Influence of unlike dispersion interactions in modeling methane clathrate hydrates

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A B S T R A C T

Studies of the thermodynamic stability of clathrate hydrates of natural gas (mostly methane) is important in fields such as offshore gas exploitation and energy storage. Two approaches were used to study the effect of unlike dispersion interactions on methane clathrate hydrates: grand canonical Monte Carlo simulations (which yield adsorption data directly and can be used to infer phase equilibria), and estimation of the heat of dissociation coupled with the Clausius–Clapeyron equation (to calculate the phase equilibria, at the expense of providing no information about the adsorption behavior). It was found that the adsorption isotherm parameters change monotonically with respect to unlike dispersion interactions, although a perfect fit to experimentally-derived values may not be possible, at least using the force fields considered in this study. The heat of dissociation changes monotonically due to changes in the unlike dispersion interaction, and a best fit value of the Berthelot correction factor is achieved.

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1. Introduction

Clathrate hydrates resemble ice, and form from a gas species trapped within a network of hydrogen-bonded water molecules. Naturally occurring clathrate hydrates contain primarily methane as the guest molecule, and are found in the deep ocean or permafrost [1]. Methane hydrates are a major concern in offshore operations [2], as it frequently forms blockages in natural gas pipelines [3]. However, methane hydrates are also of interest as an energy storage medium due to the relatively low cost of the storage material, which is essentially water [4,5].

The effect of unlike dispersion interactions on adsorption in methane clathrate hydrates has not yet been studied in detail, although such a study has recently been undertaken for argon clathrate hydrates [6]. The effects of dipole moment, molecular size, and other parameters on the stability of clathrate hydrates have been studied by laboratory experiments [7,8]. However, such experiments do not allow for full control of molecular parameters, which is possible with molecular computations. By varying the molecular properties, the physical mechanisms of guest molecule adsorption can be studied directly.

The standard Lorentz [9] and Berthelot [10] combining rules are commonly used for specifying the parameters of unlike Lennard–Jones (LJ) interactions [11] between different molecule types [12]. However, their applicability to systems containing nonpolar and polar molecules may not be optimal. For instance, gas–water interactions are not well described by these combining rules [13]. Extensive discussions on the general use of combining rules can be found in the literature [6,13–17], although there is little work with respect to clathrate hydrates. The use of the standard Lorentz and Berthelot rules for clathrate hydrate systems has only recently been discussed in the literature [18].

An extensive study was performed recently to determine the effects of the Lorentz and Berthelot combining rules on adsorption in argon clathrate hydrates [6]. Changes in the Lorentz and Berthelot combining rules resulted in significant changes in adsorption for the sII and sH clathrate hydrate structures, due to the size differential between the cages present in these structures. The effects were considered to be weak for the sI argon clathrate hydrate. It should also be noted, however, that the LJ parameters of argon were adjusted, and not the unlike interactions between argon and water.

The study focuses on the Berthelot rule, since previous studies [18–20] have shown that for spherical (e.g., argon) or approximately spherical molecules (e.g., methane), an additional 'polarizability' contribution to the guest–water interactions must be considered. This is achieved in a computationally expedient way

[18] through the introduction of a correction factor to the Berthelot rule. The polarizability contribution is purely a dispersion/energetic effect, and so the size parameter remains unaffected.

2. Theory and methods

2.1. Clathrate hydrate phase equilibria

Phase equilibria of clathrate hydrates are described using the van der Waals–Platteeuw theory [21]. The phase equilibrium criterion is the equality of the chemical potential of water in the hydrate and liquid phases, each relative to the hypothetical empty hydrate ($\Delta\mu_W^H$ and $\Delta\mu_W^L$, respectively). Calculation of each of these terms can be achieved by [22]:

$$\Delta\mu_W^H = -R \cdot T \cdot \sum_j \left[\nu_j \ln \left(1 - \sum_j \theta_{ij} \right) \right] \tag{1}$$

$$\Delta\mu_W^L = -R \cdot T \cdot \frac{\Delta\mu^0}{R \cdot T_R} - \int_{T_R}^{T} \frac{\Delta H_W}{R \cdot T^2} \, dT + \int_0^P \frac{\Delta V_W}{R \cdot T} \, dP \tag{2}$$

where the indices i and j refer to the gas species and cavity type, respectively, ν_j is the ratio of water molecules per unit cell to cavity type j, θ_{ij} is the fractional occupancy of cavity type j by gas species i, $\Delta\mu^0$ is $\Delta\mu_W^H$ at $T_R = 273.15$ K and $P_R = 0$ MPa (i.e., the reference state), and ΔH_W and ΔV_W are the differences in enthalpy and molar volume, respectively, between liquid water and the hypothetical empty hydrate in the reference state. Therefore, once the dependence of the fractional occupancy on temperature and pressure is known, phase equilibria can be estimated using the above relationships.

The fractional occupancy, θ, is the number of adsorbed methane molecules per unit cell divided by the total number of adsorption sites per unit cell, N/N_T, and is calculated by using the Langmuir adsorption constant C and the fugacity of the gas species f:

$$\theta = \frac{C \cdot f}{1 + C \cdot f} \tag{3}$$

Pressure can be substituted for fugacity in Eq. (3), since the deviation is not great [23] over the range of experimental data [24,25] for methane clathrate hydrates. A temperature dependence relationship for the Langmuir adsorption constant [26] was fitted [27] to the simulated adsorption isotherms using two parameters A and B:

$$C = \left(\frac{A}{T} \right) \cdot \exp \left(\frac{B}{T} \right) \tag{4}$$

In order to estimate the phase equilibria, Eq. (4) can be combined with Eqs. (1)–(3).

It was recently found [28,29] that in order to accurately simulate hydrates under equilibrium, the water force field should reproduce the experimental value for the melting point of ice I$_h$. However, GCMC simulations assume a priori that the hydrate structure is stable under the conditions considered, and moreover, phase equilibrium is not simulated directly using GCMC simulations. GCMC simulations only consider the phenomenon of adsorption into a stable clathrate lattice, and so can only directly provide information on the loading behavior of clathrate hydrates. Once the loading behavior is known, the influence of pressure and temperature on occupancy can be ascertained. Since van der Waals–Platteeuw theory [21] can be used to express the chemical potential of the hydrate phase using the occupancy, the dissociation pressure can then be estimated using adsorption isotherms fitted to experimental data [30]. Thus, the phase equilibria are inferred using the pressure- and temperature-dependence of the occupancies.

By expressing the natural logarithm of the dissociation pressure as a function of the reciprocal of temperature, the heat of dissociation ($\Delta H_{Diss.}$) can be related to the slope of the dissociation pressure curve by the Clausius–Clapeyron equation [31]:

$$\frac{d \ln P}{d(1/T)} = \frac{-\Delta H_{Diss.}}{Z \cdot R} \tag{5}$$

where Z is the compressibility factor of methane. Methane was considered as an ideal gas when employing Eq. (5) in this study, since over the range of experimental temperature and pressure values, the deviation from ideality is not significant [23]. In the case of using GCMC simulations (the first approach considered in this study), the heat of dissociation can only be inferred by examining the effect of adsorption isotherm parameters on the slope of the dissociation pressure curve. In the second approach in this study, the heat of dissociation itself was estimated directly by computing the enthalpies of the hydrate phase, gaseous methane, and liquid water. These calculated values were subsequently used in the integrated form of Eq. (5) to determine the dissociation pressure curve.

2.2. Intermolecular interactions

The LJ potential is frequently used to describe intermolecular interactions [32]. In this work, the adsorption isotherms and the heat of dissociation of methane clathrate hydrate were studied directly for different values of the unlike LJ well depth, ε_{ij}. This was achieved through application of a binary correction factor, k_{ij}, to the Berthelot rule:

$$\varepsilon_{ij} = k_{ij} \cdot (\varepsilon_{ii} \cdot \varepsilon_{jj})^{0.5} \tag{6}$$

where ε_{ii} and ε_{jj} are for the intermolecular interactions between like LJ sites. The reference case is $k_{ij} = 1.0$ (i.e., the Berthelot rule). It should be noted that ε_{ij} (and by extension, k_{ij}) values fitted to data for clathrate hydrate systems are limited in their application to other data for bulk systems [33]. Moreover, molecular interaction parameters fitted to clathrate hydrate data do not match those obtained by fitting to, for example, second virial coefficient, gas viscosity, or molecular beam scattering data [34]. This problem has been discussed in further detail and at great length in the literature [35–46].

It can be noted that the Berthelot rule is a special case of a more general formulation by Reed [47] and extended upon by Hudson and McCoubrey [48], which makes use of both the molecular size parameters and ionization potentials when calculating ε_{ij}. The Berthelot rule is returned from the Hudson and McCoubrey rule when the two molecules possess similar sizes and ionization potentials. Therefore, it is not surprising that the unmodified Berthelot rule may be insufficient to describe interactions between methane and water in clathrate hydrate systems [49].

The LJ parameters ($\varepsilon_{ii}/k_B = 145.27$ K and $\sigma_{ii} = 0.3821$ nm) of the united atom (UA) methane were calculated [50] from the critical properties [51], and the Simple Point Charge (SPC) water force field [52] was chosen since it has successfully been used in describing clathrate hydrates (albeit without directly considering phase equilibria) [27,53]. Since the structure-forming properties of water systems obtained from simulations using different force fields are similar [54], and since methane force field parameters are not significantly different [18], it is expected that trends observed in this study should be similar for other force field combinations. Ewald summation [55] was used for the long-range electrostatic interactions up to a real space cut-off distance of 1 nm, and the LJ interactions were truncated at 1 nm. The force field parameters are shown in Table 1.

2.3. Grand canonical Monte Carlo simulations

The General Utility Lattice Program (GULP) [56] was employed to perform grand canonical Monte Carlo (GCMC) computer