Classical interaction model for the water molecule

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The authors propose a new classical model for the water molecule. The geometry of the molecule is built on the rigid TIP5P model and has the experimental gas phase dipole moment of water created by four equal point charges. The model preserves its rigidity but the size of the charges increases or decreases following the electric field created by the rest of the molecules. The polarization is expressed by an electric field dependent nonlinear polarization function. The increasing dipole of the molecule slightly increases the size of the water molecule expressed by the oxygen-centered σ parameter of the Lennard-Jones interaction. After refining the adjustable parameters, the authors performed Monte Carlo simulations to check the ability of the new model in the ice, liquid, and gas phases. They determined the density and internal energy of several ice polymorphs, liquid water, and gaseous water and calculated the heat capacity, the isothermal compressibility, the isobar heat expansion coefficients, and the dielectric constant of ambient water. They also determined the pair-correlation functions of ambient water and calculated the energy of the water dimer. The accuracy of theirs results was satisfactory. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2730510]

I. INTRODUCTION

One of the evergreen topics of physical chemistry is to understand the behavior of water in molecular details in pure form or as a solvent. The popularity of water studies stems from two sources: the ubiquity of this substance in nature and the complex properties of materials containing water. Since the appearance of powerful computers the most obvious way to study water theoretically is to build a model based on quantum or classical mechanics and perform computations based on the concepts of statistical mechanics. In engineering applications or in complex biological systems the computational demand is still large enough to require classical models composed of fixed (or stretching and bending) bonds, partial charges, and simple functions of repulsions and attractions.

The most frequently used models of this kind represent water as a rigid, planar molecule. The geometry of atoms is fixed, partial charges are placed on the hydrogens and the bisector of the HOH angle, and the model is completed by a Lennard-Jones interaction centered on the oxygen atom. There are numerous parametrizations of this archetype. The most frequently used versions are the TIP4P (Ref. [1]) and the SPC/E (Ref. [2]) models. The former has the geometry of the gas phase molecule (0.9752 Å for the OH bond length and 104.52° for the HOH angle) with the negative partial charge $(2 \times 0.52$ esu) placed at 0.15 Å from the oxygen, while the latter has perfect tetrahedral geometry (1.0 Å and 109.47°) with a negative partial charge $(2 \times 0.4238$ esu) being on the oxygen atom. The best overall performance[3–7] is shown by two recent parametrizations of this model family: the TIP4P-EW (Ref. [3]) and the TIP4P-2005.[4] All the above models are computationally economic and easy to implement in simulations.

It is remarkable that some nonpolarizable models fitted to the properties (internal energy, density, and structure at the level of pair correlations) of ambient water can provide reasonable predictions at a range of state points in liquid state and, in some cases, even including high temperature hexagonal ice. Still, any water model which is unable to respond to the polarizing forces of the surrounding by varying its electric moments will perform poorly in the vapor phase and in the ice phases in general.[5,6] The need for a model being correct independently from macroscopic state variables and the actual molecular environment is an aim of researchers from the beginning of molecular simulations. This is the aim of this paper too. In the following we propose a model and report the first results of an approach we opted to follow.

There are several dozen water models in the literature.[8,9] Some of them are polarizable and intend to remedy the shortcomings of the simple models. It is not our aim of reviewing and assessing the performance of these models but, for the most recent and most successful ones, we refer the reader to the literature.[10–18] As for strategies, there are two extremes to follow. One is to build a sophisticated model and try to match the experimental properties as done, for instance, by Fanourgakis and Xantheas and Burnham and Xantheas.[19] The other is to create a simpler model at the expense of some loss in physics but gain in terms of the easiness of code implementation and the moderate increase in computational cost as done by Lamoureux *et al.*[20] In this respect our approach is much closer to the latter. We wanted a model which is based on plausible assumptions and straightforward coding. In this paper we dealt primarily with the solid-liquid region of the phase diagram, although we simulated a vapor phase and determined the energy of the water dimer.

In the next section we describe our strategy of potential

derivation. Then in Sec. III we provide the details of the calculations and present the results. In the last section we conclude our study.

II. DESCRIPTION OF THE ENLARGEABLE CHARGES MODEL FOR WATER

The basic attributions of the enlargeable charges (ENCS) model are as follows:

(1)   The shape of the molecule corresponds to the geometry of TIP5P: 0.9752 Å for the OH bond length and 104.52° for the HOH angle; there are two weightless sites (C) placed 0.7 Å from the oxygen with 109.47° for the COC angle in the plane perpendicular to the HOH plane.[21]

(2)   The partial charges are set to match the gas phase dipole of the water molecule: 1.855 D.[22] So, both the H and C sites carry a charge of 0.195 esu.

(3)   The polarization happens as the result of the electric field created by the partial charges of the other water molecules in the system.

(4)   The response for the electric field is manifested by the variation of the magnitude of charges on the H and C sites, while the geometry of the molecule remains fixed.

(5)   The polarizability α of the molecule is expressed by a nonlinear function. In this way the dipole moment varies as $\mu = \alpha(E)E$.

(6)   In addition to the dipole moment, i.e., the magnitude of the partial charges, we change the size of the molecule in the form of changing the σ parameter of the Lennard-Jones potential. The increase of the dipole moment increases the magnitude of σ.

The justifications are as follows:

(1)   A planar model could not represent the almost isotropic polarizability of water.[9] While the actual geometry might change later to match the quadrupole moment and possibly the energy of water clusters, the roughly tetrahedral arrangement gives more room for variations. In fact, the ENCS can be seen as an improvement of the TIP5P interaction.

(2)   The simplest way to calculate the polarizing electric field is to use the direct part of the Ewald sum.[23] For large enough system the net force originating from charges far from the actual one is practically isotropic. (Its time or ensemble average is very close to zero.) This assumption should be checked for each system in question. For ambient water 250 particles proved to be sufficient to fulfill this criterion. We checked it by performing calculations on 500 particles. For ice phases we need more than ~150 particles. In the case of hexagonal ice we used 432, and for the vapor phase we used 2000 molecules.

(3)   The price to be paid for this method is the loss of rigorous energy conservation. This is caused by the assumption of the zero net force beyond the Ewald cutoff radius. This assumption is correct in the average but should not be correct instantaneously. However, the code maintains its simplicity. The only extra cost comes

from the need of an iterative force—charge calculation to preserve the self-consistency of the method. The importance of these iterations depends on the particular property to be calculated. Properties determined from fluctuations proved to be more sensitive in this respect.

(4)   While the charges of different molecules are different, we keep the four partial charges in each molecule identical. Clearly, this approach prevents the out-of-plane polarizability of water because the dipole vector of the molecule is always aligned along the bisector of the HOH angle. At this stage we accept this limitation of physics for the sake of computational simplicity. We calculate the component of the polarizing force parallel with the OH or OC bonds for each site. Such a way we determine forces which "stretch" or "compress" the OH or OC bonds depending on the direction. Then we add up these plus or minus components as scalars to create the independent variable of molecule i for the polarizability function as follows:

$$F_i = \sum_{\alpha=1,2,3,4} -z_\alpha \frac{\partial \Phi}{\partial \mathbf{r}_i^\alpha} \frac{(\mathbf{r}_i^\alpha - \mathbf{r}_i^O)}{|\mathbf{r}_i^\alpha - \mathbf{r}_i^O|}, \tag{1}$$

where α identifies the four charged sites, $z_\alpha = \pm 1$ is the sign of the charge α, Φ is the Coulomb potential created by the rest of the molecules as expressed by the direct part of the Ewald sum, and r_i^O is the position of the oxygen atom.

This method might seem as an oversimplification because we pay no attention to theories describing responses of the charge distributions within the molecule to the impact of an external field. (See, for instance, the principle of electronegativity equalization.[11]) However, at this stage our primary intention merely is to check whether such a method as an improvement of the rigid TIP5P model can work.

(5)   The polarizability function [in fact, we used the total $\alpha(E)E$ term which provided the total dipole moment of the molecule] has a trivial fixed point. At zero electric field the dipole moment of the gas phase molecule is applied.[22] In addition to that, using the ACES II quantum mechanical code[24] we determined the linear, gas phase polarizability of the molecule and fitted the close to zero field moments to this value (see Fig. 1).

(6)   A classical model is inherently unable to mimic effects of quantum mechanical origin. This prompted us to match the dilatation of the freezing water by increasing the size of the molecule. It might be a plausible assumption to increase the size of the molecule with the size of its dipole moment, and it is mandatory if one wishes to match energy and density values in the liquid-solid coexistence region. Even rigid models with fixed dipole moment overestimate the density of the hexagonal phase. This error would be larger for polarizable models because the molecule due to the stronger field would have a larger dipole moment in the crystalline than in the liquid phase. Interestingly, this aspect was neglected in most of the previous polarizable mod-
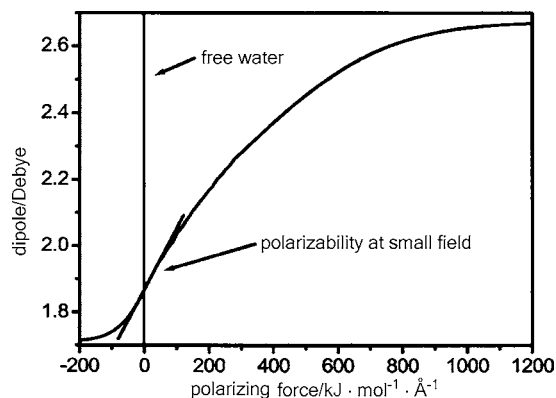
FIG. 1. The nonlinear polarizing function is shown as the dipole moment in terms of the polarizing Coulomb force. The linear change of the dipole moment at small fields is marked by a linear line.

els. These studies were more focused on the correct liquid-gas features.

The importance of the repulsion was pointed out in our recent studies.[25] The most remarkable finding was that potential models fitted to the density of ambient water overestimate the energy of the high pressure ice phases (ice VII and VIII) by $4-6$ kJ/mol.[5,25] This is caused by the fact that in liquid water and in the low pressure ice phases the water molecule has four neighbors, while in the high pressure phases the number of neighbors is eight, and only four of them is connected by hydrogen bonds. The fixed repulsive part of the interaction is unable to adjust itself to this situation, in contrast to real molecules. The impact of an ion on its hydration shell can be seen as a pressure in the range of 10^2 GPa. The correct reproduction of high pressure phase energies and structures can improve our understanding of ion hydration.

We emphasize that in the classical models the charge-charge and the Lennard-Jones interactions cannot be separated. In these models the fitting procedure does not make a clear distinction between the charge-charge and the Lennard-Jones contributions. In addition to this, the actual estimate of the dipole moment in liquid water or ice depends on how the electron density is partitioned on to molecules. So, models having dipole moments around 2.5 D are reasonable, despite recent calculations where this arbitrariness and the classical

character of the model are responsible for the fact that the size of the dipole moment in ambient water as obtained from *ab initio* molecular dynamics[26] and from the analysis of experimental data[27,28] is 2.95 D, and recent calculations provided 3.09 D for hexagonal ice.[29] The typical dipole moment for the simple models is much smaller typically in the range of $2.1-2.6$ D.[8,9]

Since classical models were fitted to the parameters of ambient water their fixed geometry and dipole moment produced poor matches for gas phase properties.[5,6] We showed previously that neither their second virial coefficients in terms of the temperature nor the estimated critical constants were close to the experimental value.[5,6] To present a property straightforward to compute and visualize we calculated the dimer energy of some of the most frequently used nonpolarizable, rigid models. For comparison we show results for the polarizable models too (Table I).

Our approach has two differences with respect to other polarizable models in the literature. The first is the tabulated nonlinear polarizability function. Although the test to find the optimal form of this function has not been completed yet, there is a large freedom to adjust this function. While other models tried to find a simple physical theory of polarization to justify their model, we state that if the basic principles are correct it is more important to match the experimental data, than to constrain the performance of the model with approximate theories. The other difference is the variable size of the water molecule. While we pointed to the importance of correct repulsion in the case of crystalline solids, it cannot be neglected if transport processes are concerned either. Even correct static structures can produce false transport coefficients because the system is too "tight" or too "loose." A similar approach was taken by Chen *et al.* by coupling electronic properties to Lennard-Jones parameters in order to obtain better liquid-vapor coexistence properties.[30]

III. DETAILS AND RESULTS OF CALCULATIONS

We wrote a Monte Carlo program with the Ewald summation.[5,23] Since the shape of the molecule has not changed during the simulation, we could retain the standard random displacement and rotation technique trying to keep the 1/2 acceptance ratio.[5,23] First we carried out a trial move and rotation one by one for each water particle. After finishing this cycle, we changed the volume of the system in a

TABLE I. Dimer energies for different rigid and polarizable models of water. The experimental values is 22.6 ± 3.0 kJ/mol. (Refs. 37 and 38).

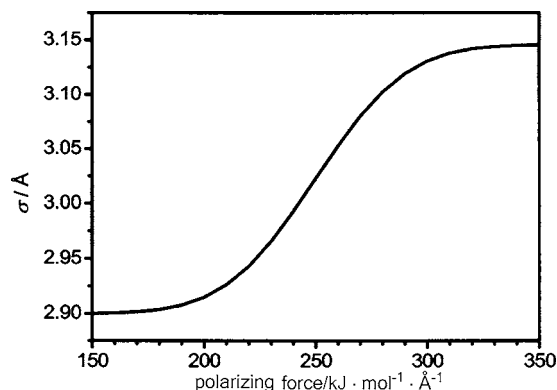| Rigid models	TIP4	TIP4P-EW	TIP4P-2005	TIP4P-ice	TIP5P	TIP5P-E	TIP3P
$-$Energy (kJ/mol)	25.9	28.5	29.8	31.3	28.4	28.5	27.2
Reference	1	3	4	33	39	40	41
Polarizable models	POL3	TIP4P-FQ	Burnham *et al.*	MCDHO	SWM4-DP	ENCS	*Ab initio*
Energy (kJ/mol)	19.6	18.9	22.3	20.9	21.7	22.6	20.9
Reference	14	11	43	15	20	This work	42

FIG. 2. The Lennard-Jones σ parameter in terms of the polarizing force.

Parinello-Rahman fashion[5] and if this was successful we repositioned the particles accordingly. While the Monte Carlo procedure does not need the calculation of forces, for the sake of polarization, we had to determine the electrostatic forces acting on each charged site of a molecule by using the direct part of the Ewald sum.[5,23] The result of this force calculation, as it was described in the previous section, was used as an input for the nonlinear polarizing function. Thus, following the successful or unsuccessful attempt to change the volume, the program calculated the forces and adjusted the charges of each water molecule. Since their polarizing environments were different, the molecules obtained different charges. (But the four sites of a molecule remained identical.) Then the program returned to start the random move and turn attempts again. Such a way we considered a Monte Carlo cycle as a time step.

The self-consistency of the above algorithm requires an iterative charge alteration procedure (while keeping the position of the molecules) because the change of neighboring charges would alter the electric field acting on the molecule in question. We involved this possibility in the code. The iteration was less important in the case of obtaining an accurate average energy or structure than for properties calculated from fluctuations. Typically, five iterations were sufficient.

In Fig. 1 we present the nonlinear polarizing function applied in these simulations. The electric field is expressed in the form of a force acting on the sites of a molecule. At zero electric field, the function correctly crosses the value of 1.855 D. The zero field polarizability was determined by the ACES II quantum chemical package for the given rigid geometry.[24] The polarization function has a saturation character with a saturation value of 2.673 D. This value resulted from a simultaneous trial and error fit together with the σ parameter of the Lennard-Jones interaction. In principle, there is no need for a maximum possible value of the water dipole moment because the increasing size could prevent a polarization catastrophe. From the point of view of the simulation control, however, it was better to limit the maximum value for both functions (see Fig. 2). The function applied for the size σ_i of water molecule i was the following:

$$\sigma_i = \sigma_{\min} + \Delta\sigma[\text{erf}(x) + 1.0]/2.0, \qquad (2)$$

where $x = a(F_i - F_0)$. The parameter values applied in this paper were as follows: $\sigma_{\min} = 2.9$ Å, $\Delta\sigma = 0.2445$ Å, F_i is the

TABLE II. Values of the polarizing functions as shown in Fig. 1.

F (kJ/mol/Å)	D (D)
−200	1.714
−150	1.721
−100	1.741
−50	1.786
0	1.855
50	1.959
100	2.036
150	2.106
200	2.169
250	2.230
300	2.282
350	2.327
400	2.372
450	2.414
500	2.454
550	2.490
600	2.523
650	2.551
700	2.576
750	2.597
800	2.614
850	2.628
900	2.640
1000	2.655
1100	2.664
1200	2.668

force of Eq. (1), $F_0 = 25.0$ kJ/mol/Å, and $a = 0.22$ mol Å/kJ.

While in the case of the polarizing function we started to use a similar functional form, and it turned out that the convenient parameter adjusting of Eq. (2) should be replaced by a tabulated function. The tabulated values of Fig. 1 are shown in Table II.

While the maximum value was determined following the requirement of matching macroscopic data, the minimum values are somewhat arbitrary. The dipole moment of the molecule as a result of polarization in the linear regime at a rigid geometry is a line crossing the zero field axes. The minimum value may be fitted to match gas phase and water cluster properties. (This part of the function needs further refinement.) In the case of the size function both the mini-
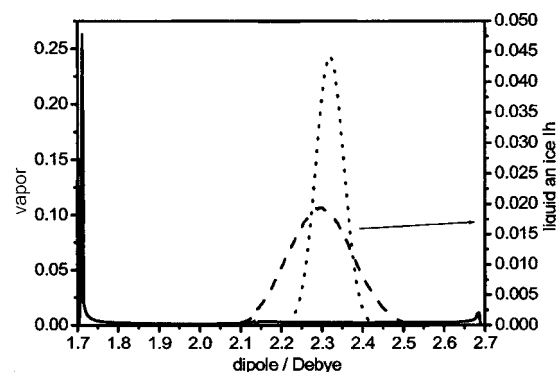

FIG. 3. Distribution of the dipole moments (in arbitrary units) at 273.15 K in hexagonal ice (dotted line), water (dashed line), and gas phase (solid line).
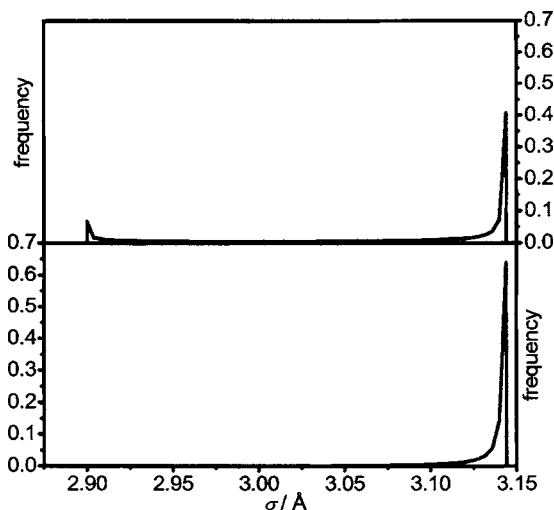
FIG. 4. Size distribution of water molecules (in arbitrary units) at 273.15 K in water (top) and hexagonal ice (bottom).
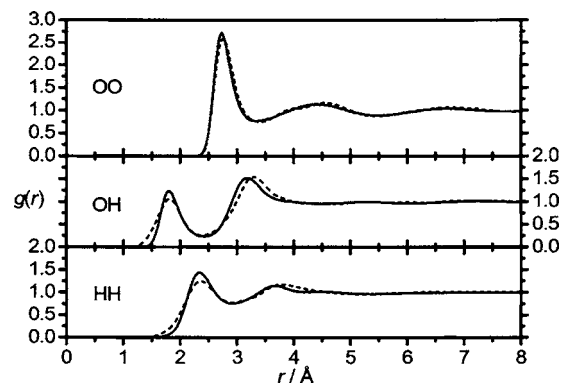

FIG. 5. Partial pair correlation functions for ambient water. [Solid lines: our calculation; dotted line: from the measurement of Soper *et al.* (Ref. 30)].

mum and the maximum values were fitted in order to give a good match for experimental properties. Clearly, our choice of parameters is not unique. There is a range of variables within the combination of the Lennard-Jones and the Coulombic parts that provide an acceptable accuracy. This is true, in particular, for the minimum value of the Lennard-Jones size parameter σ.

In Fig. 3 we present the distributions of dipoles in three phases. In hexagonal ice the distribution is narrower than in the liquid phase and its expectation value is higher. This is in accordance with the measurement and the quantum chemical computational evidence. In the case of the gas phase the minimum accessible value of the polarization function (see Fig. 1) influences the place of the sharp maximum of the distribution. In addition to this big peak, there is a smaller one at fairly high dipole moment values which indicates some kind of closeness of a small amount of molecules.

In Fig. 4 we show the distribution of the Lennard-Jones σ parameter for the hexagonal ice and liquid water at 273.15 K. In the ice phase most of the molecules have the highest possible σ value of the distribution with a long but quickly diminishing tail towards lower values. In the case of water roughly 40% of the σ-s can be found at the maximum

value. The rest is relatively evenly distributed in the available range of σ with an artificial peak at the lowest possible value of 2.9 Å. Roughly 10% of the molecules have this size parameter.

In Fig. 5 we present the partial pair-correlation functions of ambient water. Our curves are in very good agreement with the experimental ones,[31] in particular, the overlap of the O–O distributions is remarkable.

In Table III we present the results of our simulations for ice polymorphs. The agreement in densities is excellent in the case of ice Ih, ice III, and ice VII. For the other phases the agreement is poorer. In this respect the results obtained by the TIP4P-2005 rigid model are somewhat better than our results.[4] It might be an interesting question to answer why our approximate polarization scheme adapts selectively to crystal structures. In order to compare the energy data to the theoretical calculations of Handa *et al.*[32] we show the results at 5 K too. It seems that the energy of the high pressure polymorphs (ice VII and VIII) is still to high.

We also carried out simulations for identifying the density maximum of water. Our result was 272 ± 3 K which is a reasonable estimation. Due to the labor intensive character we have not identified the melting temperature of the model yet. However, it seems certain that in this respect the ENCS model will provide a much better performance than most of the water models. The rigid TIP4P-ice model[33] was parameterized to produce the correct melting temperature for hex-

TABLE III. Ice phase densities and internal energies with the ENCS potential model. N is the number of particles in the simulation. T and P are the temperatures and pressures, respectively, at which the structure determination of the phase were carried out (Ref. 44). The numbers in parentheses mark the difference from the measurement values. The last two columns refers to simulation results applying the same pressure but at 5 K.

Ice	N	T (K)	P (GPa)	$-U$ (kJ/mol)	Density (g/cm^3)	$-U$ (kJ/mol)	Density (g/cm^3)
Ih	432	250	0.0001	49.4	0.919(1)	58.2	0.985
Ic	216	78	0.0001	54.8	0.962(31)	57.8	0.981
III	324	250	0.28	46.5	1.161(4)	53.6	1.199
VI	270	225	1.10	46.7	1.407(34)	51.4	1.444
VII	432	295	2.4	42.4	1.600(1)	48.1	1.663
VIII	216	10	2.4	47.0	1.671(43)	47.1	1.673
IX	324	165	0.28	50.8	1.169(25)	55.8	1.208
XI	432	5	0.0001	58.3	0.987(53)	58.3	0.987
XII	192	260	0.50	45.4	1.344(52)	50.7	1.377

TABLE IV. Several simulation properties for liquid and hexagonal ice. Experimental data taken from Ref. 9.

T (K)	Phase	$-U$ (calc.) (kJ/mol)	$-U$ (Expt.) (kJ/mol)	Density (calc.) (g/cm^3)	Density (Expt.) (g/cm^3)
273.15	Hexagonal ice	48.6±0.1	48.8	0.911±0.001	0.917
273.15	Water	43.5±0.3	42.8	1.002±0.003	1.000
298.15	Water	42.0±0.1	41.5	1.001±0.005	1.000

agonal ice. The model has a relatively high dipole moment (2.425 D) and very poor liquid-vapor and vapor property prediction ability.[34] The larger dipole moment provides a larger cohesive energy of hexagonal ice (and an incorrectly high density) which prevents the crystal to melt 30–60 K below its correct melting temperature as it is done by the rest of the rigid models.[33] There is no need to increase the dipole moment to very high values in our case because for the ENCS model the average dipole moment of the hexagonal phase is larger than that in the liquid (see Fig. 3). A similar conclusion was demonstrated recently by Nicholson *et al.*[35] These authors could obtain the correct melting temperature for hexagonal ice by increasing the Lennard-Jones σ parameter of the TIP4P-FQ interaction model.[36]

Our estimation for our heat of melting is reasonable as it can be seen from Table IV. The internal energy difference between the ice and liquid phase at 273.15 K is 5.1 kJ/mol instead of the correct value of 6.0 kJ/mol. The estimates of other energies and densities have acceptable quality too.

In Table V we present additional properties calculated for ambient water. With the exception of the isothermal compressibility the agreement is satisfactory. Especially, the dielectric behavior is promising because as it is shown by Lamoureux *et al.*[20] the relative permittivity is typically overestimated by the polarizable models and underestimated by the rigid models (see Fig. 5 in Ref. 20.)

IV. CONCLUSIONS

We presented a new approach to develop a classical polarizable water model for computer simulations. The model intends to cover the entire phase diagram from the gas to the high pressure solid phases. We created a nonlinear polarizability function describing the response of the water molecule to the impact of the varying electric field. In addition to polarizability, we introduced the size dependence for the model by varying the magnitude of the Lennard-Jones σ parameter as a function of the dipole moment of the molecule.

Such a way, we intended to increase the ability of the molecule to adapt to all possible changes of the surroundings and state variables.

Despite that the presented results represent the first parameter sets of the ENCS (rigid geometry but enlargeable charges) model, the results have a reasonably good quality. As for comparison with probably the best rigid model in the liquid-solid region, the TIP4P-2005 gives somewhat better results for ice densities.[4,5] This points to the need of further parameter refining of the ENCS model in order to overcome the disadvantage of polarizable models by having water molecules with higher dipole moments in the ice phases than in the liquid. Nevertheless, the TIP4P-2005 model is also unable to decrease the internal energy of high-pressure ice phases;[4] its melting temperature is ~250 K and its relative permittivity is ~60.[4] The gas phase properties of the TIP4P-2005 are poor.[5] This is true for all rigid, nonpolarizable models.[5,6] In the present paper, the simplest manifestation of this is the calculated dimer energies shown in Table I.

The polarizable model of Lamoreux *et al.*,[20] termed as SWM4-DP, develops an interaction system fitting its parameters to the gas and certain liquid properties simultaneously ensuring reasonably good estimates for the coefficients they calculated. Nevertheless, it seems probable that the model will give fairly inaccurate estimates for ice properties because the enhanced dipole moment tends to contract the system and increase its energy and density. This should be true for all polarizable models.

As we emphasized previously,[5] water molecules in the hydration shells of ions or highly polar parts of molecules experience an energy density corresponding to the pressure of 10–200 GPa. This is the region where dense ice phases exist. Clearly, the environment of a hydrating molecule in aqueous solution is different from that in a crystal. Nevertheless, the knowledge of the deformation and polarization of water under high pressure in ice can provide information valuable in aqueous solutions as well.

As a summary, we believe that the basic approach of our interaction model is promising. Applying further refinement of the parameters and removing unnecessary simplifications, the model might be able to cover the entire phase diagram of water with acceptable accuracy.

TABLE V. Several properties calculated for ambient water. C_p is the isobar heat capacity, α_p is the isobar heat expansion, κ_T is the isotherm compressibility, and ε is the relative permittivity.

Property	Calculated	Experimental[a]
C_p (kJ mol^{-1} K^{-1})	83.4	75.2
α_p (K^{-1})	3.06×10^{-4}	2.56×10^{-4}
κ_T (MPa^{-1})	24.0×10^{-5}	46.0×10^{-5}
ε	80.0	78.4

[a]Reference 9.

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