ON THE APPLICATION OF BINARY CORRECTION FACTORS IN LATTICE DISTORTION CALCULATIONS FOR METHANE CLATHRATE HYDRATES

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ABSTRACT

The lattice distortion theory of Zele and co-workers is an attractive method for amending calculated phase equilibria of clathrate hydrates, since only two molecular computations are required. The perturbation energy between the empty and loaded clathrate hydrate lattice is the quantity of interest. The effect of binary correction factors applied to the Lorentz and Berthelot combining rules for the intermolecular interaction between gas and water particles is investigated. There are clear trends for the perturbation energy and lattice constant in terms of the binary correction factors, although there is significant sensitivity to the force field parameterization of the gas species.

1. INTRODUCTION

1.1. CLATHRATE HYDRATES

Clathrate hydrates consist of hydrogen-bonded networks of water molecules trapping gas particles in a crystal lattice. Superficially, this material resembles ice and is found in natural deposits in the deep ocean and in permafrost in the tundra [1]. In clathrate hydrate systems, water can be considered as the "host" species, and the enclathrated gas as the "guest" species.

Three different clathrate hydrate structures are found in natural or industrial settings: Structure I (sI), structure II (sII), and structure H (sH). The distinguishing characteristics of these structures are the ratios and types of cavities present in the crystal lattice at the nanometer scale. These cavities are essentially "cages" in which gas particles are enclosed by water molecules, with oxygen atoms forming the vertices of these polygonal cages. The relative sizes of the cavities (i.e. small, medium and large) are used as references within the unit cell. A brief summary of clathrate hydrate crystal structures is presented in Table 1 [2]. The sI and sII structures are most common, since these can form

with a single gas species. The sH clathrate hydrate, however, requires a small gas species (such as methane) and a large gas species (such as cyclopentane) to simultaneously stabilize the small and large cages, respectively. Thus, the sH structure can only form in the presence of specific gas mixtures that usually do not occur in the natural environment.

Clathrate hydrate structure	sI		sII		sH		
Crystal system	Primitive cubic		Face-centered cubic		Hexagonal		
Space group	*Pm3n*		*Fd3m*		*P6/mmm*		
Cavity type	Small	Large	Small	Large	Small	Medium	Large
Cavity description	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^3 5^6 6^3$	$5^{12}6^8$
Cavities/unit cell	2	6	16	8	3	2	1
Cavity radius (nm)	0.395	0.433	0.391	0.473	0.391	0.406	0.571
H_2O/unit cell	46		136		34		
Unit cell formula	$2S \cdot 6L \cdot 46H_2O$		$16S \cdot 8L \cdot 136H_2O$		$3S \cdot 2M \cdot 1L \cdot 34H_2O$		

Table 1. Table summarizing the crystalline structures and properties of the structure I, II, and H clathrate hydrates [2]. The small, medium, and large cavities are denoted in the unit cell formula by S, M, and L, respectively.

1.2. LATTICE DISTORTION (LD) THEORY

Phase equilibrium calculations for clathrate hydrate systems often use thermodynamic models based on the theory of van der Waals and Platteeuw (vdWP) [1,3], which employs the Lennard-Jones-Devonshire cell model to describe interactions between enclathrated gas molecules and the host water network. The vdWP theory has several shortcomings related to assumptions made in its original formulation [4-14]: No interactions between particles of the guest gas species, and fixed spatial positions of the water molecules. One attempt at amending the vdWP theory is the LD theory of Zele and co- workers [15]. LD theory includes a term for distortion of the host lattice, which was not accounted for in the original vdWP theory. The present paper seeks to examine the effects of a further adjustment to LD theory through the use of binary correction factors to the Lennard-Jones (LJ) potential describing the intermolecular interactions between water and methane.

1.3. BINARY CORRECTION FACTORS

The cross-interactions between LJ sites are often accounted for by the Lorentz [16] and Berthelot [17] (L-B) combining rules. However, these simple rules cannot always adequately account for all of the complexities of interactions between unlike LJ sites, and thus a binary correction factor (k_{ij}) can be introduced into the dispersion term (ε_{ij}) for the cross-interaction between unlike sites i and j, through a variant of the Berthelot rule:

$$\varepsilon_{ij} = k_{ij} \left(\varepsilon_{ii} \, \varepsilon_{jj} \right)^{0.5} \tag{1}$$

It should be noted that the Berthelot rule can be considered as a special case of a more general combining rule which considers the ionization potentials and the molecular size parameters when calculating the unlike intermolecular LJ well in depth [18,19]. When considering this general combining rule, the Berthelot rule arises when the two particles are of a similar size and similar ionization potential. Therefore, it can be expected that the unmodified Berthelot rule can be insufficient when describing the interactions between water and gas molecules in the clathrate hydrate phase [20].

In addition, another binary correction factor (l_{ij}) can be applied to account for the cross-interaction in the size term (σ_{ij}) of the LJ potential, using a modified form of the Lorentz rule:

$$\sigma_{ij} = 0.5 \, l_{ij} \left(\sigma_{ii} + \sigma_{jj} \right) \tag{2}$$

The binary correction factors kij and lij can be determined in a systematic manner provided that experimental data, with calculated data such as structural energies, are available for comparison. In the context of LD theory, the most useful data type for comparison is dissociation pressure data, as these are computed via the phase equilibrium calculations described above. In the present study, kij was held fixed at unity, while lij was varied and vice versa.

Previous studies have investigated binary correction factors applied to intermolecular
LJ potentials in clathrate hydrate systems; determination of these factors can be indirect, using the excess chemical potential of dilute methane in water [21] or through direct coexistence of molecular dynamics simulations [22]. In both of these prior studies, however, a binary correction factor was only applied to the dispersion term of the LJ potential. It was found that increasing the binary correction factor for this term by 7% improved the fit of the molecular simulations to the experimental measurements.

It should be noted that the aforementioned studies used significantly more computations than the present contribution. Since LD theory requires only two computations per gas species, it is an attractive option if computational costs are to be reduced. Therefore, it is desired to assess the usefulness of LD theory in the context of binary correction factors applied to the intermolecular LJ potential between the guest gas species and the water lattice.

2. THEORY AND METHODS

2.1. LD VAN DER WAALS-PLATTEEUW THEORY

The phase equilibrium criterion of interest here is the equality between the chemical potential of liquid water (μ_W^L) and water in the hydrate phase (μ_W^H):

$$\mu_W^L = \mu_W^H \tag{3}$$

For convenience, both of these quantities are expressed relative to the chemical potential of water in the hypothetical empty hydrate (μ_W^β):

$$\Delta\mu_W^L = \mu_W^\beta - \mu_W^L = \Delta\mu_W^H = \mu_W^\beta - \mu_W^H \tag{4}$$

The empty hydrate is considered, even though it does not exist in nature, because it represents a useful reference state. The difference between the chemical potential of water in the empty hydrate and water

in the loaded hydrate ($\Delta\mu_W^H$) can be calculated in terms of the fractional occupancy (θ) of the gas species enclathrated in the hydrate [3]:

$$\Delta\mu_W^H = - R\,T\,\Sigma_j [\ \nu_j \ln (1 - \Sigma_i\ \theta_{ij})] \tag{5}$$

The index *i* refers to the gas species, *j* is a reference to the cavity type (i.e. small, medium, large), νj is the ratio of cavities of type j to water molecules in the hydrate unit cell, and θ_{ij} is the fractional occupancy of cavity type *j* by gas species *i*. The fractional occupancy is often described in terms of a Langmuir-type adsorption isotherm.

The difference between the chemical potential of water in the hypothetical empty hydrate and the chemical potential of water in liquid water ($\Delta\mu_W^L$) can be expressed as the difference between two pure phases at reference conditions of T_R = 273.15 K and zero absolute pressure. The chemical potential difference at these conditions is the so-called "reference potential", $\Delta\mu^0$. Appropriate corrections (f) for the actual temperature, pressure, and gas solubility of the system in question are then applied [23]:

$$(\Delta\mu_W^L) / (R\,T) = (\Delta\mu^0) / (R\,T_R) + f \tag{6}$$

The corrections necessary to account for temperature, pressure, and solubility shall not be elaborated upon here, since the quantity of interest in LD theory is the reference potential, $\Delta\mu^0$. The other quantities are elaborated upon in the literature [23].

LD theory attempted to introduce an adjustment to the reference potential to account for the distortion of the host water lattice by the guest molecules. This correction becomes especially significant for large molecules, such as cyclopentane or tetrahydrofuran (both of which can be found in clathrate hydrate systems). This correction takes the form of a perturbation potential, $\Delta(\Delta\mu^0)$ [15]:

$$\Delta(\Delta\mu^0) = \Delta U_H - T_R\,\Delta S \tag{7}$$

ΔU_H is the change in the energy of the host lattice due to the distortion associated with enclathration of gas molecules, and $T_R\,\Delta S$ represents the entropic effect of expansion. The host energy consists of a summation of static and vibrational contributions, details of which are given in the following sections. This entropic term can be calculated as [15]:

$$T_R\,\Delta S = T_R (\beta / \kappa)\,\Delta V_H \tag{8}$$

β and κ are the thermal expansivity and the isothermal compressibility of the hydrate, respectively, and ΔV_H is the change in molar volume of the host lattice due to the distortion associated with the presence of the guest species. ΔU_H and ΔV_H can be readily determined from molecular-level computations, whereas β and κ can be found in the literature [24,25]. The entropic term is, however, negligible compared to the other contributions to the perturbation energy [15].

The left-hand side of Equation (7) is a perturbation term which can be added to the (unperturbed) reference potential to produce a "perturbed" reference potential ($\Delta\mu^*$), which can then be used instead of the reference potential when evaluating Equation (6) [15]:

$$(\Delta\mu^*) = \Delta\mu^0 + \Delta(\Delta\mu^0) \tag{9}$$

The LD theory of Zele, Lee, and Holder showed that there is indeed a distortion of the host lattice, and that the trends obtained from their simulations were the same as for their empirically determined perturbed reference potentials [15]. It should be noted that for relatively small changes in the lattice constant (i.e. for cell constants in the region of approximately up to 101% of the "fixed" value of the vdWP theory) [15], the results of the previous molecular simulations agreed favourably with the values obtained empirically.

2.2. STATIC ENERGY

As stated above, the host energy consists of static and vibrational contributions. The static contribution is usually significantly larger than the vibrational contribution. Therefore, it can be reasonable to neglect the vibrational contributions altogether (i.e. $U_{STATIC} >> U_{VIB}$). This is discussed below for the system studied in this work.

The General Utility Lattice Program of Gale and Rohl [26] was used in this study. In order to determine the static contribution, a geometry optimization was undertaken to obtain the lowest energy configuration, which is the most stable. Optimization was performed using the steepest descent method, similar to previous computations [27]. An energy-minimized crystal lattice structure [28] was used as the starting point for this study. Only the sI structure was considered, since it is well known that methane clathrate hydrate occurs in this form [1]. The lattice optimization was undertaken at zero absolute temperature and zero absolute pressure, and the static energy was determined at this configuration. The spatial coordinates of the energy-minimized lattice associated with each value of the binary correction factors were used as the starting point for the next calculation, such that the calculations proceeded in an incremental fashion. For example, the set of spatial coordinates $\{x\}$ of m

water molecules obtained from the minimized structure for the base value of k_{ij} = 1 would be used as the starting point for k_{ij} = 1.01, and so forth. This helps to avoid the problem of the lattice optimization locating a local minimum structure, as opposed to the desired global minimum structure [28]. A preliminary series of computations that did not follow this incremental procedure showed that local minima were obtained in many of the optimisations; and hence, an erraticand non-monotonic function for ΔU_H as a function of k_{ij} was obtained. The results of these initial calculation attempts can be seen in Figure 1, wherein it is also apparent that the nonincremental approach did not yield minimum energy structures.

2.3. VIBRATIONAL ENERGY

The spatial coordinates of the water molecules were subsequently processed to compute the vibrational contribution to the host energy. This was achieved by means of a vibrational partition function calculation at the reference conditions. This incorporates the effect of temperature, which was not done in the calculation of the static contribution.

The collective vibrational excitations in the elastic crystal lattice are calculated by considering the reciprocal lattice of the clathrate hydrate crystal. This was achieved by computing the force matrix (using the potential energy between sites) and the Hessian matrix to determine the vibrational frequencies. The electrostatic charges on the atoms were included using the Born effective charges [29,30]. Once the vibrational frequencies were calculated, the vibrational partition function ($Z_{VIB.}$) and vibrational energy ($U_{VIB.}$) were computed over m vibrational modes [31]. These are shown below:

$$Z_{VIB.} = \Sigma_m \Sigma_k \exp(- h\omega / 2k_BT) / (1 - \exp(- h\omega / k_BT)) \quad (10)$$

$$U_{VIB.} = \Sigma_m \Sigma_k w_k (0.5\, h\omega + h\omega / (\exp(h\omega / k_BT) - 1)) \quad (11)$$

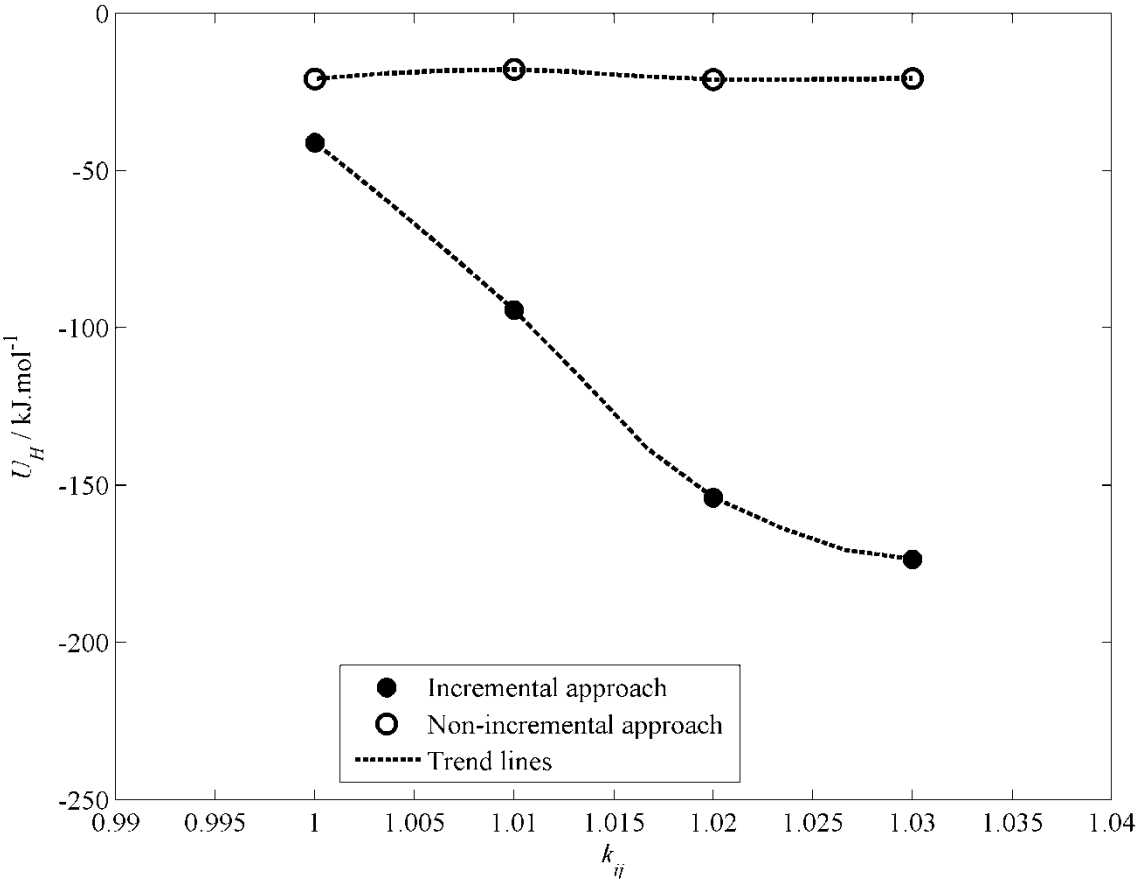

Figure 1. Comparison of lattice energies of the empty sI methane clathrate hydrate calculated using incremental and non-incremental approaches in k_{ij}.

In Equations (10) and (11), ω is the relevant vibrational frequency, and in Equation (11), w_k is the weight of each point in reciprocal space, such that the sum of all weights is unity. The calculation of the host energy is the sum of the static and vibrational contributions.

2.4. INTERMOLECULAR POTENTIALS

The Simple Point Charge (SPC) force field [32] was used to represent water molecules, and a united atom particle with an intermolecular LJ potential [33] was used for methane. The LJ parameters (εii and σii) of the methane–methane intermolecular interactions are adjusted using [34] the critical temperature (T_C = 190.6 K) and critical pressure (P_C = 4.61 MPa) of methane [35]. The force field parameters are shown in Table 2. Ewald summation [36] accounted for electrostatic interactions of the system, and a cutoff radius of 1 nm was used for LJ interactions.

The aforementioned force fields provide adequate descriptions of pure water [15] and methane [34] systems, and therefore the present study focuses on the cross-interaction terms applicable to the

clathrate hydrate phase only. Moreover, a previous study [37] has found a significant phase dependence on binary correction factors between unlike LJ interactions, further motivating this approach.

Molecular species	Non-bonded interactions (Lennard-Jones)	Charges	Bond angle
SPC water [21]	ε_O / k_B = 78.21 K	q_O = -0.82 e	$\alpha_{(H\text{-}O\text{-}H)}$ = 109.47 ^{o}
	σ_O = 0.3166 nm	q_H = +0.41 e	
United atom LJ methane [23,24]	ε_{CH4} / k_B = 145.27 K		
	σ_{CH4} = 0.3821 nm		

Table 2. Force field parameters used in this study.

3. RESULTS AND DISCUSSION

3.1. LATTICE VIBRATIONS

Figures 2 and 3 show that there is no significant dependence of the phonon densities of state on kij or lij. This suggests that adjusting the size or dispersion terms of the unlike LJ interaction does not significantly influence the vibrations of the clathrate hydrate lattice.

Averaging across all computations, vibrational energy amounted to 10.5 ± 0.4 kJmol^{-1}. This value was approximately constant, regardless of whether the host lattice was distorted or not, which can be expected since lattice vibrations are largely dependent upon temperature. Since the differences in host energy are of interest in this study, the vibrational term can be ignored, since it is approximately constant for the distorted and undistorted lattices.

As expected, it was found that $U_{STATIC} >> U_{VIB.}$ in all cases investigated in this study. Therefore, any influence of k_{ij} or l_{ij} on the vibrational energy would have to be profound for it to influence the results of this study. Moreover, since the vibrational contribution is significantly smaller than the static contribution, it can be neglected in perturbation energy calculations.

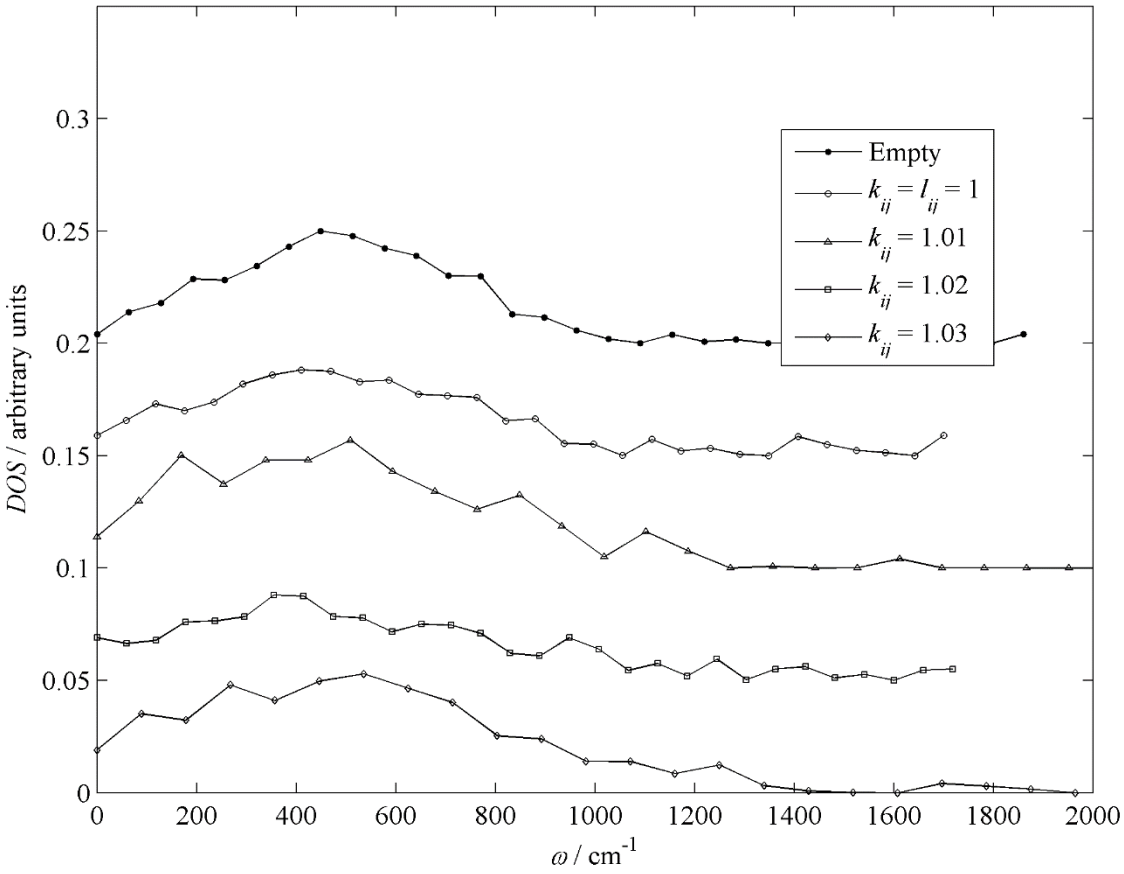

Figure 2. Influence of LJ dispersion correction factor (k_{ij}) on phonon DOS of sI methane clathrate hydrate over the vibrational frequency (ω). Each plot is shifted upward from the curve below by 0.05 units for clarity.

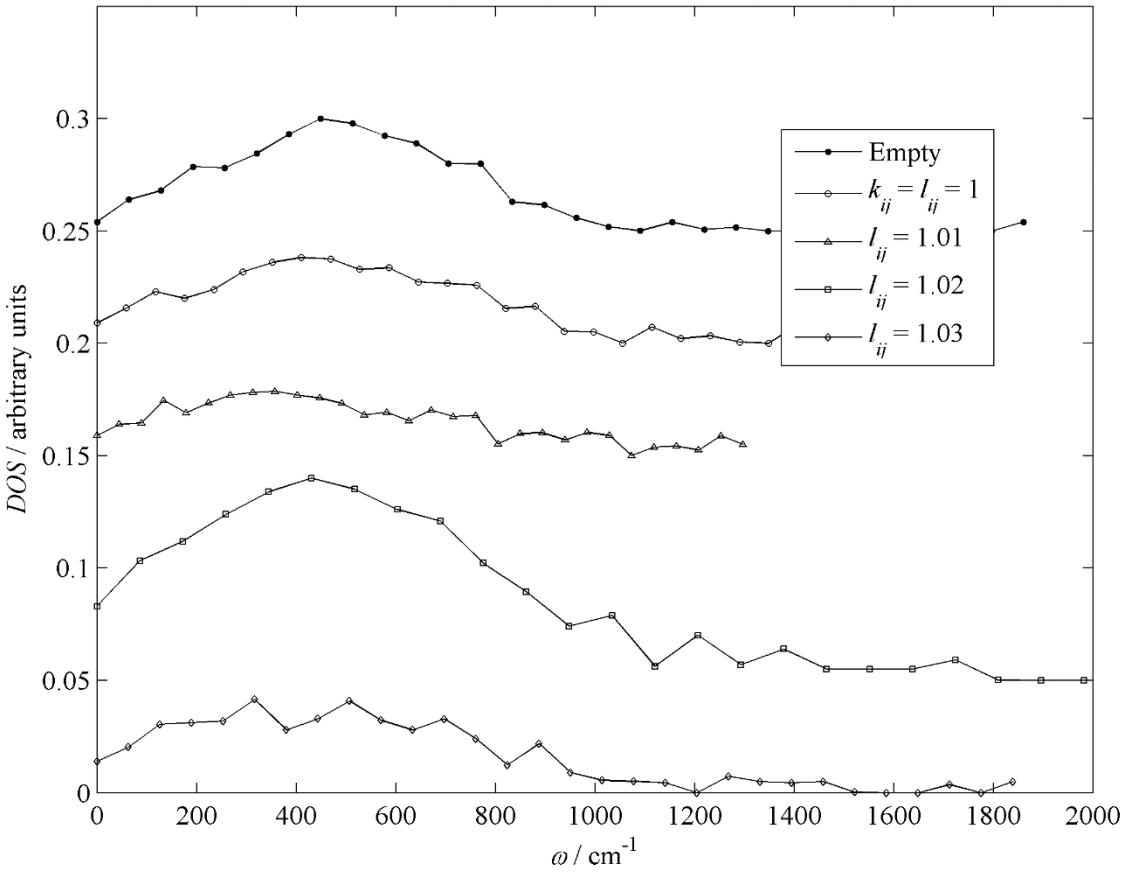

Figure 3. Influence of LJ size correction factor (l_{ij}) on phonon DOS of sI methane clathrate hydrate over the vibrational frequency (ω). Each plot is shifted upward from the curve below by 0.05 units (except l_{ij} = 1.01, which is shifted up by 0.1 units) for clarity.

3.2. EFFECT OF BINARY CORRECTION FACTORS ON THE PERTURBATION ENERGY

The phonon density of states (DOS) was also used to determine the entropic term for the lattice configurations in Equation (7), $T_R \Delta S$. On average, it was found that $T_R \Delta S$ was two to three orders of magnitude lower than ΔU_H. This concurs with previous observations [15], and therefore the entropic contribution was neglected in the presentation of the results.

The result of interest from the computations is the perturbation potential energy of the hydrate lattice, represented by ΔU_H in Equation (7). This quantity can be determined directly by calculating the energy of the empty hydrate lattice (which has been optimized at the conditions of interest, namely T = 273.15 K and P = 0 MPa) and comparing it to the energy of the water molecules in the loaded lattice at the same conditions, as per the original LD theory. The host energy of the empty lattice was −84.6 kJ mol^{-1}.

Figure 4 shows that the perturbation energy decreases with an increase in both k_{ij} and l_{ij}. It is also clear that the desired value for the perturbation potential (~20 J mol^{-1}) results in values of k_{ij} = 1.002 ± 0.009 and l_{ij} = 1.015 ± 0.011 obtained through quadratic and linear fitting, respectively. For comparison, k_{ij} = 1.07 was previously obtained for methane + water cross-interactions [21]. It should be noted, however, that different water and methane force fields were used in Ref. [21]. The desired value of the perturbation energy was determined from the experimental phase equilibrium data [38,39] by applying the method of Parrish and Prausnitz [40] and making use of the Peng–Robinson cubic equation of state [41] for the vapour phase fugacity.

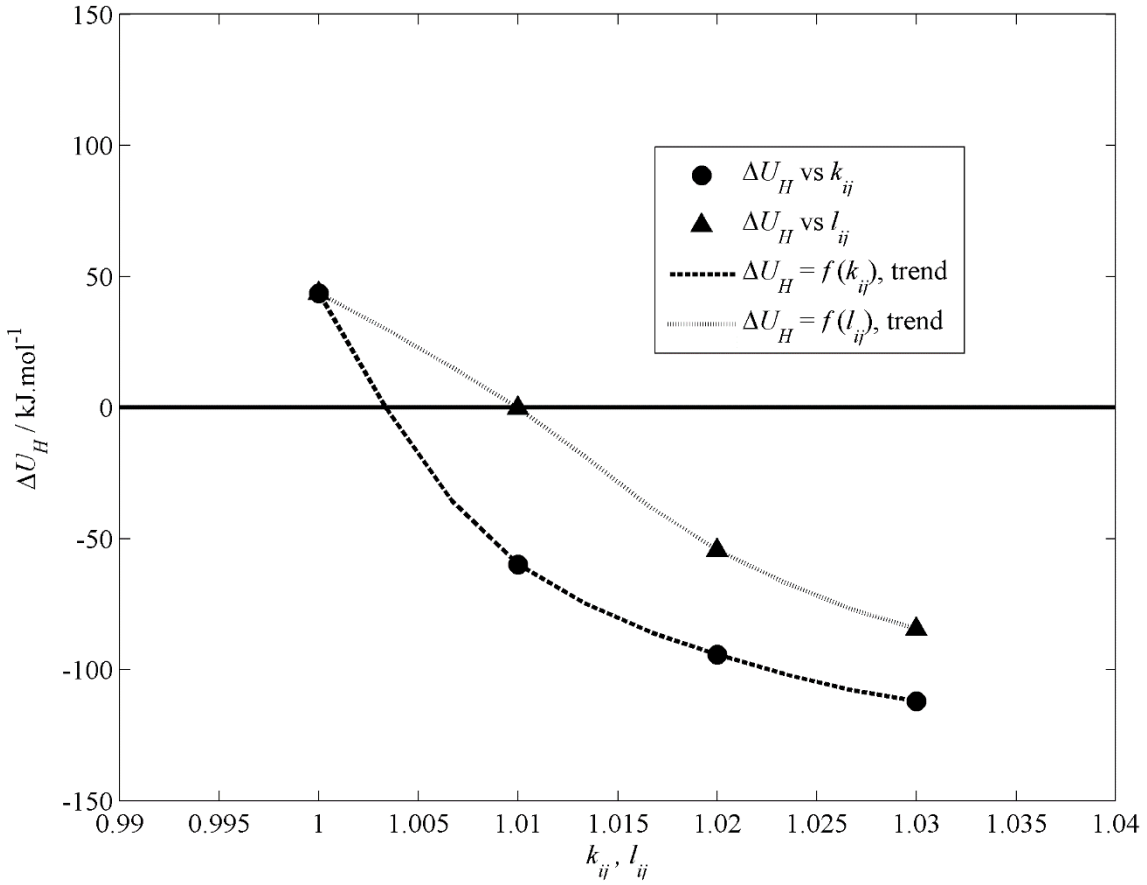

Figure 4. Effect of k_{ij} and l_{ij} on ΔU_H. The solid horizontal line is the value of ΔU_H calculated from experimental phase equilibrium data (≈20 J mol^{-1}). The trends are fitted as guides for the eye.

Figure 4 also reveals that the perturbation energy is extremely sensitive to changes in the value of either binary correction factor, especially if the order of magnitude of the perturbation energy is considered relative to the aforementioned desired value. This may also be evidenced in the aforementioned values obtained for k_{ij}, compared to the literature [21]. For both of the values mentioned above, changes of less than 1% the binary correction factors result in changes of the order of 50–100 kJ mol^{-1}. These changes are more than three orders of magnitude larger than the desired

value of the perturbation energy.

Another point to be noted is the degree of sensitivity of the perturbation energy to changes in the binary correction factors relative to each other. Figure 4 shows that ΔU_H is slightly more sensitive to changes in k_{ij} than l_{ij}. However, the difference is not very large, given that $\Delta U_H \approx 20$ J mol^{-1} is achieved over a range of 1–1.011 for k_{ij} or l_{ij}, due to the pronounced sensitivity of the perturbation energy to both parameters. Therefore, adjustment of either the size or dispersion terms of the cross-interaction between water and methane will change the perturbation potential approximately equally.

It can also be seen in Figure 4 that the L – B rules without binary correction factors (i.e. $k_{ij} = l_{ij} = 1$) result in values for the perturbation potential which would provide a poor fit to the experimental data. The aforementioned lack of suitability of an unmodified Berthelot rule [18–20], coupled with the results shown in Figure 4 suggest that the LD theory used in this study can produce results which fit the experimental data when binary correction factors are employed.

A cause for lack of robustness in determination of the binary correction factors can arise from shortcomings in the force fields used (namely SPC for water and a united atom LJ force field for methane in this study). However, the SPC force field has been used in the original LD study with some success. The united atom LJ force field for methane in this study is similar to other united atom methane force fields [21] which have been used successfully for clathrate hydrate studies, such as the united-atom OPLS force field [42] or the transferable potentials for phase equilibrium (TraPPE) [43]; in fact, the force field used in this study is almost identical to the two aforementioned force fields. Therefore, it cannot simply be a shortcoming of the employed force fields which has resulted in the sensitivity to the binary correction factors.

It is expected that an increase in the binary correction factors lead to a larger (more negative) value for the perturbation energy. This is because increasing the binary correction factors increases the strength of the methane–water interactions (for k_{ij}) or the equilibrium distance between the methane and water molecules (for l_{ij}). As discussed below with reference to Figure 5, this results in a larger expansion of the clathrate when methane is present. Since, the perturbation energy is the energy of this expanded structure relative to the structure in the absence of methane, there is a larger perturbation energy for larger binary correction factors (the negative sign arises merely because the energy of the pure clathrate is subtracted from the expanded substrate and not vice versa).

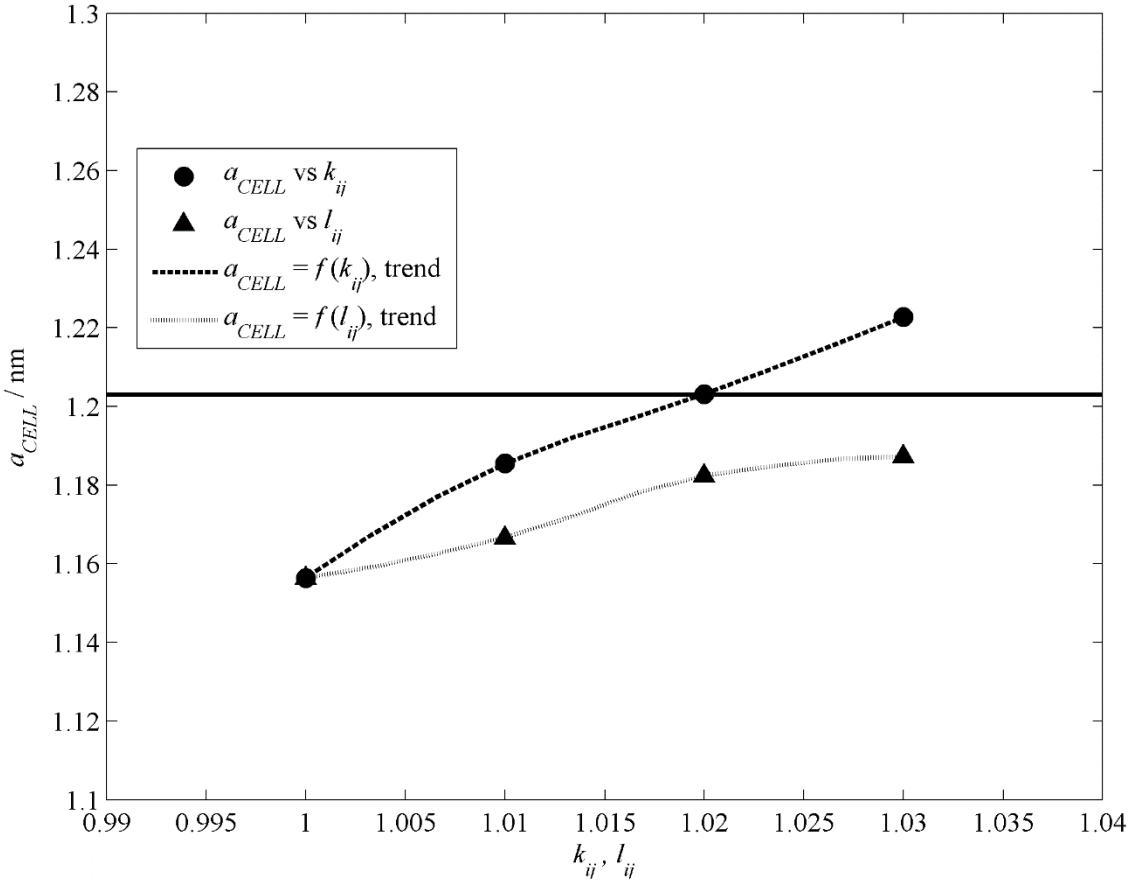

Figure 5. Effect of k_{ij} and l_{ij} on a_{CELL}. The solid horizontal line is the experimental value of a_{CELL} (1.203 nm) [15]. The trends are fitted as guides for the eye.

3.3. EFFECT OF BINARY CORRECTION FACTORS ON THE CELL CONSTANT

The relationship between the lattice or cell constant of the clathrate hydrate unit cell and the binary correction factors, is shown in Figure 5. The experimental lattice constant is generally accepted to be 1.203 nm [15], and is also considered in this analysis. In this case, it can be seen that setting k_{ij} = 1.020 ± 0.014 reproduces the experimental lattice constant. This is different to the value of k_{ij} found when fitting to the perturbation potential. Moreover, whilst the value of l_{ij} fitted to the experimental lattice constant was not determined, it is apparent that it will be greater than 1.03 (provided the trend observed in Figure 5 continues), which also differs to the value required for l_{ij} to reproduce the desired perturbation energy. Therefore, the value of the binary correction factors for the size and energy parameters of the LJ potential fitted to the experimental data varies according to the type of experimental data which are being considered.

Figure 5 also shows that there is an approximately linear trend of the cell constant with changes in the binary correction factors. In this case, however, increasing the binary correction factors result in an

increase of the cell constant. It can also be seen that the cell constant is more sensitive to variations of k_{ij} than l_{ij}. This can be due to the size of the methane molecule relative to the diameter of the cavities in the sI clathrate hydrate. In nature, methane is known to occupy both the small and large cavities [1] due to its small size. Therefore, larger changes to the size term of the LJ cross-interaction are required to perturb the crystal lattice significantly from the configuration of the empty clathrate hydrate as compared to the dispersion term. It can then be deduced that the intermolecular energy between the gas species and water plays a more significant role in the distortion of the clathrate hydrate lattice than the molecular size of the gas species, at least for approximately spherical gas species.

The dependence of the perturbation energy on the lattice constant is shown in Figure 6. Here, it can be seen that these two quantities are related in an approximately linear fashion, with increases in the lattice constant resulting in larger negative values of the perturbation energy. This is to be expected, as Figures 4 and 5 both suggest that increasing the strength of the intermolecular LJ potential results in more negative perturbation energies and an increase in the lattice constant. This is due to the greater deviation in the size of the crystal unit cell as compared to the empty lattice, which is the chosen reference state in LD theory.

A further point illustrated in Figures 4, 5, and 6 is that k_{ij} or l_{ij} cannot be fitted simultaneously to match the experimental value for the lattice constant and the perturbation energy. This is evidenced by the perturbation energy (≈ -100 kJ mol^{-1}) which corresponds to the experimental lattice constant (1.203 nm). Therefore, it can be supposed that the experimental or calculated quantity which is desired should be carefully selected (depending on the property of interest), since the results of the computations do not yield results which are quantitatively similar to experimental results for all data types.

3.4. FORCE FIELD SENSITIVITY

The error limits of the calculated perturbation energies and lattice constants (see Figures 7, 8, and 9) have been estimated by analysing their sensitivity to uncertainties in the critical properties used to calculate the LJ parameters of methane (standard deviations for experimentally measured critical temperature and pressure from an aggregated data-set are σ_{Tc} = 0.3 K and σ_{Pc} = 0.03 MPa [44], respectively). Although the LJ potential is only an approximation of the intermolecular interaction for methane, LD theory in this study is being examined within the context of LJ-type gas molecules distorting the water lattice of clathrate hydrates. For real gases, LJ parameters can be readily estimated using critical properties, and thus some measure of the allowed values of the perturbation energy and lattice constant, k_{ij} and l_{ij} are necessary, since there are a large number of data-sets which researchers can use to obtain T_C and P_C. The ranges between the upper and lower limits in Figures 7, 8, and 9

represent the possible allowed values for ΔU_H, a_{CELL}, k_{ij}, and l_{ij} for the SPC water + united atom LJ methane sI clathrate hydrate system. The values for k_{ij} and l_{ij} obtained in this study clearly lie within the bounds of the error limits.

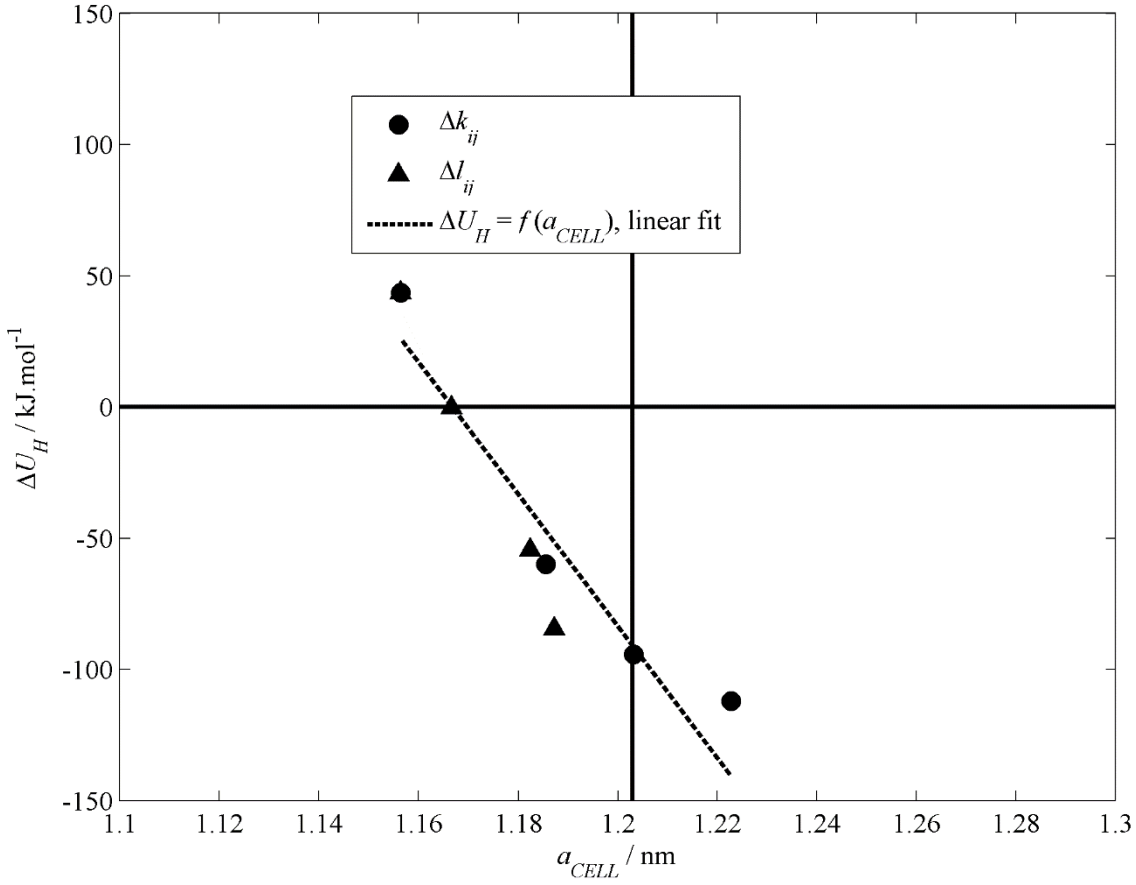

Figure 6. General trends for ΔU_H vs. a_{CELL} determined by separately changing k_{ij} and l_{ij}. The horizontal solid line represents the value of ΔU_H determined from experimental phase equilibrium data (≈20 J mol^{-1}), and the vertical solid line represents the experimental lattice constant (1.203 nm) [15]. The dashed line is a linear trend fitted as a guide for the eye.

To determine the error limits, the LJ parameters of methane were recalculated for every combination of addition/subtraction of each of σ_{Tc} and σ_{Pc} . For each set of reevaluated LJ parameters for methane, the lattice energies were recalculated and compared to the values obtained using the mean critical properties. The maximum deviations were then considered as the limits of allowed values of ΔUH, a_{CELL}, k_{ij}, and l_{ij}.

Plausible values for the binary correction factors can also be considered for the entire allowed range of possibilities afforded by the error limits. If the ranges allowed by the error limits are considered, then fairly large ranges are found: $0.999 \leq k_{ij} \leq 1.021$ and $1.003 \leq l_{ij} \leq 1.029$.

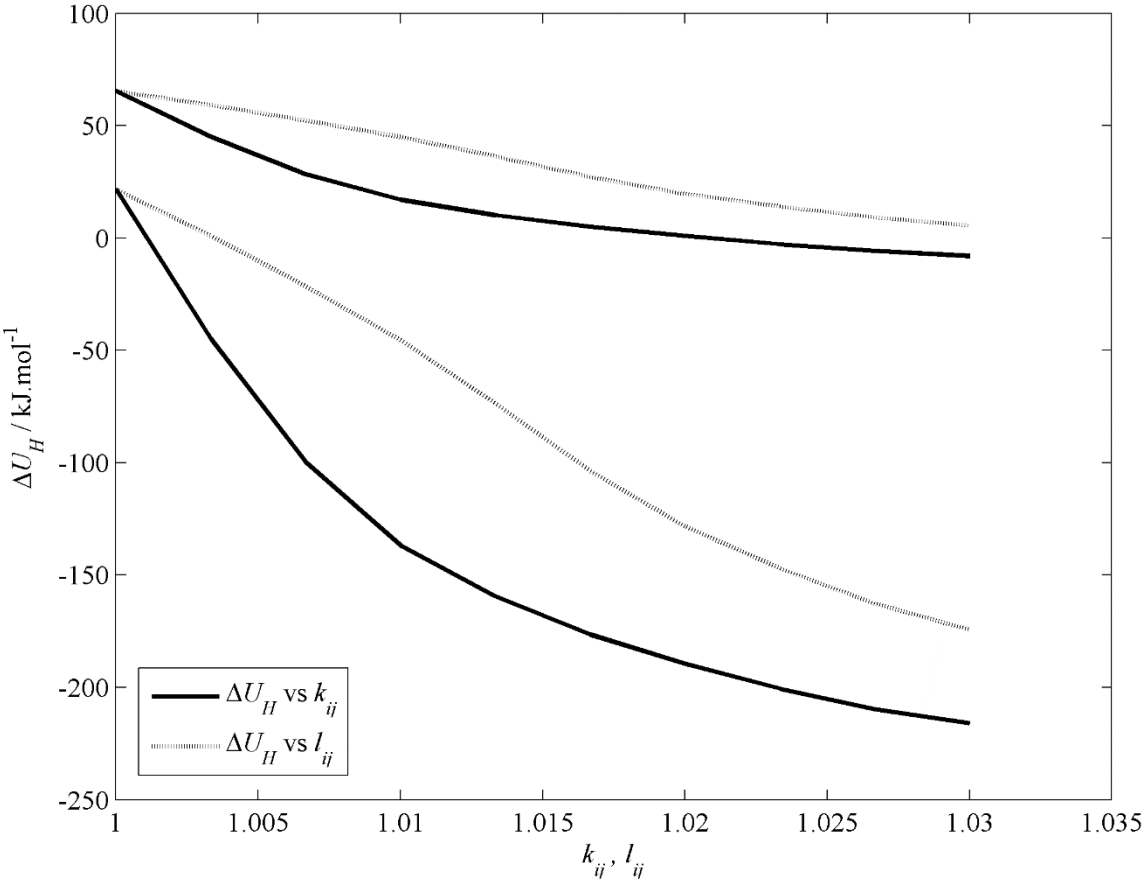

Figure 7. Estimates of allowed limits of ΔU_H.

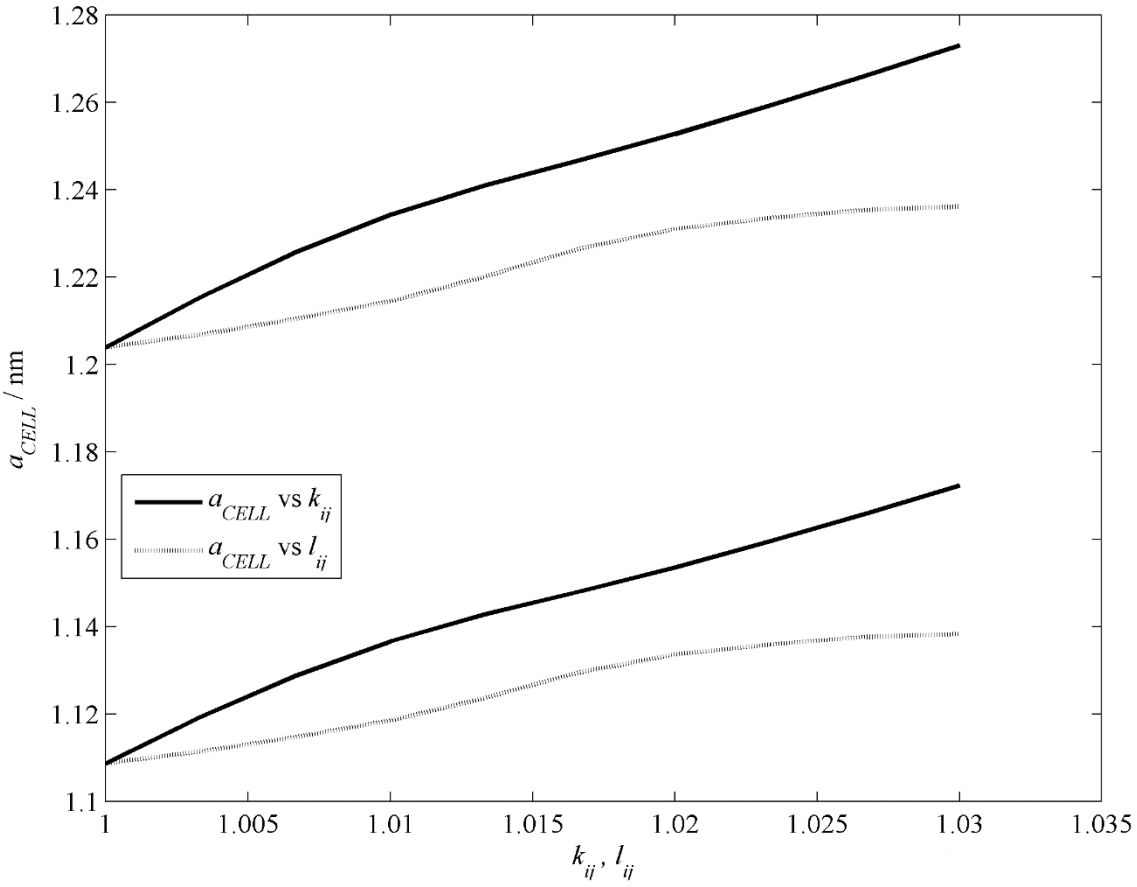

Figure 8. Estimates of allowed limits of a_{CELL}.

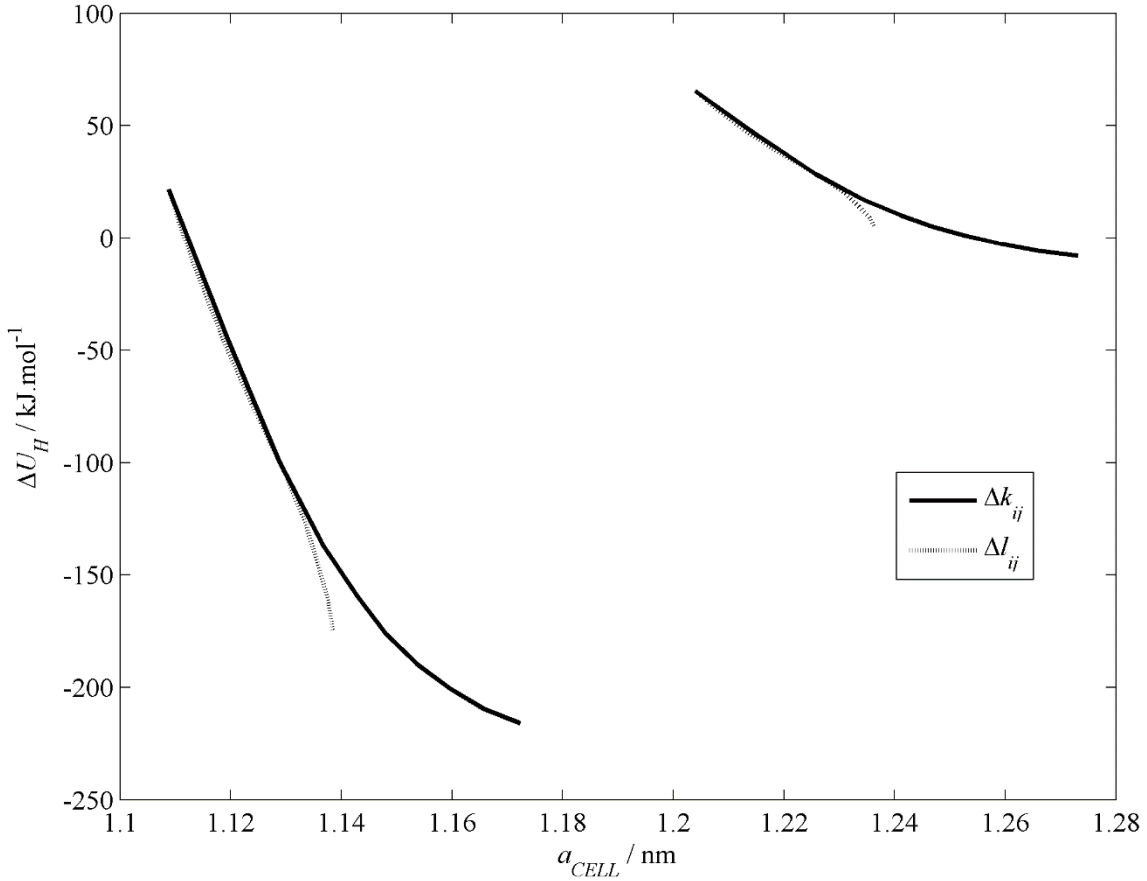

Figure 9. Estimates of allowed limits of ΔU_H and a_{CELL} determined by separately changing k_{ij} and l_{ij}.

3.5. GENERAL TRENDS

It is important to consider how the force fields used in this study compare with other force fields which have been used to describe clathrate hydrate systems. The parameters of the SPC force field are very similar to the parameters of the extended SPC (SPC/E) force field [45] as well as the TIP4P force field [46]. The similarities of computations performed for clathrate hydrates using both the SPC/E and TIP4P force fields have been established in the literature [2,47,48]. As stated previously, the parameters of the united atom LJ force field used in this study for methane are very similar to the LJ parameters of other commonly used methane force fields (such as the OPLS-UA and TraPPE force fields). Thus, using the similarities evident in the parameters used for both the water and methane molecules in this study, it can be presumed that a similar response of the perturbation energy and lattice constant to LJ binary correction factors can be valid for water + LJ clathrate hydrates in general, when using optimized lattice structures.

However, even though the trends observed in this study can be very similar to other united atom

methane force fields, the sensitivity of ΔU_H and a_{CELL} to σ_{Tc} and σ_{Pc} should be considered. This sensitivity suggests that any combination of k_{ij} and l_{ij} obtained for a particular force field combination does not have general applicability, since the values obtained for k_{ij} or l_{ij} are specific to the particular LJ parameterization of methane. Thus, although ΔU_H and a_{CELL} can behave similarly as a function of k_{ij} or l_{ij} for each force field combination, the actual values of k_{ij} and l_{ij} can be very different.

An additional factor to consider when determining the general application of the results of this study is the structure forming capacity of the various water force fields. The structure forming capacity describes the capability of a force field to form ordered water dimers, trimers, tetramers, and so on. For pure water, this can be expressed as the frequency of occurrence of each geometric structure as a function of temperature. If results of this study were to have general application, it is important to consider how SPC water compares to other simulated species when forming regular, geometric networks.

A recent study [49] on the structure-forming capacity of SPC, SPC/E, TIP3P [50], TIP4P, TIP4P-Ew [51], TIP4P/2005 [52], and TIP5P [53] water force fields found that the capability of each of these water force fields to form ordered structures was qualitatively the same. Similar quantitative results were obtained for these water force fields if a "temperature shift" was applied. Hence, if the system temperature was adjusted, then all of the force fields form the same quantity of ordered structures, and the amount of each type of structure exhibits almost an identical temperature dependence. Therefore, since a great number of water force fields behave in the same way when forming ordered structures, it can be concluded that the results from this study have general application, at least when using a LJ gas species.

4. CONCLUSIONS

Both the perturbation energy and cell constant were found to be approximately linearly dependent on the values of the binary correction factors; the magnitude of the perturbation energy increases, whilst the cell constant increases with increasing binary correction factor values. It should be noted that both quantities are sensitive to small changes in k_{ij} and l_{ij}.

Different values for the binary correction factors can be calculated, depending upon which experimental data type is selected for comparison. Both k_{ij} and l_{ij} were found to have different values when either the lattice perturbation energy or the lattice constant were used for fitting. Fitting for the lattice constant resulted in a poor value for the perturbation energy and vice versa.

The magnitude of the perturbation potential was found to correlate positively with the lattice constant.

This was expected as increasing the lattice constant causes the system to deviate further from the reference state (the empty lattice) in LD theory.

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