymbol{\mu}_0)_i$ and $(\boldsymbol{\mu}_{\text{ind}})_i$ are the permanent and the induced dipole moments on the i th molecule, respectively, and $(\mathbf{E}_0)_i$ is the electric field at the position of the i th molecule produced by the permanent dipoles of all other molecules.¹⁴ After the introduction of the electric field produced by the induced dipoles of all other molecules at the position of molecule i , $(\mathbf{E}_{\text{ind}})_i$, the induced dipole moment of the i th molecule is defined as

$$(\boldsymbol{\mu}_{\text{ind}})_i = \alpha [(\mathbf{E}_0)_i + (\mathbf{E}_{\text{ind}})_i] \quad (11)$$

In general, α is a tensor, but in this study, we restrict ourselves to a scalar polarizability. For the nonpolarizable case, $U_{\text{ind}} = 0$, and U_{el} reduces to the sum of the dipole–dipole pair potentials

$$u_{\text{DD}}(ij) = -\mu_0^2 \left(\frac{3(\mathbf{n}_i \cdot \mathbf{r}_{ij})(\mathbf{n}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} - \frac{\mathbf{n}_i \cdot \mathbf{n}_j}{r_{ij}^3} \right) \quad (12)$$

where ij is a notation for $\mathbf{r}_{ij}, \mathbf{n}_i, \mathbf{n}_j$ and $\mathbf{n}_i = \boldsymbol{\mu}_i / \mu_0$ is the unit vector in the direction of the i th dipole.

3. Methods

3.1. Nonpolarizable Case. It is more convenient to introduce the PT approach for the DHS system and to describe the two different methods of taking into account the polarizability afterward. To calculate the relative permittivity of a bulk fluid, the starting point is the Kirkwood equation¹²

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} = y_0 g_K \quad (13)$$

where the Kirkwood factor g_K takes care of the short-range correlations between the dipoles and it is obtained from the fluctuation of the total dipole moment \mathbf{M} of the system

$$g_K = \frac{\langle M^2 \rangle}{N\mu_0^2} = 1 + \int \langle g(12)(\mathbf{n}_1 \cdot \mathbf{n}_2) \rangle_{\omega_1 \omega_2} d\mathbf{r}_{12} \quad (14)$$

where the ensemble average is determined using the pair-correlation function $g(12)$ and $\langle \dots \rangle_{\omega_1 \omega_2}$ denotes the average over the orientations. The pair-correlation function is expanded into

a perturbation series developed by Barker and Henderson.²³ In the framework of the Gubbins–Gray–Pople–Stell perturbation theory,²⁴ the Kirkwood factor can be expressed as^{8,13,18,25,26}

$$g_K = 1 + y_0^2 \frac{9I_{\text{dd}\Delta}}{16\pi^2} \quad (15)$$

where $I_{\text{dd}\Delta}$ denotes a triple integral. The values of the integral have been tabulated by Tani et al.¹³ for the DHS fluid and by Goldman¹⁸ for the Stockmayer fluid. In this paper, we use the values calculated for our previous work²⁷ by the Fourier transform convolution theorem method.^{18,24,26} In the case of the DHS fluid, the integral depends only on the dimensionless reduced density $\rho^* = \rho\sigma^3$, and the ρ^* -dependence can be given by the following polynomial

$$I_{\text{dd}\Delta}(\rho^*) = 18.6426 - 0.0352\rho^* + 2.2950\rho^{*2} + 2.9831\rho^{*3} - 0.0665\rho^{*4} + 2.3666\rho^{*5} \quad (16)$$

By substitution of eq 15 into eq 13, the Kirkwood equation can be rewritten as

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} = y_0 \left(1 + y_0^2 \frac{9I_{\text{dd}\Delta}}{16\pi^2} \right) \quad (\text{DHS1}) \quad (17)$$

The results calculated from eq 17 are not in good agreement with the simulation data, so Tani et al.¹³ expanded $\epsilon(y_0)$ as a Taylor series on the basis of the above equation and obtained that

$$\epsilon(y_0) = 1 + 3y_0 + 3y_0^2 + 3y_0^3 \left(\frac{9I_{\text{dd}\Delta}}{16\pi^2} - 1 \right) + \dots \quad (\text{DHS2}) \quad (18)$$

Note that in the low-density limit $I_{\text{dd}\Delta} = 17\pi^2/9$ and eq 18 becomes identical to eq 6.

Tani et al.¹³ have shown that the results obtained from the above series expansion of the Kirkwood equation are in better agreement with the simulation data than those calculated from the Kirkwood equation itself (eq 17). Goldman¹⁸ has found the same for the Stockmayer fluid. In the introduction, we have already reasoned that such a series expansion is not merely a computational trick, but it is an equation that is independent of the boundary conditions and the shape of the sample. Equations written in the form of the Kirkwood, the ONS, or the CM equations explicitly include the information about the boundary conditions (left-hand side of the equations). Accordingly, the Kirkwood factor on the right-hand side of the equations will also depend on the boundary conditions because the resulting relative permittivity should be independent of them. This is a practice in simulations where the system is finite even if periodic boundary conditions are applied. In theory, the bulk system is considered as infinite, and the $I_{\text{dd}\Delta}$ integral includes information only on the short-range correlations of a central dipole and its local environment and knows nothing about boundary conditions of the macroscopic sample. Therefore, it is reasonable to express the relative permittivity in a form that is independent of boundary conditions.

Note that eq 18 can be obtained from the response of the system to an applied external field. Szalai et al.²⁸ have expressed the field-dependent Helmholtz free energy of the DHS system from which the polarization can be obtained. From the polarization, the relative permittivity follows using eq 1. The resulting equation for ϵ is the same as eq 18. The approach based on the response to an external field can be applied in the frame of the

MSA^{29,30} and for the calculation of the magnetic susceptibility of magnetic fluids using simulations.^{31–34}

3.2. Continuum Approach. In the above section, the polarizability α of the molecules was not taken into account. In our previous work,⁴ we have proposed a simple continuum approach on the basis of the Kirkwood–Fröhlich equation³⁵

$$\frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} = y_0 g_K = y_0 \left(1 + y_0 \frac{9I_{dd\Delta}}{16\pi^2} \right) \quad (\text{KF1}) \quad (19)$$

It is seen that the difference between this equation and the ONS equation (eq 3) is that the Kirkwood factor is present on right-hand side representing the correlation between the permanent dipoles of the molecules. This factor is calculated from the expression derived in the previous section (eq 15). We emphasize that y_0 is calculated by using the permanent dipole moment μ_0 .

This treatment makes it possible to approach the problem from two different points of view. (A) If we examine a certain real substance, then its high-frequency relative permittivity is used as an additional macroscopic physical parameter as an input for the equation. In this work, we use the relation $\epsilon_\infty = n^2$, where n is the inner refractive index. (B) If we examine a molecular model (such as the PDHS model used in this work), then the input is the molecular polarizability α . In this case, the high-frequency relative permittivity can be obtained from the CM equation (eq 4).

Following the reasoning given in the previous section, we can assume that the series expansion of the above equation might also give a more general equation for the relative permittivity. Performing the same series expansion for the Kirkwood–Fröhlich equation as Tani et al.¹³ did for the Kirkwood equation, we obtain⁴

$$\epsilon(y_0) = \epsilon_\infty + \frac{\epsilon_\infty(\epsilon_\infty + 2)^2}{2\epsilon_\infty + 1} y_0 + \frac{\epsilon_\infty(\epsilon_\infty + 2)^4}{(2\epsilon_\infty + 1)^3} y_0^2 + \frac{\epsilon_\infty(\epsilon_\infty + 2)^2}{2\epsilon_\infty + 1} \left[\frac{9I_{dd\Delta}}{16\pi^2} - \frac{(2\epsilon_\infty - 1)(\epsilon_\infty + 2)^4}{(2\epsilon_\infty + 1)^4} \right] y_0^3 \quad (\text{KF2}) \quad (20)$$

Note that with $\epsilon_\infty = 1$ eq 20 yields eq 18.

3.3. Molecular Approach. In the previous section, the polarizability was taken into account in a continuum approach. If we want to treat the molecular polarizability in a self-consistent way on the molecular level, then we have to use a theory that is able to treat the nonadditive many-body interactions. Wertheim³⁶ developed a graph theory in which a renormalized effective dipole moment μ is defined as a sum of the permanent dipole moment μ_0 and the induced dipole moment resulting from the mean electric field E acting on the molecules

$$\mu = \mu_0 + \alpha E \quad (21)$$

Gray et al.^{37–39} showed that the mean electric field can be given as

$$E = - \left(\frac{\partial f}{\partial \mu} \right)_{\alpha VT} \quad (22)$$

where f is the one-particle Helmholtz free energy of the system. The above two equations provide a self-consistent iteration route that can be solved for the effective dipole moment. For the free energy, a Padé approximant can be given with free energy perturbation terms that can be calculated if one knows the g_0 radial distribution function of the reference HS system. The

exact forms of these perturbation integrals can be found elsewhere.^{24,40}

After the renormalized iteration procedure, we obtain the effective dipole moment as a function of α and μ_0 . The following expression can be used as a starting point to estimate the dielectric constant of polarizable model fluids

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} = \frac{4\pi}{3} \alpha \rho + y g_K \quad (23)$$

It is important to note that the effective dipole moment μ should be used in the calculation of the dipole strength function $y = 4\pi\rho\mu^2/9kT$ in the above equation (subscript 0 is missing). As it was discussed in our previous publication,⁵ an expression can be developed for $y g_K$. Using the density as a variable instead of y , we obtained

$$y g_K = \frac{4\pi\mu^2}{9kT} \rho + \frac{4\pi}{3} I_{dd\Delta} \left[\left(\frac{\mu^2}{3kT} + \alpha \right)^3 - \alpha^3 \right] \rho^3 \quad (24)$$

By introduction of the parameters

$$a = \frac{4\pi}{3} \left(\frac{\mu^2}{3kT} + \alpha \right) \quad (25)$$

and

$$b = \frac{4\pi}{3} I_{dd\Delta} \left[\left(\frac{\mu^2}{3kT} + \alpha \right)^3 - \alpha^3 \right] \quad (26)$$

eq 23 can be expressed as

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} = a\rho + b\rho^3 \quad (\text{MOL1}) \quad (27)$$

By performance of the same series expansion as in the case of nonpolarizable fluids,¹³ the following equation is obtained for the relative permittivity

$$\epsilon(\rho) = 1 + 3a\rho + 3a^2\rho^2 + 3(b - a^3)\rho^3 \quad (\text{MOL2}) \quad (28)$$

3.4. Monte Carlo Simulation. In our previous papers,^{5,14} we have already shown that eq 28 gives a reasonable estimate for the relative permittivity of the polarizable Stockmayer fluid. Here, we present MC results for the PDHS fluid to prove the applicability of our theoretical equations in the case of the PDHS system as well. We restrict ourselves to reduced parameters that are in the region of the state points considered in this work (for the estimation of the reduced parameters, see the next section). A systematic study of the relative permittivity of the PDHS fluid for a broader range of density, dipole moment, and polarizability will be published elsewhere.⁴¹

The treatment of nonadditive potentials in molecular dynamics simulations is straightforward since the works of Vesely.^{42,43} Its basis is the iteration procedure hidden in eq 11. For a given configuration of dipoles, the electric fields $(\mathbf{E}_{\text{ind}})_i$ of the induced dipoles $(\mu_{\text{ind}})_i$ are given, from which a new set of the induced dipoles is calculated from eq 11. From the new induced dipoles, a new set of electric fields follows, and this iteration is performed until a prescribed accuracy is attained. In the case of MC simulations, where single particle moves are used, the main problem is the time-consuming step of calculating the electric fields of the induced dipoles in this iteration procedure. Předota et al.⁴⁴ have suggested a method called “pair approximation for polarization interaction” to overcome this difficulty. This method was used in our earlier study;⁵ the

technical parameters given in that paper are used in this work. For details, the reader is referred to the original papers of Předota et al.⁴⁴

Our MC simulation procedure is standard and detailed in excellent books,^{45–47} here, we give only the formula necessary to calculate the relative permittivity. The basic equation is²²

$$\frac{(\epsilon - 1)(2\epsilon_{\text{RF}} + 1)}{3(2\epsilon_{\text{RF}} + \epsilon)} = \frac{(\epsilon_{\infty} - 1)(2\epsilon_{\text{RF}} + 1)}{3(2\epsilon_{\text{RF}} + \epsilon_{\infty})} + \frac{4\pi\rho}{9kT} \frac{\langle \mathbf{M}^2 \rangle}{N} \quad (29)$$

where \mathbf{M} is the total (permanent and induced) dipole moment of the system, whose quantity is straightforwardly determined in the simulation. The high-frequency dielectric constant is calculated from the CM equation (eq 4). Theoretically, the relative permittivity of the medium surrounding the spherical sample (ϵ_{RF}) should be equal to the relative permittivity of the sample (ϵ). Since ϵ is not known in advance, it is usual to use the conducting boundary condition ($\epsilon_{\text{RF}} \rightarrow \infty$) in simulations. This corresponds to using the reaction field method to estimate the long-range corrections. Canonical (constant NVT) simulations have been performed with 256 particles. The length of the simulations varied between 300 and 500 000 MC cycles depending on the dipole moment and the polarizability.

4. Estimation of the Parameters

When we consider a real liquid, the following experimental parameters are available⁴⁸ as inputs for the calculations: the mass density, the molar mass (from these, the number density ρ follows), the temperature, the refractive index, and the dipole moment. Whether it is the permanent dipole moment μ_0 or the effective (total) dipole moment μ is an important question. The measurements for the dipole moment are usually performed in dilute solution in nonpolar solvent. Although there is a mutual polarization between the polar solute molecule and the surrounding nonpolar solvent molecules, this effect is small compared to the mutual polarization between the polar molecules in the liquid phase. Therefore, we assume that the dipole moments determined from these experiments correspond to the permanent dipole moment.

It is conventional to describe the properties of the model fluids by reduced quantities. In the case of the PDHS fluid, the reduced parameters are the reduced density ($\rho^* = \rho\sigma^3$), the reduced dipole moment ($\mu_0^* = \mu_0/\sqrt{kT\sigma^3}$), and the reduced polarizability ($\alpha^* = \alpha/\sigma^3$). Realize that almost every important parameter in the theoretical equations is dimensionless: y , $\alpha\rho$, $a\rho$, and $b\rho^3$.

To calculate reduced quantities, we have to make some assumptions about the HS diameter σ . Since the shape of real molecules is rarely spherical, it is hard to relate the HS diameter to any dimensional parameter on the molecular level. Instead, we propose the reverse route; let us fix the reduced density ρ^* at a prescribed value, from which a HS diameter can be calculated from $\sigma = (\rho^*/\rho)^{1/3}$. For the reduced density, we have chosen the value $\rho^* = 0.8$. This value is characteristic of the packing of molecules in the liquid phase and is frequently used in the literature. Furthermore, this density is below the density where the solid–liquid-phase transition appears. Certainly, other values for ρ^* would be equally reasonable. Nevertheless, its effect appears only in the higher-order terms of the series expansion with the $I_{\text{dd}\Delta}(\rho^*)$ integral; therefore, its effect on the relative permittivity is relatively small. In the case of the MOL1 and MOL2 equations, the ρ^* -dependence of ϵ is larger due to the renormalization procedure. This question will be discussed in the next section.

5. Results and Discussion

Before presenting our results, we summarize our theories. The basic model is the DHS potential, which is a hard sphere with a point dipole in its center. Neglecting the polarizability and applying the PT for the model, we obtain an expression for the Kirkwood factor (eq 15). The relative permittivity is determined from the Kirkwood equation (DHS1; eq 17) or its series expansion (DHS2; eq 18). The polarizability can be taken into account in a continuum or a molecular approach. In the continuum approach, we start from the Kirkwood–Fröhlich equation (KF1; eq 19), where the Kirkwood factor is calculated in the same way as in the case of the DHS model. The ONS equation (ONS; eq 3) corresponds to the KF1 equation with $g_K = 1$. In the molecular approach, the polarizability is built into the model on the molecular level (MOL1; eq 27) with the help of a renormalization procedure. In both the KF1 and the MOL1 approaches, the series expansion forms are also available (KF2; eq 20 and MOL2; eq 28). In the limit of $\alpha \rightarrow 0$, equations MOL1 and MOL2 become equivalent to DHS1 and DHS2, respectively. In this limiting case, $\epsilon_{\infty} \rightarrow 1$, and equations KF1 and KF2 also become equivalent to DHS1 and DHS2, respectively.

5.1. Comparison of Theory and Simulation. In this work, our main purpose is to apply the above-described models and theoretical methods to real substances. The distinction between model and method is important. We can state that the model is good for a real liquid if the results obtained for the model from simulations agree with experiments. We can state that the theory is good for a given model if the results obtained from the theory agree with simulations. So, in this sense, simulations play the role of a bridge between theories and experiments. This means that before we compare the results obtained from theories to experimental data, we have to justify the theories, namely, we have to compare theoretical results to simulations.

In this paper, we show results only for state points that are relevant to the theory–experiment comparison of the next subsection. The reduced parameters characteristic of the real compounds considered in this study can be found in Table 1. It is seen that in most cases the reduced dipole moment (μ_0^*) is in a range between 0.2 and 1.1, while the polarizability (α^*) varies between 0.05 and 0.1. Therefore, we have performed several MC simulations for a grid in the above parameter range with increments $\Delta\mu_0^* = 0.1$ and $\Delta\alpha^* = 0.01$ for the fixed value of the reduced density ($\rho^* = 0.8$).

Figure 1 shows the MC results compared to those calculated from different theories as a function of α^* for a lower ($\mu_0^* = 0.5$) and a higher ($\mu_0^* = 0.9$) reduced dipole moment. Henceforth, we will use the above notations (DHS2, ..., MOL2) for the various theories, while the notations MC and EXP will be used for the simulation and experimental data, respectively. For the lower dipole moment, the continuum theories reproduce the MC data well, while the MOL2 equation overestimates the simulation data. With an increase in the value of the dipole moment, the MOL2 equation becomes more successful. The ONS equation underestimates ϵ considerably for $\mu_0^* = 0.9$. The KF1 equation seems reasonable in this case, but this is a coincidence in our opinion. Our simulations for even higher dipole moments (these results are published elsewhere⁴¹) showed that the nonexpanded equations (DHS1, KF1, MOL1) overestimate the MC data. The DHS2 approach corresponds to $\alpha^* = 0$, so this equation is unable to reproduce the α^* -dependence of the relative permittivity for the nonzero molecular polarizabilities. The MOL1 equation overestimates the relative permittivity, while its series expansion (MOL2) gives better results

TABLE 1: HS Diameter, Reduced Polarizability, and Reduced Permanent Dipole Moment of Sulfur Compounds, Amines, Ethers, Halogenated Compounds, and Hydroxy Compounds as Calculated by the Procedure Given in Section 4 at $\rho^* = 0.8^a$

compound	σ	α^*	μ_0^*	μ^*	compound	σ	α^*	μ_0^*	μ^*
Sulfur Compounds									
carbon disulfide	4.3146	0.1054	0.0330	0.3920	1-butanethiol	5.2313	0.0787	0.6305	0.8290
thiophene	4.7259	0.0916	0.2496	0.5125	ethyl sulfide	5.2430	0.0787	0.6612	0.8587
benzenethiol	5.1479	0.1003	0.5192	0.7859	Methyl sulfide	4.6102	0.0774	0.7222	0.9144
Amines									
triethylamine	5.7073	0.0720	0.3146	0.5050	butylamine	5.0842	0.0726	0.5942	0.7763
dibutylamine	6.0851	0.0752	0.3445	0.5433	propylamine	4.7838	0.0704	0.6320	0.8073
dipropylamine	5.6696	0.0726	0.3794	0.5681	<i>m</i> -toluidine	5.2382	0.0973	0.5963	0.8493
diethylamine	5.1734	0.0695	0.4651	0.6411	<i>o</i> -toluidine	5.2311	0.0979	0.6593	0.9103
isobutylamine	5.1062	0.0715	0.5427	0.7227	aniline	4.9538	0.0998	0.6752	0.9306
Ethers									
<i>p</i> -dioxane	4.8466	0.0756	0.2079	0.4211	phenyl ether	5.9633	0.0988	0.3927	0.6644
dimetoxymethane	4.8861	0.0648	0.3407	0.5058	acetal	5.7592	0.0672	0.4923	0.6607
pentyl ether	6.4624	0.0739	0.3601	0.5539	isopropyl ether	5.7244	0.0668	0.4429	0.6110
isopentyl ether	6.4660	0.0737	0.3720	0.5645	veratrole	5.5356	0.0925	0.4997	0.7443
furan	4.5855	0.0757	0.3595	0.5593	phenetole	5.5282	0.0885	0.5159	0.7475
butyl ether	6.0832	0.0722	0.3911	0.5779	ethyl ether	5.1678	0.0646	0.4867	0.6475
propyl ether	5.6767	0.0688	0.4812	0.6546	anisole	5.2559	0.0899	0.5094	0.7455
Halogenated Compounds									
pentachloroethane	5.4317	0.0882	0.3661	0.6060	1-chlorobutane	5.1769	0.0727	0.8021	0.9791
bromoform	4.8873	0.1015	0.4518	0.7270	1,1,1-trichloroethane	5.0977	0.0783	0.6783	0.8742
1,2-dibromethane	4.8561	0.0934	0.5715	0.8148	iodoethane	4.7478	0.0897	0.8555	1.0743
chloroform	4.7496	0.0791	0.5478	0.7501	1,1,2,2-tetrachloroethane	5.1989	0.0864	0.7112	0.9281
diiodomethane	4.7556	0.1201	0.5135	0.8391	bromoethane	4.6383	0.0757	0.9378	1.1179
bromobenzene	5.1942	0.0961	0.6456	0.8923	1,1-dichloroethane	4.8280	0.0745	0.9202	1.0981
chlorobenzene	5.1401	0.0914	0.6515	0.8849	1,2-dichloroethane	4.7253	0.0790	0.8928	1.0828
iodomethane	4.3663	0.0917	0.7998	1.0266					
Hydroxy Compounds									
2-methyl-2-butanol	5.2590	0.0727	0.6950	0.8751	1-pentanol	5.2372	0.0739	0.6993	0.8826
<i>trans</i> -3-methylcyclohexanol	5.4805	0.0814	0.6782	0.8827	3-methyl-1-butanol	5.2544	0.0732	0.7450	0.9250
phenol	4.7976	0.0940	0.6638	0.9038	cyclohexanol	5.1599	0.0825	0.7824	0.9857
<i>p</i> -cresol	4.9929	0.0935	0.6806	0.9182	<i>cis</i> -3-methylcyclohexanol	5.4922	0.0813	0.7378	0.9398
1-octanol	5.9478	0.0767	0.5982	0.7920	2-butanol	4.9687	0.0715	0.7123	0.8887
<i>o</i> -cresol	5.0206	0.0942	0.6355	0.8776	1-butanol	4.9617	0.0719	0.7807	0.9563
<i>m</i> -cresol	5.1854	0.0936	0.6430	0.8829	2-methyl-1-propanol	4.9787	0.0714	0.7944	0.9683
3-methylcyclohexanol	5.4894	0.0814	0.7345	0.9368	2-propanol	4.6666	0.0687	0.8188	0.9849
2-methyl-2-propanol	5.0137	0.0699	0.7290	0.9008	2-propene-1-ol	4.5080	0.0738	0.8327	1.0116
3-pentanol	5.2261	0.0740	0.6825	0.8664	2-propyn-1-ol	4.2872	0.0771	0.9886	1.1700
benzyl alcohol	5.1670	0.0934	0.6968	0.9334	ethanol	4.2639	0.0661	0.9375	1.0939
1-hexanol	5.4996	0.0752	0.5976	0.7871	1,2-propanediol	4.6033	0.0775	1.1328	1.3089
2-methylcyclohexanol	5.4726	0.0819	0.7574	0.9602	1,3-propanediol	4.5775	0.0786	1.2693	1.4412
4-methylcyclohexanol	5.4988	0.0812	0.7327	0.9345	1,2-ethanediol	4.1991	0.0774	1.3175	1.4845
2-pentanol	5.2494	0.0734	0.6863	0.8683					

^a The last column contains the values of the reduced effective dipole moment given by the renormalization PT.

compared to simulations. This is in agreement with the findings of Tani et al.¹³ for the DHS fluid.

Figure 2 shows the relative permittivity as a function of $(\mu_0^*)^2$ for a lower ($\alpha^* = 0.05$) and a higher ($\alpha^* = 0.08$) reduced polarizability. In both cases, the continuum approaches work better at low dipole moments. With an increase in the dipole moment, the MOL2 equation becomes superior over the continuum equations. As we mentioned above, the KF1 equation overestimates ϵ at high dipole moments. It is clearly seen from the results for $\alpha^* = 0.05$. The KF2 and ONS equations underestimate the MC data for high dipole moments, which indicates that modeling the polarizability on the molecular level is necessary for high dipole moments.

5.2. Comparison with Experiment. In this work, we consider two main groups of compounds, (1) nonassociative compounds (sulfur compounds, amines, ethers, and halogenated compounds) and (2) associative (hydroxy) compounds near room temperature at atmospheric pressure. The molecules belonging to the first group are weakly polar, and their relative permittivities are relatively low. The relative permittivities of hydroxy compounds are higher but still moderate (below 25). For

compounds of even higher relative permittivities, molecular models more complex than the PDHS model considered here would be necessary. From the comparison to MC data in the previous subsection, we found that MOL2 is the best theory at higher dipole moments, while KF2 works better at low dipole moments. The MOL1 and KF1 equations overestimate the MC results; therefore, we will concentrate mainly on the theories using series expansions (DHS2, KF2, and MOL2). We will always show the results of the classical Onsager theory (ONS).

Before presentation of our results for a number of real substances, it is worthwhile to discuss the effect of the value of the reduced density. In the procedure for the calculation of reduced quantities given in section 4, the reduced density is the only parameter that can be chosen freely. Figure 3 shows the relative permittivity of two selected compounds, a non-associative (chloroform) and an associative (phenol) compound as obtained from the ONS, KF2, and MOL2 equations. The ONS equation does not depend on ρ^* . The KF2 equation also gives nearly ρ^* -independent results. The MOL2 equation is more sensitive to the value of the reduced density. Its explanation is that the value of ρ^* influences the Helmholtz free energy; at

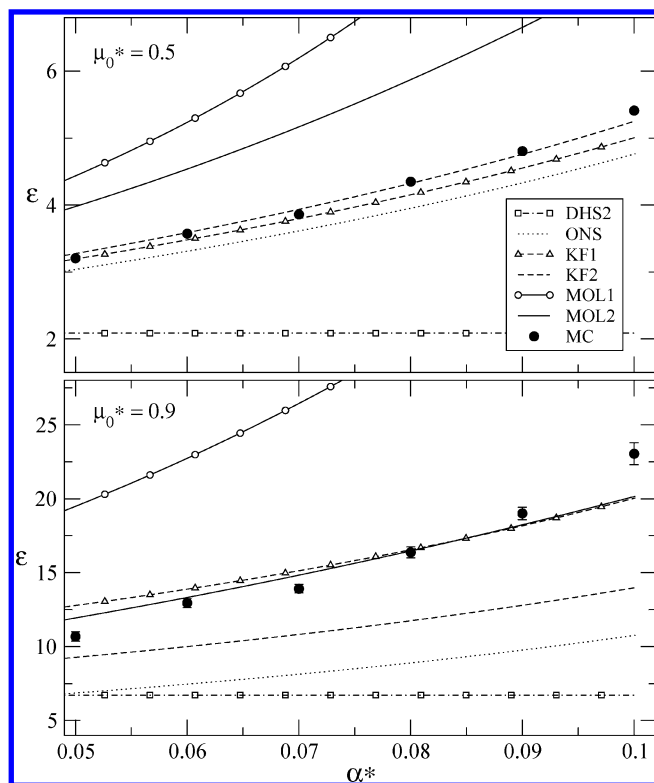


Figure 1. Relative permittivity of the PDHS fluid as a function of the reduced polarizability for dipole moments $\mu_0^* = 0.5$ and $\mu_0^* = 0.9$ as obtained from different theories and MC simulations. The reduced density is $\rho^* = 0.8$.

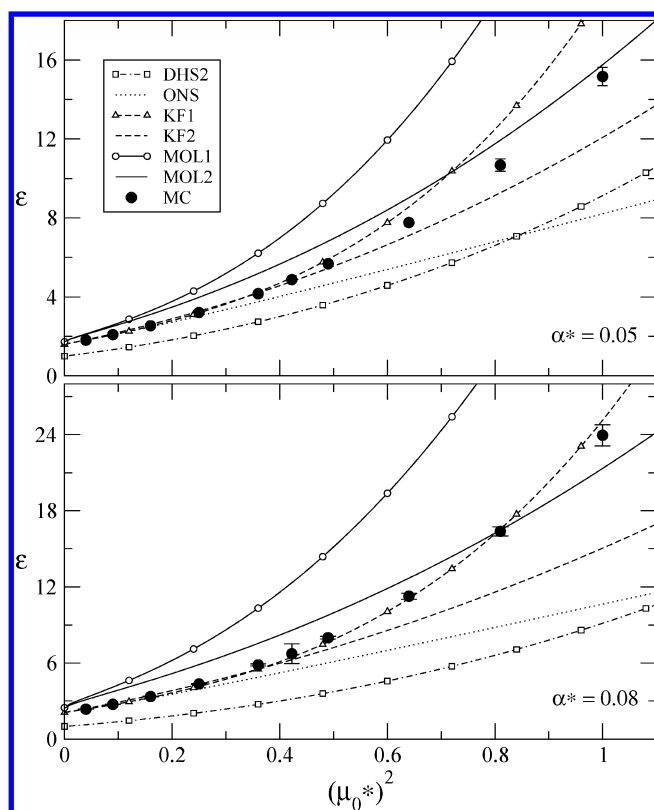


Figure 2. Relative permittivity of the PDHS fluid as a function of the square of the reduced permanent dipole moment for $\alpha^* = 0.05$ and $\alpha^* = 0.08$ as obtained from different theories and MC simulations. The reduced density is $\rho^* = 0.8$.

higher ρ^* , the mean electric field, thus the induced dipole moment, becomes larger. As a consequence, the effective dipole

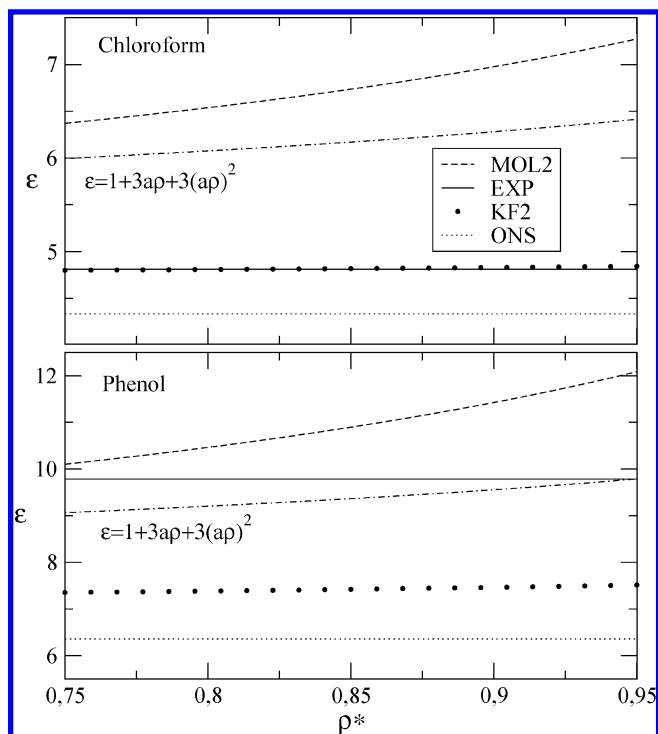


Figure 3. Relative permittivity of chloroform and phenol as a function of the reduced density calculated from various theories compared to the experimental values (solid lines). The dot-dashed lines refer to the MOL2 equation, neglecting the third-order term.

moment is larger at higher densities. This increases the value of the parameters ap and $b\rho^3$. In Figure 3, we also displayed the value of ϵ calculated by truncating eq 28 before the third-order term ($\epsilon = 1 + 3ap + 3a^2\rho^2$). Even this quantity increases with ρ^* , so the increase of the I_{dd} integral is not the only source of the increase of ϵ ; the renormalization procedure causes the stronger ρ^* -dependence. Our systematic simulation studies have shown that the MOL2 theory reproduces the ρ^* -dependence of the relative permittivity of both the polarizable Stockmayer⁵ and the PDHS⁴¹ fluid reasonably.

Nonetheless, the observed ρ^* -dependence of the MOL2 equation does not influence our qualitative conclusions seriously. Choosing, say, $\rho^* = 0.9$ instead of $\rho^* = 0.8$ would change the relative permittivity from $\epsilon = 6.54$ to $\epsilon = 6.97$ in the case of chloroform and from $\epsilon = 10.46$ to $\epsilon = 11.41$ in the case of phenol. These deviations are not too large compared to the deviations between the various theories and the experimental data as we will see from the next figures. We do not expect accurate quantitative agreement from our theories; our intention is to produce results based on a model that is, although very simple, able to take into account molecular correlations.

The relative permittivities of the various compounds calculated from different theories are tabulated in Table 2 with a comparison to experimental data. The MC results are interpolated values computed from the MC data obtained for the grid described in subsection 5.1. To make it easier to draw qualitative conclusions, we illustrate our results graphically. We plot the relative permittivities as calculated from the DHS2, ONS, KF2, and MOL2 equations as well as MC simulations against experimental relative permittivities. The straight lines denote the experimental values, while every symbol corresponds to a given compound, which can be identified from Table 2. We show the results for sulfur compounds, amines, ethers, halogenated compounds, and hydroxy compounds in Figures 4–8, respectively.

TABLE 2: Relative Permittivity of Sulfur Compounds, Amines, Ethers, Halogenated Compounds, and Hydroxy Compounds as Calculated from Various Theories^a

compound	DHS1	DHS2	KF1	KF2	ONS	MOL1	MOL2	MC	EXP
Sulfur Compounds									
carbon disulfide	1.00	1.00	2.65	2.65	2.65	3.57	3.34	2.67(2)	2.64
thiophene	1.22	1.22	2.79	2.89	2.79	4.37	3.93	2.79(1)	2.71
benzenethiol	2.23	2.20	5.28	5.51	4.97	11.02	7.90	6.78(10)	4.38
1-butanethiol	3.15	2.99	5.99	5.88	5.14	11.24	8.03	6.36(78)	5.07
ethyl sulfide	3.49	3.27	6.62	6.35	5.48	12.55	8.70	7.11(78)	5.72
methyl sulfide	4.35	3.91	8.09	7.33	6.15	15.35	10.05	9.55(24)	6.20
Amines									
triethylamine	1.37	1.37	2.59	2.69	2.58	3.74	3.47	2.65(2)	2.42
dibutylamine	1.45	1.45	2.81	2.94	2.79	4.25	3.85	2.92(3)	2.98
dipropylamine	1.57	1.56	2.94	3.08	2.91	4.48	4.02	2.85(2)	3.07
diethylamine	1.93	1.91	3.47	3.61	3.35	5.50	4.71	3.72(3)	3.58
isobutylamine	2.39	2.34	4.32	4.42	4.00	7.32	5.86	4.28(8)	4.43
butylamine	2.80	2.70	5.06	5.07	4.51	8.92	6.79	4.71(8)	4.88
propylamine	3.17	3.00	5.59	5.47	4.79	9.85	7.3	5.66(8)	5.31
<i>m</i> -toluidine	2.82	2.71	6.40	6.45	5.69	13.58	9.19	6.88(9)	5.95
<i>o</i> -toluidine	3.47	3.25	7.88	7.58	6.54	17.04	10.81	9.06(21)	6.34
aniline	3.67	3.40	8.47	8.04	6.89	18.56	11.49	9.78(21)	6.89
Ethers									
<i>p</i> -dioxane	1.15	1.15	2.29	2.34	2.29	3.12	2.97	2.37(1)	2.21
dimetoxymethane	1.44	1.44	2.55	2.64	2.53	3.56	3.32	2.63(1)	2.65
pentyl ether	1.50	1.50	2.87	2.99	2.84	4.34	3.91	2.88(2)	2.77
isopentyl ether	1.54	1.54	2.93	3.06	2.90	4.47	4.01	2.90(2)	2.82
furan	1.50	1.50	2.91	3.04	2.88	4.47	4.00	2.99(2)	2.94
butyl ether	1.61	1.60	3.00	3.14	2.96	4.60	4.10	2.86(2)	3.08
propyl ether	2.01	1.99	3.58	3.72	3.44	5.71	4.86	3.71(3)	3.39
phenyl ether	1.61	1.61	3.84	4.07	3.79	7.22	5.79	3.97(3)	3.69
acetal	2.07	2.05	3.63	3.77	3.47	5.76	4.89	3.62(3)	3.80
isopropyl ether	1.82	1.81	3.21	3.35	3.12	4.90	4.31	3.45(3)	3.88
veratrole	2.11	2.09	4.66	4.87	4.43	9.07	6.86	4.42(4)	4.09
phenetole	2.21	2.18	4.68	4.87	4.42	8.93	6.79	5.73(8)	4.22
ethyl ether	2.04	2.02	3.50	3.63	3.35	5.42	4.66	3.40(3)	4.33
anisole	2.17	2.14	4.66	4.66	4.41	8.95	6.80	5.90(8)	4.33
Halogenated Compounds									
pentachloroethane	1.52	1.52	3.30	3.47	3.27	5.60	4.78	3.49(2)	3.73
bromoform	1.86	1.85	4.50	4.76	4.37	9.05	6.84	5.11(4)	4.39
1,2-dibromomethane	2.61	2.53	5.73	5.85	5.20	11.71	8.26	5.91(10)	4.78
chloroform	2.43	2.37	4.69	4.81	4.33	8.48	6.54	5.40(8)	4.81
diiodomethane	2.20	2.16	6.34	6.67	5.98	14.96	9.81	10.25(10)	5.32
bromobenzene	3.31	3.12	7.40	7.20	6.24	15.78	10.23	8.23(12)	5.40
chlorobenzene	3.38	3.18	7.22	6.99	6.04	14.94	9.85	7.88(21)	5.62
iodomethane	5.85	4.95	12.36	10.14	8.20	25.42	14.39	11.37(36)	7.00
1-chlorobutane	5.90	4.98	10.46	8.62	6.91	19.11	11.76	11.16(36)	7.39
1,1,1-trichloroethane	3.71	3.43	6.99	6.61	5.66	13.27	9.05	7.38(78)	7.53
iodoethane	7.32	5.86	15.12	11.44	8.96	30.09	16.24	17.66(42)	7.82
1,1,2,2-tetrachloroethane	4.18	3.79	8.45	7.74	6.53	17.04	10.82	10.27(31)	8.20
bromoethane	10.29	7.55	18.61	12.47	9.17	33.05	17.39	18.71(84)	9.39
1,1-dichloroethane	9.56	7.15	17.13	11.82	8.79	30.48	16.41	17.36(84)	10.00
1,2-dichloroethane	8.53	6.57	15.92	11.44	8.70	29.41	15.99	15.69(36)	10.36
Hydroxy Compounds									
2-methyl-2-butanol	3.94	3.61	7.04	6.55	5.57	12.86	8.85	6.99(78)	5.82
<i>trans</i> -3-methylcyclohexanol	3.71	3.43	7.19	6.80	5.82	13.96	9.39	7.43(78)	8.05
phenol	3.53	3.29	7.71	7.38	6.36	16.27	10.46	8.56(21)	9.78
<i>p</i> -cresol	3.74	3.46	8.12	7.66	6.55	17.11	10.85	8.94(21)	9.91
1-octanol	2.83	2.73	5.32	5.32	4.72	9.70	7.21	5.34(8)	10.34
<i>o</i> -cresol	3.20	3.03	7.03	6.90	6.00	14.79	9.77	7.75(12)	11.50
<i>m</i> -cresol	3.28	3.10	7.16	6.98	6.06	15.02	9.88	7.83(12)	11.80
3-methylcyclohexanol	4.55	4.06	8.77	7.83	6.53	17.10	10.86	8.87(31)	12.30
2-methyl-2-propanol	4.46	3.99	7.76	6.98	5.83	13.93	9.38	9.21(22)	12.47
3-pentanol	3.77	3.48	6.82	6.42	5.49	12.54	8.70	6.96(78)	13.02
benzyl Alcohol	3.96	3.63	8.58	7.97	6.77	18.09	11.29	9.34(21)	13.10
1-hexanol	2.83	2.72	5.24	5.24	4.65	9.44	7.07	5.12(8)	13.30
2-methylcyclohexanol	4.96	4.35	9.59	8.34	6.87	18.74	11.59	9.34(31)	13.30
4-methylcyclohexanol	4.52	4.04	8.70	7.78	6.50	16.94	10.78	8.78(31)	13.30
2-pentanol	3.82	3.52	6.87	6.45	5.51	12.59	8.72	6.95(78)	13.82
1-pentanol	4.00	3.66	7.23	6.70	5.69	13.33	9.09	7.21(78)	13.90
3-methyl-1-butanol	4.73	4.19	8.46	7.48	6.20	15.58	10.16	8.47(24)	14.70
cyclohexanol	5.46	4.69	10.59	8.93	7.27	20.71	12.45	9.89(31)	15.00
<i>cis</i> -3-methylcyclohexanol	4.61	4.10	8.87	7.89	6.57	17.29	10.94	8.89(31)	16.47
2-butanol	4.19	3.80	7.41	6.78	5.72	13.44	9.14	7.61(24)	16.56
1-butanol	5.43	4.67	9.57	8.10	6.58	17.43	11.01	8.42(24)	17.51

TABLE 2: (Continued)

compound	DHS1	DHS2	KF1	KF2	ONS	MOL1	MOL2	MC	EXP
Hydroxy Compounds (Continued)									
2-methyl-1-propanol	5.73	4.87	10.04	8.35	6.73	18.20	11.36	8.39(24)	17.93
2-propanol	6.31	5.24	10.78	8.69	6.89	19.10	11.76	12.61(30)	19.92
2-propene-1-ol	6.67	5.47	11.91	9.40	7.41	21.79	12.91	12.09(36)	21.60
2-propyn-1-ol	12.76	8.82	23.33	14.30	10.16	40.54	20.13	21.36(84)	24.50
ethanol	10.28	7.54	17.08	11.55	8.42	28.71	15.73	16.46(45)	24.55
1,2-propanediol	23.51	13.65	43.04	20.36	12.96	67.86	29.27	33(1)	32.00
1,3-propanediol	41.34	20.45	76.3	28.18	16.09	108.86	41.53	40(1)	35.00
1,2-ethanediol	50.18	23.52	91.57	31.2	17.05	125.76	46.29	41(1)	37.70

^a The last column contains the experimental data.⁴⁸ The MC data are interpolated values using the simulations performed on the grid described in the text. The numbers in parentheses denote the statistical uncertainties in the last digits calculated from the block average method.

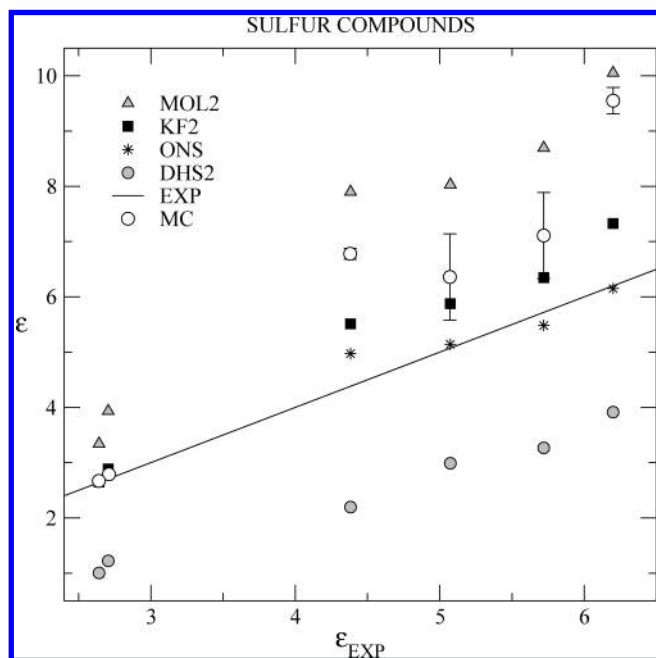


Figure 4. Relative permittivity of sulfur compounds as obtained from different theories and simulation plotted against the experimental values (solid line).

The DHS2 equation underestimates the experimental data considerably in every case. This means that the nonpolarizable DHS model is inappropriate and taking the polarizability into account in some way is necessary.

If we want to draw a clear distinction between model and theories, then we have to discuss the agreement between MC and experimental data separately from the comparison of theory and experiment. Let us compare the open circles to the straight lines in Figures 4–8. We can conclude that in the cases of amines (Figure 5) and ethers (Figure 6) the agreement between the MC results and experimental data is quite good. This is valid for sulfur (Figure 4) and halogenated (Figure 7) compounds if the relative permittivity is not too large (below 6).

For nonassociative liquids with relative permittivities higher than 6, the MC results based on the PDHS model overestimate the experimental values. A possible explanation of this result is that the PDHS model overemphasizes the role of the electrostatic interactions (modeled by polarizable point dipoles) compared to the van der Waals forces. Specifically, the shape of the molecules is a much more important factor in this regime; the hard sphere core of the PDHS model probably allows much more orientation polarization than is possible in real liquids. The molecules have irregular shapes, and they are close to each other in the liquid; consequently, their ability to orient each other (orientation polarization) is smaller than in the case of the PDHS model.

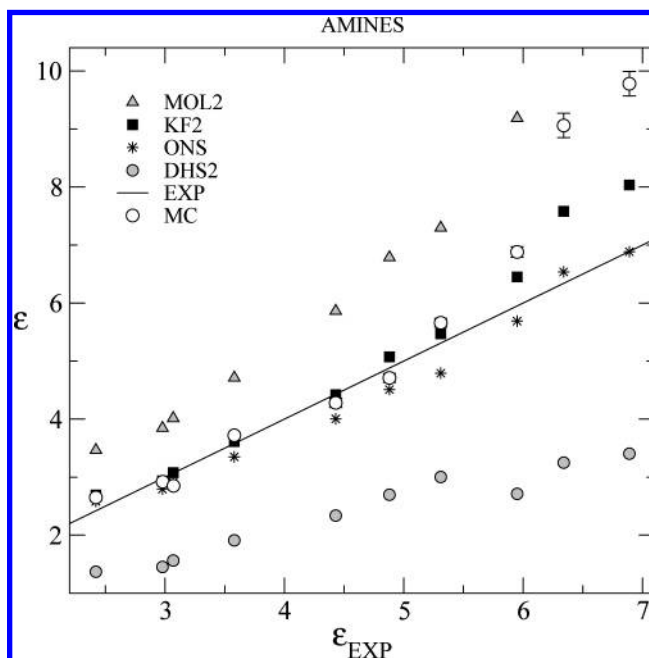


Figure 5. Relative permittivity of amines as obtained from different theories and simulation plotted against the experimental values (solid line).

In the case of hydroxy compounds (Figure 8), the situation is reversed. Here, the PDHS model is quite good in some cases, and it underestimates the experimental data in other cases. The explanation is also the reverse of that given above for the case of nonassociative liquids. For associative liquids, the electrostatic interactions are stronger, hydrogen bonds form, and the shape of the molecules is probably less important. As a consequence, the error introduced by the simple spherical shape of the PDHS model is smaller in these cases. For the materials where the MC results underestimate the relative permittivities, the polarizable point dipole model is probably no longer satisfactory to describe association. In these cases, more detailed model potentials are necessary.

When we compare the results given by various theories to experimental data, the conclusions we can draw are less definite. There are cases when a theory works well for a given model (agrees with simulation), but it fails for real liquids. The typical example is the case of hydroxy compounds at intermediate relative permittivities; the MOL2 theory is very good in reproducing the MC data, but both fail to reproduce experiment. In this case, it is the model that fails not the theory.

On the contrary, if a theory seems to work well in reproducing experiment, but it fails for the model, then we cannot state that the theory is appropriate to calculate the relative permittivities of the real liquids. The theory contains some approximation that results in a positive (or negative) error in ϵ compared to

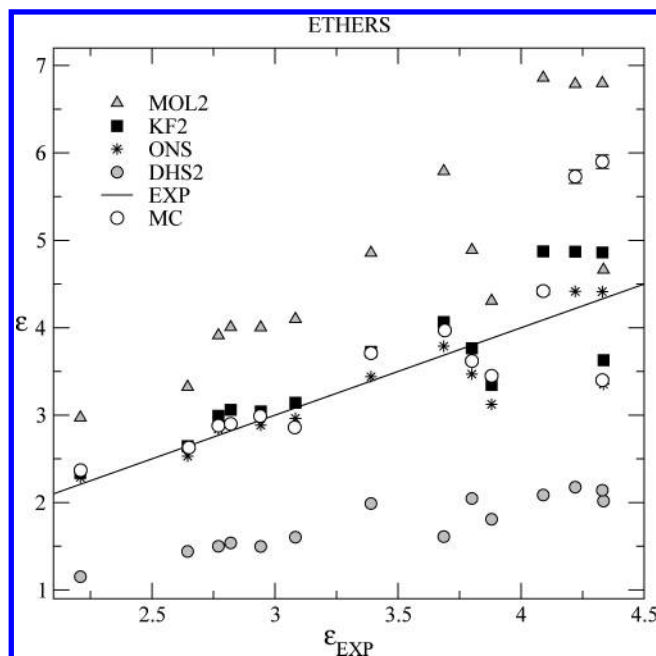


Figure 6. Relative permittivity of ethers as obtained from different theories and simulation plotted against the experimental values (solid line).

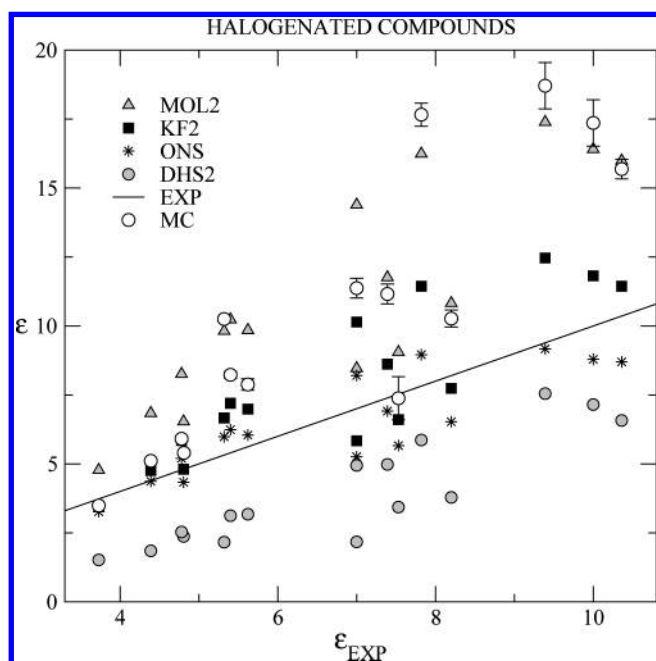


Figure 7. Relative permittivity of halogenated compounds as obtained from different theories and simulation plotted against the experimental values (solid line).

simulation. If the errors caused by the weakness of the model introduce an error of the opposite sign, then these two contributions might cancel each other. This might result in a false belief that the theory is good for the real liquid, but this is not the case. Good examples are the halogenated compounds where the KF2 equation seems to work well, but the MC data overestimate the experimental values. The reason that the KF2 equation gives good estimates is probably that the errors introduced by the unsatisfactory modeling of the molecule's shape (sphere) and the electrostatic forces (point dipoles, continuum description of polarizability) cancel each other.

In this respect, it is interesting that the ONS equation gives surprisingly good results in some cases (sulfur compounds,

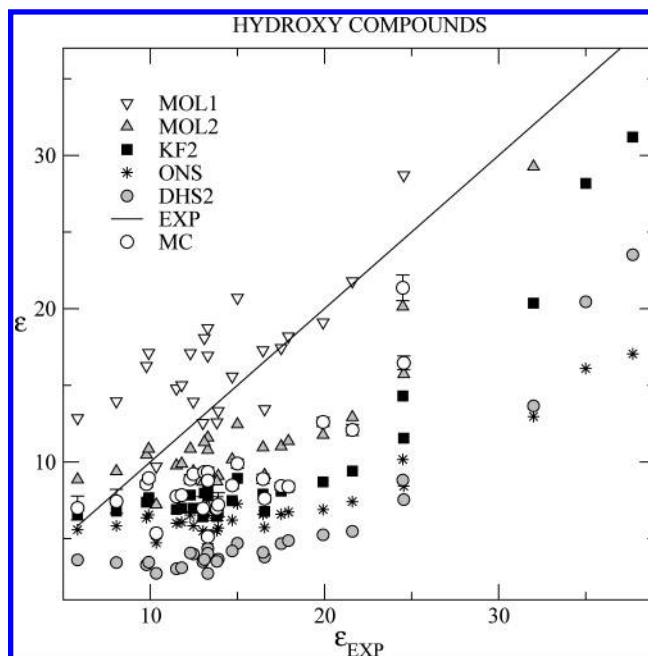


Figure 8. Relative permittivity of hydroxy compounds as obtained from different theories and simulation plotted against the experimental values (solid line).

ethers, halogenated compounds). The model of the Onsager approach is very simple (a point dipole in a cavity) for which Onsager's solution is exact. On the basis of the reasoning given in the above paragraph, we cannot state that the ONS equation is appropriate for these compounds. If the PDHS model, which is a more developed model than that of the Onsager approach, does not work well for a given liquid, then we cannot state that a weaker model is good even if it accidentally gives reasonable results. What we can say is that there are fortunate cancellations in the Onsager model.

6. Summary

Whether it is the spherical HS core or cutting the multipole expansion at the point dipole term that contains the stronger approximation is an open question. In the case of liquids with stronger dipolar interactions, the latter is probably more important. This is supported by the results of Goldman et al.^{19,20} for the SPC and TIP4P models of water. Furthermore, Goldman and Joslin²¹ included quadrupole moments in their PT calculations to represent molecules that are able to hydrogen bond. They found that, by supplementing the DHS model with a quadrupole moment, experimental relative permittivities of hydrogen-bonded liquids could be reproduced. We emphasize that molecular polarizability was not taken into account in the studies of Goldman et al.;^{18–21} therefore, a generalization of Goldman's equations for more complex charge distributions in the spirit of our KF2 or MOL2 method would be worthwhile.

We have proposed various theoretical equations based on the DHS model of pure polar liquids. The main point of our work is that we take into account the molecular polarization in two approaches, in a continuum approach based on the Kirkwood–Fröhlich equation and in a molecular approach based on a renormalization PT treatment of the PDHS model. We tested our theories against MC results in the parameter range of real compounds considered in this work and found that the continuum approach (KF2) works better for lower dipole moments, while the molecular approach (MOL2) is better at higher dipole moments. The results obtained from the PDHS model using MC

simulations overestimate the relative permittivity of compounds of intermediate dipolar strength due to the spherical shape of the molecular model. In the case of some associative liquids, the PDHS model provides an underestimation of experimental values due to the unsatisfactory treatment of electrostatic forces. If we want to consider molecules acting through specific interactions (first of all, hydrogen bonds), then models that are more sophisticated than the PDHS potential are needed.

In this paper, we considered pure liquids and stressed the importance of taking into account the polarizability and dipole–dipole correlations. If we have usable models and theories for pure liquids, then we can also calculate the relative permittivity of their mixtures. This issue was considered in our earlier paper,⁴ where we extended our continuum approach to mixtures and showed that it correctly reproduces the mole fraction dependence of the relative permittivity as obtained from experiments.⁴⁹ With a reasonable equation for the $\epsilon(x)$ function, we can determine the composition of polar mixtures from simple dielectric measurements. Lee and Ladanyi⁵⁰ found that the series expansion used in eq 18 is very efficient in reproducing the relative permittivity of mixtures of DHS molecules. This supports the thought that our theoretical approaches might provide promising tools to study the dielectric properties of mixtures of polar liquids.

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