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A potential model for methane in water describing correctly the solubility of the gas and the properties of the methane hydrate

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We have obtained the excess chemical potential of methane in water, over a broad range of temperatures, from computer simulation. The methane molecules are described as simple Lennard-Jones interaction sites, while water is modeled by the recently proposed TIP4P/2005 model. We have observed that the experimental values of the chemical potential are not reproduced when using the Lorentz-Berthelot combining rules. However, we also noticed that the deviation is systematic, suggesting that this may be corrected. In fact, by introducing positive deviations from the energetic Lorentz-Berthelot rule to account indirectly for the polarization methane-water energy, we are able to describe accurately the excess chemical potential of methane in water. Thus, by using a model capable of describing accurately the density of pure water in a wide range of temperatures and by deviating from the Lorentz-Berthelot combining rules, it is possible to reproduce the properties of methane in water at infinite dilution. In addition, we have applied this methane-water potential to the study of the solid methane hydrate structure, commonly denoted as sI, and find that the model describes the experimental value of the unit cell of the hydrate with an error of about 0.2%. Moreover, we have considered the effect of the amount of methane contained in the hydrate. In doing so, we determine that the presence of methane increases slightly the value of the unit cell and decreases slightly the compressibility of the structure. We also note that the presence of methane increases greatly the range of pressures where the sI hydrate is mechanically stable.
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I. INTRODUCTION

Methane is a simple molecule and it is thus not surprising to learn that it was one of the main components of the early Earth's atmosphere.[1] In addition to this, it is found in the atmosphere of Titan,[2] one of the moons of Saturn, as well as in outer space. From an economical perspective, methane is becoming increasingly important as a source of energy, and from a climatic perspective is an important greenhouse gas. Here on Earth, methane is in contact with water in many situations, and so it is important to understand the interactions between these two molecules.

Let us begin by briefly describing two good reasons to study the behavior of methane in water. First, methane is a hydrophobic molecule, and as such its solubility in water is rather low, and methane molecules tend to aggregate when solvated in water. This behavior is more clearly exhibited by longer *n*-alkane chains, which may be considered as polymers of methane, and is of critical relevance in understanding the tertiary structure of proteins, as well as the important role it plays as a driving force in a number of processes occurring within living cells.[3,4] Therefore, although the solubility of methane in water may seem of rather limited importance, the correct description of the interactions between methane and water can be considered as a first step to improve our understanding of hydrocarbons and other more complex organic molecules in water.

A second reason to study the behavior of methane in water is the formation of methane hydrates. Methane hydrates are crystalline solids, with nonstoichiometric composition, which are formed when methane under pressure is cooled in contact with liquid water at temperatures around the melting temperature of water. Their presence in gas pipelines is considered, correctly, a major problem since they throttle and block the flow of gas causing enormous damage and expense. On a more positive note, it is thought that the amount of methane stored in the form of hydrates, typically in deep seas, is many times greater than that currently available from regular extractions.[5,6] For this reason, the possibility of recovering methane stored in the form of hydrates, for energetic purposes, is receiving increasing attention and simulation and theoretical studies of methane hydrates are becoming more and more popular in recent years.[7–14] A review of each of these areas may be found in two recent review papers. The first is by Chandler[15] and focuses on a molecular description of the hydrophobic effect, while the second is by Sloan[16] and deals with gas hydrates. For the two

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reasons detailed above, it can be safely stated that it is important to describe, and understand, the interaction between methane and water.

In modeling methane, it is often assumed that although methane is a nonspherical molecule, it may be described by a spherical Lennard-Jones (LJ) interaction site. In fact, although for certain situations a more realistic description is needed, it has been found that the vapor liquid equilibria and a number of properties of methane in the liquid phase can be reproduced using this relatively simple potential. In the case of water, a number of potentials consisting of a LJ interaction site located on the oxygen and two positive charges located on the hydrogens have been proposed. The main difference between these models is the location of the negative charge, which is located on the oxygen for the extended simple point charge (SPC/E) potential,[17] on the H–O–H bisector on the TIP4P model[18,19] and on the electron "lone pairs" for the TIP5P model.[20] All these popular water potentials are rigid and nonpolarizable. In addition, the interaction between the methane and the water molecules is often described using a LJ potential with the cross interactions parameters chosen according to the Lorentz-Berthelot rules.

Following from this, and pertinent to the topic of this work, is the question of whether or not these models are capable of reproducing one of the most basic properties of methane in water, namely, its excess chemical potential at infinite dilution. This issue has been studied in a recursive manner over the last two decades[21–24] and, in a recent work, Paschek[25] analyzed in detail the results using the SPC/E, TIP4P, and TIP5P models of water. A main conclusion of his work is that none of these models is able to reproduce the excess chemical potential of methane in water in the temperature range of 270–370 K. Although this simple conclusion is rather deceptive, Paschek made two other important observations.

The first of Paschek's observations is that the SPC/E, TIP4P, and TIP5P models of water are not able to describe correctly the density of pure water in the temperature range of 270–370 K (they describe correctly the density of water at room temperature but fail to describe the density of water in this temperature range). Thus the failure to describe the behavior of methane in water, may just be a failure of the water models to describe the density of pure water. In the last two years, two new models have been proposed that, for the first time, describe correctly the density of pure water in this temperature range. These are the TIP4P/Ew proposed by Horn *et al.*[26] and the TIP4P/2005 proposed by Abascal and Vega.[27] The evaluation of the chemical potential of methane in water for these new water models would seem a logical next step and in fact this was done quite recently for the TIP4P/Ew model. Using this model, Krouskop *et al.*[28] have tested Paschek's hypothesis of a link between the accuracy of the calculation of the density of water and that of the chemical potential. They demonstrate that this model provides better values for the density of water than any of those presented by Paschek[25] and go on to show that it does indeed produce more accurate values for the chemical potential of methane in water.

The second observation of Paschek, already pointed out by Guillot and Guissani,[21] is that when a spherical guest molecule, such as Xenon (Xe), dissolves in water, it experiences a high local electrical field from the solvent. This field induces a dipole moment, creating an extra energy interaction between Xe and water. In other words, the polarizability of the guest molecule is important in describing its interaction with water properly, and as such should not be ignored. Following this idea, there would seem to be little hope to describe correctly the interaction between methane in water without including such polarizability. Although including the polarizability is probably the rigorous route, such a calculation is also computationally very expensive. Since the presence of polarizability increases the strength of the interactions between methane and water, it seems reasonable to expect that this effect can be mimicked by allowing deviations from the Lorentz-Berthelot rules such that an increase in the strength of the methane water interaction is achieved. This is a simpler and computationally less expensive route worth exploring.

In this work we aim to develop a model able to describe correctly the excess chemical potential of methane in water in a wide range of temperatures. To this end, we use the TIP4P/2005 model for water, as it has been shown to reproduce the density of water very accurately in the temperature range of 270–370 K. In addition, we account for polarizability by increasing the cross interaction energy from that obtained from Lorentz-Berthelot rule. We will show that this combination is sufficient to describe the excess chemical potential of methane in water. The use of the TIP4P/2005 model for water has an additional advantage. This model provides a correct description of the phase diagram of water and is able to describe (with an error smaller than 1%) the density of many of its solid structures.[27] The TIP4P/2005 is not only a reliable model for the liquid phase, but also for the solid phases of water. Because of this, it is tempting to think that it would also be a good model for describing methane hydrates. This seems reasonable as the model describes well the different polymorphs of water, and the methane hydrate could be considered as an ice, with cavities filled by methane. In this work we show that, as well as describing correctly the excess chemical potential of methane in water, the model is also quite successful in describing the density of methane hydrate. In this respect, the methane-water model proposed in this work can be considered a general purpose model to describe in a simple way the interaction between methane and water, both in the liquid, and in the solid phase.

II. SIMULATION DETAILS

A detailed description of the TIP4P/2005 as well as a comparison to the TIP4P and TIP4P/Ew models can be found in the paper of Abascal and Vega.[27] Here we highlight only the main aspects of the model. The location of the oxygen and hydrogen atoms in TIP4P/2005 is identical to that of TIP4P. The value of the LJ parameter σ and the distance from the oxygen to site M containing the negative charge are quite similar in TIP4P/2005 and TIP4P. The main difference between TIP4P/2005 and TIP4P is that the magnitude of the partial charges and of the ϵ/k parameter of the LJ interaction

TABLE I. Potential parameters for the water-water interactions (TIP4P/2005), methane-methane interaction (Refs. 21, 25, and 29) (CH_4), and for the water-methane interactions as obtained from Lorentz Berthelot rules ($\chi=1$) and from the optimized potential of this work ($\chi=1.07$).

Model	ϵ/k (K)	σ (Å)	q_H (e)	d_{OM} (Å)
Water TIP4P/2005	93.2	3.1589	0.5564	0.1546
CH_4	147.5	3.730		
Water-CH_4 ($\chi=1$)	117.25	3.4445		
Water-CH_4 ($\chi=1.07$)	125.45	3.4445		

are larger in TIP4P/2005 when compared to TIP4P. Table I contains the parameters for the TIP4P/2005 model. Also in Table I can be found the Lennard-Jones parameters for methane used in this work. These were proposed by Hirschfelder *et al.*[29] and used by Guillot and Guissani[21] and Paschek.[25] Other popular models for methane are the TraPPE (Ref. 30) and OPLS-UA (Ref. 31) models which, as well as being practically identical to each other, are similar to the model used here. In fact, the value of σ is the same and the value of ϵ/k differs only slightly, being about 148 K instead of 147.5 K as used in this work. In all our simulations, the Lennard-Jones potentials are truncated at 9.0 Å and a standard long range correction to the energy is added.[32] Meanwhile, the Coulombic interaction between charged particles is accounted for using the Ewald summation technique with a real space cutoff of 9.0 Å, a screening parameter of 0.33/Å. The reciprocal space is restricted to the vectors $\mathbf{h}$ such that the modulus of the vector is $|\mathbf{h}|^2 < 60$.

Our determination of the excess chemical potential of methane in water was carried out in two steps. In the first step, long Monte Carlo isobaric-isothermal NpT simulations of pure water were performed. The simulations consist of 360 water molecules located in a cubic box with isotropic scaling used when changing the size of the simulation box. The length of each run was about 1.5×10^6 cycles, where a cycle denotes a trial move per particle plus an additional trial volume change. The pressure was set to $p=0.1$ MPa and several runs were performed at temperatures between 250 and 370 K. In this way the average density at a certain temperature and pressure is obtained with a relatively high accuracy. This is important because, as mentioned previously, it has been noted that the excess chemical potential is sensitive to the system density. Since for the TIP4P/2005 these runs have already been reported,[27] we refer the reader to the results of this previous work for further details.

Once the average densities for normal pressure (i.e., 0.1 MPa) have been obtained at several temperatures, a second step involves the calculation of the chemical potential of methane at infinite dilution. We have accomplished this by performing canonical (NVT) Monte Carlo simulations with 360 water molecules, at the average density obtained from the NpT runs, together with the Widom test particle method[33] with a methane molecule as test particle. Specifically, 20 000 trial insertions of methane were attempted every 10 cycles for runs of 400 000 cycles in length giving a total of 800×10^6 trial insertions per run. For each temperature, we performed six independent runs of this type such that the number of attempted insertions for each temperature and pressure is approximately 5000×10^6. As in all the simulations presented here, the LJ methane-water interaction was truncated at 9.0 Å and long range corrections to the chemical potential of methane in water were also included. We estimate that the chemical potentials calculated in this manner have an accuracy of 0.2 kJ/mol. The excess chemical potential was estimated from the simple Widom test particle method,[33]

$$\mu_{ex} = -kT \ln\langle \exp(-\beta U_{test})\rangle. \tag{1}$$

As a test of the methodology used in this work we attempted to reproduce the values of the chemical potential of methane in SPC/E water reported by Paschek[25] at 0.1 MPa and 300 K (parameters of Table I using Lorentz-Berthelot rules for the water-methane interaction). We obtain a value of 9.65 kJ/mol for the excess chemical potential. This compares well with the values of 9.71 kJ/mol obtained by Paschek for 256 particles at the same temperature, hence confirming the validity of our method. In summary, to obtain an accuracy of about 0.2 kJ/mol in the excess chemical potential about 5000×10^6 insertions are needed.

The cross interaction between methane and water molecules is of Lennard-Jones type with the parameters obtained from

$$\epsilon_{CH_4-H_2O} = \chi\sqrt{\epsilon_{CH_4-CH_4}\epsilon_{H_2O-H_2O}} \tag{2}$$

and

$$\sigma_{CH_4-H_2O} = \frac{(\sigma_{CH_4-CH_4} + \sigma_{H_2O-H_2O})}{2}. \tag{3}$$

In Eqs. (2) and (3) it can be seen that the standard Lorentz-Berthelot rule[34] is retained in the cross interaction diameter ($\sigma_{CH_4-H_2O}$), while for the energetic cross interaction the Lorentz-Berthelot combining rule is recovered when $\chi=1$. Deviations from the Lorentz-Berthelot rule are obtained with values of χ different from 1.

Let us now describe briefly the simulation details of the methane hydrate. The methane hydrate is a cubic structure, usually denoted as sI, with space group $Pm3n$. In this structure the unit cell has 46 water molecules.[35–37] Each unit cell consists of two small and six large cavities, each capable of containing a methane molecule. It seems that the optimal ratio between the size of the guest molecule and the size of the cavity is of 0.75.[16] When formed in nature methane hydrates sI usually present most (but not all) the cavities occupied by methane molecules. For this reason methane hydrates are nonstoichiometric compounds, meaning that the ratio of methane to water molecules is not fixed. Typically the ratio of cavities occupied is high; commonly higher than 0.95.[38] When methane hydrates are formed in research laboratories, the occupancy ratio tends to be higher and very close to 1, i.e., in this case all cavities are occupied by methane molecules. When the occupancy is complete the methane hydrate can be described by the simple formula $CH_4(H_2O)_{5.75}$. It is important to note at this stage that, because methane hydrates are nonstoichiometric compounds and because in many cases it is not possible to know precisely the occupancy ratio, the density, expressed as mass per unit of volume, is not typically reported in experimental works. Rather, it is more common for the parameters of the unit cell to be given. In this work we have placed a methane molecule in all the cavities of the hydrate and thus the occupancy ratio in our modeled hydrates is exactly one (i.e., 100%). This is slightly larger than the occupancy ratio of naturally-formed methane hydrates and close to those formed in experimental research labs. There are several interesting reviews on hydrates and we refer the reader to those references for further details.[39–41]

In our hydrate simulations we have used boxes consisting of eight unit cells. The number of water molecules was $46 \times 8 = 368$, and the number of methane molecules was exactly 64. The position of the oxygens can be easily obtained from the space group and from the positions obtained from x-ray diffraction studies.[13] It is, however, not as trivial to locate the position of the hydrogens in the initial configuration because, in the hydrate sI, the protons are disordered. This is not surprising since a number of water solid structures, including the common hexagonal ice Ih, present proton disorder.[19,42] In the sI hydrate, the hydrogen atoms are located such that the Bernal Fowler rules are satisfied and, since the hydrate is not ferroelectric, the dipole moment of the initial configuration must be zero. In order to generate a proton disordered structure, satisfying the Bernal Fowler rules and with zero dipole moment we have used the algorithm proposed by Buch *et al.*[43] The use of this algorithm made possible the generation of a proton disordered configuration, with 368 water molecules, satisfying Bernal Fowler rules and with almost zero dipole moment (i.e., smaller than 0.1 D for the whole system). This initial proton-disordered configuration is available upon request.

In our simulations of methane hydrate, the methane-methane interaction is of the LJ type, as described in Table I, and the water-water potential is the TIP4P/2005 model. For the methane-water interaction we used the LJ potential, with the cross interaction parameters given by Eqs. (2) and (3) with $\chi = 1.07$. The choice of $\chi = 1.07$ for the crossed interaction of ϵ is motivated by the fact that this value was necessary to describe the excess chemical potential of methane in pure liquid water; more details are given in the next section. The simulations of the methane hydrate consisted of an equilibration period of about 20 000 cycles, followed by 100 000 cycles to obtain averages. They were all performed in the NpT ensemble. As before, the LJ interactions and the real part of the Ewald sum were truncated at 9 Å, long range corrections to the LJ contribution were included, and since the sI hydrate is cubic, isotropic scaling was used in the volume changes.

TABLE II. Calculated excess chemical potentials for methane in water at 0.1 MPa. The data for SPC/E and TIP4P are from the paper of Paschek (Ref. 25). The TIP4P/2005 data are from our Monte Carlo simulations using the Lorentz-Berthelot rule with $\chi = 1$ and with $\chi = 1.07$. Densities are given in g/cm^3.

Model	T (K)	ρ_{sim}	$\mu_{\mathrm{ex,sim}}$ (kJ/mol)	$\mu_{\mathrm{ex,sim}} - \mu_{\mathrm{ex,exp}}$ (kJ/mol)
SPCE	275	1.0090	8.09	1.88
	300	0.9982	9.45	1.24
	325	0.9833	10.54	0.96
	375	0.9436	11.78	0.65
TIP4P	275	1.0053	8.38	1.88
	300	0.9935	9.78	1.31
	325	0.9765	10.71	0.85
	375	0.9294	11.44	0.06
TIP4P/2005	280	0.9994	8.14	1.19
$\chi = 1.00$	300	0.9979	9.64	1.16
	350	0.9841	11.70	0.90
	370	0.9585	12.44	1.15
TIP4P/2005	280	0.9994	7.30	0.35
$\chi = 1.07$	298	0.9979	8.27	−0.07
	330	0.9841	10.19	0.10
	370	0.9585	11.60	0.31

III. RESULTS

We first discuss the excess chemical potential of methane in TIP4P/2005 water at normal pressure (i.e., $p = 0.1$ MPa) for the case of $\chi = 1$, that is, when the Berthelot combining rule is used to describe the cross energetic interaction between methane and water. We consider four temperatures: 280, 300, 350, and 370 K. The values of the chemical potential obtained are presented in Table II and plotted in Fig. 1 together with the values for the SPC/E and TIP4P models calculated by Paschek.[25] The experimental values of the excess chemical potentials, taken from the work of Paschek,[25] are also presented in the figure. The experimental excess chemical potential μ_{ex} can be obtained from Henry's constant K_H using the general relation,[44]

$$K_H = \lim_{x \to 0} \frac{RT\rho}{M_{H_2O}} \exp(\mu_{\mathrm{ex}}/kT), \tag{4}$$

where ρ is the density of the pure solvent (obtained from the correlation of Saul and Wagner[45]) and M_{H_2O} is the molecular weight of water.

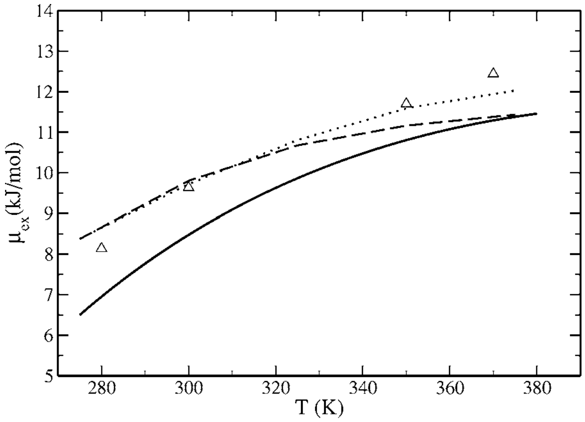

FIG. 1. Excess chemical potential at infinite dilution for methane in water as obtained from experiment (Refs. 25 and 44) (solid curve) and from computer simulations at a pressure of 0.1 MPa. In all cases methane is modeled using the potential presented in Table I, while the water-methane potential is of the Lennard-Jones type with interaction parameters obtained by applying the Lorentz-Berthelot combining rules. The open triangles represent the results of this work for TIP4P/2005 water. The dotted and dashed curves are the simulation results for SPC/E and TIP4P water, respectively, as reported by Paschek (Ref. 25).

The most obvious conclusion to be drawn from this figure is that, when water is modeled by TIP4P/2005, the experimental excess chemical potential of methane in water is not described accurately. In fact, the calculated excess chemical potential seems to be systematically above the experimental value by about 1 kJ/mol. In the case of the SPC/E model the excess chemical potential is about 1.88 kJ/mol above the experimental value at $T=275$ K and about 0.65 kJ/mol at $T=375$ K. It is noticeable that in this case the difference between simulation and experiment is not constant, but decreasing as the temperature increases. The situation is similar for the TIP4P model, the simulated values of the chemical potential are too high when compared to experiment, and the difference amounts to 1.88 kJ/mol at $T=275$ K and drops to 0.06 kJ/mol at $T=375$ K.

At this stage it is interesting to point out that since the interaction between methane and water is of LJ type, the most important variable controlling the order of magnitude of the chemical potential of methane in water is the volume fraction of pure water (i.e., the volume of space occupied by water molecules). The value σ in the SPC/E, TIP4P, and TIP4P/2005 models are practically identical, meaning that at a certain density the three models provide a practically identical value of the volume fraction. This leads us to wonder why the TIP4P gives a value for the excess chemical potential of methane of 1.31 kJ/mol above the experimental value at room temperature, while almost matching the experimental value at $T=375$ K. We note that the density variation of the TIP4P model (when Coulombic forces are treated with Ewald sums) has been considered recently[46] and it was found that, whereas TIP4P describes accurately the experimental density of pure water at room temperature, at $T=375$ K it underpredicts the experimental density of water by 0.03 g/cm^3. Thus, the volume fraction of water is underestimated by a significant amount by the TIP4P model at $T=375$ K, suggesting that the excess chemical potential of methane in water is well described at this temperature due to a fortuitous cancellation of errors. That is to say, an inaccurate methane-water potential, when used with an inaccurate water potential (i.e., a potential not describing correctly the density of water), can provide a satisfactory description of the excess chemical potential at a certain temperature.

The results of Table I suggest that, as stated by Paschek, when the magnitude of the error of the excess chemical potential of methane in water changes significantly with temperature, it may just be an indication that the water potential used is not able to describe properly the density variation of water in the temperature range considered. The data presented in Table II and the depiction of Fig. 1 suggest that none of the models is able to describe correctly the excess chemical potential of methane in water. For the TIP4P and SPC/E models, it is not obvious how to correct this situation. However, for TIP4P/2005, the difference between the calculations and the experimental values appears systematic, and since the model describes properly the density of pure water, it seems that a modification of the water-methane LJ interaction can remedy the situation. The somewhat too large excess chemical potential could have essentially two reasons, either a too large diameter or a too low well depth (or a combination of both) for the water-methane interaction. The accuracy of the data prevents a simultaneous refinement of both σ and ϵ. For this reason, in this work, we have decided to increase the value of the well depth, for the methane-water interaction, or in other words, to allow the parameter χ to change from one (Berthelot rule) to a higher value. As mentioned in the Introduction, the increase of ϵ seems physically appealing since it is an effective way of accounting for the attractive energy between the induced dipole moment of methane and the dipole moment of water. In other words, increasing the value of ϵ between methane and water is an effective way of accounting for the polarization energy between methane and water in nonpolarizable models.

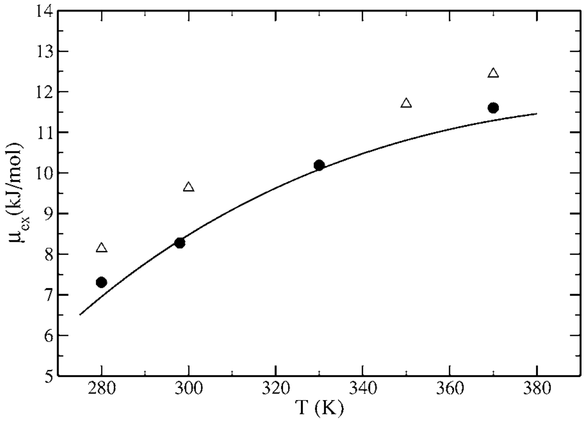

FIG. 2. Excess chemical potential at infinite dilution for methane in water as obtained from experiment (Refs. 25 and 44) (solid curve) and from computer simulations at 0.1 MPa. The methane potential is that presented in Table I, and water is modeled using the TIP4P/2005 model. In the case of the open triangles, the methane-water interaction was obtained by direct application of the Lorentz-Berthelot rules (i.e., $\chi=1$), and in the case of the filled circles, by allowing deviations from the Lorentz-Berthelot rules in the energetic parameter (i.e., $\chi=1.07$).

Motivated by this idea, the value of χ for the interaction between methane and TIP4P/2005 water was increased. In our first attempt to achieve a closer agreement with the experimental values, we increased the strength of interaction by 10% (i.e., $\chi=1.10$). Unfortunately this results in slightly too low a value for the chemical potential. However, with further refinement, we were able to estimate an optimal parameter that is approximately 7% ($\chi=1.07$) larger than that obtained using the Lorentz-Berthelot rules. In recent work, Konrad and Lankau[47] followed a similar route, allowing deviations from Lorentz-Berthelot rule for both the cross interaction diameter and interaction energy to describe the interaction between methane and water using a SPC/E water model.

Using our optimized value for χ, we have calculated the excess chemical potential at 0.1 MPa for temperatures of 280, 298, 330, and 370 K. The resulting values are presented in Table II and in Fig. 2. It can clearly be seen that this combination of the TIP4P/2005 model of water, a Lennard-Jones methane model and the Lorentz-Berthelot combining rule with a 7% increase in the interaction energy of methane and water, gives good qualitative and quantitative agreements with experimental values for the chemical potential; the deviations are of the same order of magnitude as our statistical uncertainty. Thus, for the first time, the excess

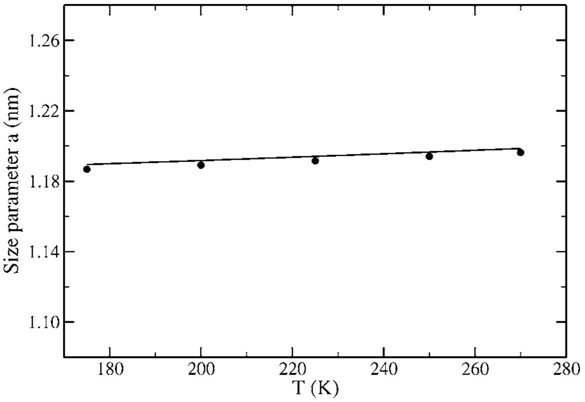

FIG. 3. Unit cell length of methane hydrate sI (cubic) as a function of temperature for a pressure of 3 MPa. Filled circles correspond to the results of this work using the TIP4P/2005 potential for water, the potential of methane described in Table I and the water-methane interaction obtained by using $\chi=1.07$. The solid line corresponds to the experimental results obtained from the correlation of Sun and Duan (Ref. 8) at 3 MPa.

TABLE III. Comparison of the clathrate unit cell parameter from simulation with experiment at 3 MPa. Simulation results were obtained with the methane filling all cavities of the clathrate (i.e., 100% occupancy). Results for two values of χ [see Eq. (2)], namely, $\chi=1.00$ and $\chi=1.07$, are presented. In the last two lines the results from English and MacElroy (Ref. 10) for $T=200$ K and 2 MPa obtained for SPC/E and TIP4P water and a slightly different model of methane are presented.

T (K)	$\chi=1.07$ a_{sim} (Å)	$\chi=1.00$ a_{sim} (Å)	a_{expt} (Å)	$a_{\text{expt}}-a_{\text{sim}}$ (Å)
175	11.866	11.868	11.895	0.030
200	11.888	11.891	11.917	0.029
225	11.913	11.915	11.941	0.028
250	11.938	11.941	11.966	0.027
270	11.960	11.963	11.986	0.026
200 (SPC/E)		11.804	11.918	0.114
200 (TIP4P)		11.825	11.918	0.093

chemical potential of methane in water is described from the melting point to the boiling point of water by a model. The success of the results of Fig. 2 reinforces the suggestion of Paschek: in order to describe the excess chemical potential of methane in water, in a broad range of temperatures, it is necessary to have a model able to describe the water densities accurately in the same temperature range, and polarization energies should be taken into account. In this work we show that the TIP4P/2005 water model satisfies the first requirement, and that the second requirement can be satisfied, at least partially, by using an effective potential between methane and water with a 7% increase of the interaction energy to compensate for the absence of polarization energies in nonpolarizable models. We believe that the approach to the problem presented in this work for methane and water, and summarized in the results of Fig. 2, may also be successful for the description of longer *n*-alkanes in water. It is not clear whether the same or a different value of χ should be used for CH_3 or CH_2 groups due to their different polarizabilities and geometries. These issues require further study and will be considered in future work.

Having obtained an improved water-methane interaction potential, we apply it to the simulation of a methane hydrate. We have calculated the unit cell parameter at 3 MPa for temperatures of 175, 200, 225, 250, and 270 K, proceeding from low to high temperatures, using the final configuration of a certain run as the initial configuration of the next run. Our results are shown graphically in Fig. 3 and numerically in Table III (results labeled as $\chi=1.07$), together with an experimental correlation proposed by Sun and Duan.[8] We find that our simulations reproduce the experimental trend, differing by only approximately 0.25% (an error of 0.25% in the unit cell amounts to an error of 0.75% in the density). It is worth noting that the average error of the TIP4P/2005 model in the prediction of densities of the different solid structures of water is typically smaller than 1%, so that it seems that the same accuracy is also kept for the clathrates. Our simulations are able to reproduce the slight increases in the side of the cubic unit cell with temperature at constant pressure. This means that the thermal expansion coefficient, which has been measured experimentally for certain hydrates[48,37] and that is considerably larger than that of ice,[37] is predicted correctly. The agreement between experiment and simulation for methane hydrates obtained with the potential parameters proposed in this work is much better than those obtained previously using other potential models for water (i.e., TIP4P and SPC/E). In the last two lines of Table III the results obtained by English and MacElroy[10] for SPC/E and TIP4P water and a different model of methane are reported. As it can be seen, the error in the estimate of the unit cell of the methane hydrate is four times larger than that obtained with the potential model of our work. An interesting issue is whether the value of χ for the water-methane interaction affects or not the density of the system. In Table III we have also included results obtained for the same model with $\chi=1.00$. As it can be seen the value of the unit cell does not depend significantly on the value of the parameter χ. In this respect the good prediction of the density reported in this work for the methane hydrate seems to be more a merit of the TIP4P/2005 model of water than of the methane-water interaction.

In order to study the effect of the amount of methane present in the hydrate, we have also performed a different type of simulation. We fix the temperature at $T=250$ K and increase the pressure from an initial value of about $p=3$ MPa to higher pressures. Again the final configuration of a certain run was used as the initial configuration of the next run. Two values of methane occupancy were considered: full occupancy (i.e., all cavities are occupied by methane) and null occupancy (i.e., all cavities are empty so that no methane is present in the hydrate). The results of the simulations for pressures up to 600 MPa are presented in Table IV and in Fig. 4. First of all, it can be seen that the volume of the unit cell shrinks considerably by when an external pressure is applied. A second interesting observation is that the volume of the unit cell depends on the methane occupancy, being slightly larger when there is methane present (i.e., full occupancy) than when no methane is present (i.e., null occupancy). The effect is small but clearly visible. This indicates that, although the methane molecule fits well within the hydrate cavities, it produces a slight increase in the unit cell parameter. An interesting remark is that, since the value of the unit cell is sensitive to the amount of methane and be-

TABLE IV. Comparison of the clathrate unit cell volume at $T=250$ K for full occupancy of methane, half occupancy of methane, and the empty hydrate structure. The unit cell volume is given in nm^3. The results were obtained from NpT simulations. The value of $\chi=1.07$ was used in the simulations.

Pressure (MPa)	100% occupancy	50% occupancy	0% occupancy
3	1.7014	1.7005	1.6965
10	1.7001	1.6990	1.6954
30	1.6969	1.6954	1.6915
50	1.6936	1.6921	1.6878
100	1.6856	1.6836	1.6785
150	1.6778	1.6752	1.6695
200	1.6702	1.6669	1.6607
300	1.6561	1.6516	1.6435
400	1.6425	1.6368	1.6266
500	1.6297	1.6226	1.6106
600	1.6174	1.6080	1.5937

cause it is difficult to establish precisely the amount of methane contained within the methane hydrate, the value of the unit cell is an indirect measure of the amount of methane contained within the methane hydrate. We have performed additional simulations with an occupancy of 0.5 (by deleting randomly half of the methane molecules of the fully occupied structure). These results are presented in Table IV. As it can be seen, in the case of half occupancy the value of the unit cell is closer to that obtained with full occupancy than to that obtained for the empty hydrate. The fact that the volume of the unit cell depends on the amount of methane shows that although methane is a host molecule, it affects slightly the properties of the host network of water molecules. This is also consistent with the slight differences found in the value of the unit cell for different guest molecules.[49] This effect is small at moderate pressures but becomes more important at high pressures. The results of Fig. 4 can be well described by a second order polynomial. In fact, the volume of the unit cell at $T=250$ K as a function of pressure for the empty and full hydrates is well described following

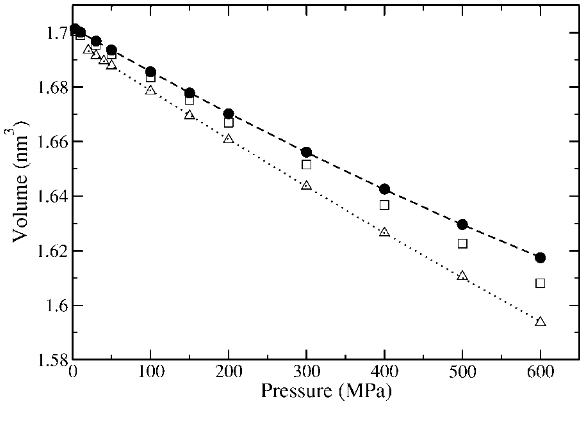

FIG. 4. Simulation results for compression (at $T=250$ K) of methane hydrate sI (cubic). Filled circles correspond to a fully occupied methane hydrate, open triangles to an empty hydrate (i.e., the cavities of the hydrate are not occupied by methane), and open squares to a 50% occupancy. The curves correspond to a quadratic regression to the simulation data. The methane potential is that of Table I, the water potential is the TIP4P/2005 model, and the water-methane interaction was obtained by using $\chi=1.07$.

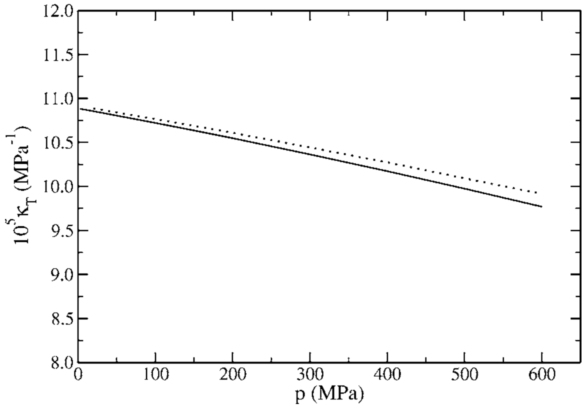

FIG. 5. Isothermal compressibility for methane hydrate sI as a function of pressure at $T=250$ K. The values were calculated using Eqs. (5)–(7) together with results from simulation. The solid line corresponds to a fully occupied methane hydrate and the dotted line to the empty hydrate structure (i.e., the cavities of the hydrate are not occupied). The methane potential is that of Table I, the water potential is the TIP4P/2005 model, and the water-methane interaction was obtained by using $\chi=1.07$.

$$V_{T,\mathrm{empty}}/(\mathrm{nm}^3) = 2.2731 \times 10^{-8} p^2 - 1.8527 \times 10^{-4} p + 1.6970 \tag{5}$$

and

$$V_{T,\mathrm{full}}/(\mathrm{nm}^3) = 4.0966 \times 10^{-8} p^2 - 1.6485 \times 10^{-4} p + 1.7018, \tag{6}$$

where the pressure p is given in Mega Pascals. From these fits it is possible to determine the isothermal compressibility in each case,

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T. \tag{7}$$

Values of the compressibility of the empty and full hydrates are presented in Fig. 5. It can be seen that the compressibility of the fully occupied hydrate is smaller than that of the empty hydrate. The compressibility changes only slightly with pressure in both cases, becoming smaller by about 10% in the 600 MPa range considered here. In the case that much larger changes with pressure are found in the unit cell parameter (i.e., higher compressibilities) in experimental work, such results must be interpreted as associated with a phase transition. This remark is interesting since several experimental groups are now involved in the search for new methane hydrate structures at high pressures (different from the well known sI hydrate considered in this work), so that the results of this work may be useful in the analysis of their experimental results.[50–52] For comparison, the compressibility of liquid water at room temperature and pressure is four times larger than those we find for the hydrate structures and, more significantly, becomes 20% smaller by applying a pressure of just 100 MPa. Based on our experience of the simulation of ices,[53–56] we believe the predictions of compressibilities of TIP4P/2005 are quite reliable for pressures up to 1000 MPa, but deteriorate somewhat at higher pressures.[27]

As an initial step to the goal of determining the fluid-solid equilibria of the methane-water mixture we have determined the excess chemical potential of methane in the clathrate by using the Widom test particle method. We have performed the calculation at null occupancy (i.e., with all cavities of the hydrate being empty) for $T=250$ K and $p=3$ MPa. We found that the excess chemical potential of methane was of −8.99 kJ/mol (for $\chi=1.07$). We also found that the value of the excess chemical potential of the methane in the clathrate was hardly affected by the value of χ. It would be of interest to determine the fluid-solid equilibria of the methane-water mixture in future work.

A final interesting issue is the mechanical stability limit of the empty and full hydrates. There is a certain range of temperatures and pressures where a solid phase is mechanically stable (at least within the length of the simulations). In previous work, Førrisdahl *et al.* have considered the stability limit of methane hydrate sI with respect to heating.[57] In this work we consider the stability limit with respect to the application of pressure for a temperature of $T=250$ K. The results presented in Fig. 4 show that both the empty and the full methane hydrate were mechanically stable up to 600 MPa. When applying higher pressures we have found that the empty methane hydrate becomes mechanically unstable at a pressure of about 700 MPa and melts. However, the full hydrate structure does not melt until pressures of about 2800 MPa are achieved. Thus the mechanical stability of the methane hydrate is extended by a factor of 4 by the presence of the methane molecule. This can be understood from the fact that the empty cavities become unstable when high pressures are applied. The presence of the methane molecule in the cavities helps to keep the rigid structure of the water molecules that form the hydrate.

IV. CONCLUSIONS

In this work we have considered two different problems in which the interaction between methane and water plays an important role. The first problem is the description of the excess chemical potential of methane in water for temperatures from the melting point up to the boiling point of water. Previous attempts to describe accurately this excess chemical potential have failed. This is rather deceptive as methane is the simplest organic molecule that one may consider in a solvent as important as water. Paschek has suggested that this failure may be due to two different effects. First, that the models of water used are not able to describe the density of water properly in a wide temperature range. Second, that polarization energies are important, and that they are not properly accounted for by nonpolarizable models when the simple Lorentz-Berthelot combining rules are used.

Recently some of the authors have proposed a new potential model for water, labeled TIP4P/2005, that describes with higher accuracy than previous models the density of water from the melting point up to the boiling point. It therefore seemed reasonable to test the ability of this model to reproduce the excess chemical potential of methane in water. Unfortunately when the simple Lorentz Berthelot rules are used for the methane-water interaction, we find this model also fails in describing the excess chemical potential. However, we find the deviation from experiment to be constant with temperature, and interpret the sign of the deviation suggesting that polarization effects may be the origin of the discrepancy.

The introduction of polarization in computer simulations is desirable but problematic, as such simulations tend to be an order of magnitude slower. For this reason, it is useful to develop more efficient ways to introduce the polarization energy, even if this is done in an empirical way. In this work we have shown that, allowing deviations from the energetic Berthelot rule and increasing the methane-water LJ interaction energy ϵ by 7%, it is possible to reproduce the excess chemical potential of methane in water. To the best of our knowledge this is the first time that this has been achieved. Motivated by the recent interest in methane hydrates, where methane water interactions are also highly relevant, we have applied the same potential to the description of the methane hydrate sI structure. We find that our model is able to describe with high accuracy the unit cell of the structure, as well as its variation with temperature and pressure. Moreover, we have analyzed the effect of methane occupancy on the unit cell and on the compressibility of the structure.

We believe that the potential model proposed in this work for methane-methane, methane-water, and water-water interactions may be useful in the study of organic molecules in water and in the study of methane hydrates. A system of methane and water is rather simple. However, the difficulties found in its study point out the fact that only quantum chemistry calculations can provide a reliable description of the interaction energies. When the solvent is a molecule such as water, which has a high dipole moment, polarization energies will be important, not only in the water-water interactions but also in the solute-water interaction, even though the solute may be a nonpolar molecule. One can guess that the use of polarizable models will increase steadily in the coming years. However, a less rigorous, but computationally less demanding method, to account for these energies is to use nonpolarizable models which include the effect of polarizability in an "effective" way. For instance, it is quite common that models of water have a dipole moment considerably larger than that of the molecule of water in the gas phase. This is also a way of introducing polarizability in an effective way. In this work we have shown that in the case of the methane-water interaction, it is also necessary to include the polarization energy in an effective way to obtain agreement with experiment. Additionally, the study of the properties of solutes in water, at infinite dilution, can be used in a practical way to propose effective potentials for the crossed solute-water interaction.

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