Microscopic model of clathrate compounds

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Abstract. The major generalization of the existing theory of clathrate hydrates, so that it can
account for phenomena such as multiple occupancy of individual cages and mutual guest-host
 couplings and guest-host interaction, are suggested. The new model allows taking into
account the influence of guest molecules on the host lattice. Atomistic modeling of structural,
dynamical and thermodynamic properties of ices and different hydrates at high pressures and a
range of temperature were performed. The influence of guest molecules (argon, methane and
xenon) on the host lattice of hydrate of cubic structures I and II was investigated. Results of
these calculations agree with known experimental data.

1. Introduction

Clathrate hydrates are supramolecular compounds of water molecules and guest components
without chemical bonds between them. Water molecules form a three-dimensional host structure (the
lattice) through hydrogen bonding; this lattice is sufficiently low density to contain a number of well-
characterized pores, or cages, in which other molecules (guests) are trapped. The first two crystal
structures (CS-I and CS-II) were characterized in the 1950’s \cite{1}. It was not until the 1980’s that third
structure with hexagonal unit cell (sH) was identified \cite{2}. More recently it has been shown that these
structures can be sensitive to pressure variation by virtue of friable packing of host framework and
relatively weak binding energy between water molecules. The recognition of this reach phase behavior
has created several important sources of interest.

The pressure-induced changes in the gas hydrate (GH) lattice are fundamentally the same as
those responsible for the rich solid phase diagram of pure water, so high pressure studies of GH should
help in the elusive goal of understanding the physical and structural properties of water itself. High
pressure experiments have been performed on Ne, Ar, Kr, N\textsubscript{2}, H\textsubscript{2} and CH\textsubscript{4} hydrates. CH\textsubscript{4} hydrate
transforms from CS-I to a hexagonal structure (MH-II) at about 9 kbar, and then to a third structure
with similarities to ice Ih at about 19 kbar. Ar also shows at least two pressure-induced phase
transitions: CS-II to sH at about 5 kbar, and then to a tetragonal structure at higher pressures; this last
structure contains up to two Ar atoms in each cage. For N\textsubscript{2} there are phase transitions at 6.5 kbar and
12.5 kbar \cite{3} with the high pressure phases again allowing multiple occupancy of the cages.

These observations have considerably undermined the existing theory of hydrate formation.
Currently, analytical theories are still based on the pioneering work of van der Waals and Platteeuw
\cite{4}. This theory, and all of its subsequent derivatives, embody four main assumptions. Three of these

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— that cages contain at most one guest; that guest molecules do not interact with each other; and that the host lattice is unaffected by the nature or number of guest molecules preset and classical statistics are valid—are clearly violated by the above data.

Some groundwork has been laid for developing such an improved theory. Dyadin and Belosludov have shown how a non-ideal solution theory can be formulated to account for guest-guest interaction [5]. In other studies, Westacott & Rodger have shown how the lattice dynamics (LD) formalism that has proved so successful in numerical simulations of GH properties can be simplified to allow for full free-energy optimization calculations for equilibrium properties [6]. A generalization of the van der Waals-Platteeuw (vdW-P) statistical thermodynamic model of clathrate hydrates, applicable for arbitrary multiple filling the cages, is formulated in [7] and [8]. However these developments do not go far enough, and a much more comprehensive theory is desperately needed.

In this work we develop a statistical thermodynamic theory of clathrate hydrates that accounts for the mutual influence of guest and host molecules (non-rigid host lattice) and guest-guest interaction—especially when more than one guest molecule occupies a cage.

2. Theory
From statistical thermodynamic well-known following precise expression for free energy:

\[ F = -kT \ln \sum_n \exp(-E_n/kT), \]  
(1)

where \( k \) – Boltzmann constant; \( T \) – absolute temperature; \( n \) – total quantum numbers which describe system state; summation on the \( n \) subscribe index mean summation on all system states; \( E_n \) – energy of the state with \( n \) quantum numbers.

Our subsequent development of a model is based only on one of the assumptions of Wan-der-Waals–Platteeuw theory: the contribution of guest molecules to the free energy is independent of mode of occupation of the cavities at designated number of guest molecules. This assumption allows to separate the entropy part of free energy:

\[ F = F_1(N_N, N) + F_2(N, N), \]  
(2)

where \( F_i \) is the part of the free energy of clathrae hydrate for the case of clathrate with one type of cavity and one type of guest and a cavity can hold one guest molecule only at given arrangement of guest molecules in the cavities, the entropy part of free energy of guest system \( F_2 \) can be wrote as

\[ F_2 = -kT \ln W_i(N, N) = \ln N! / N_i! (N - N_i)! \geq -N_i \ln y - (N - N_i) \ln (1 - y), \]  
(3)

were \( W_i(N, N_i) \) – the number of ways to order \( N_i \) guest molecules on \( N \) cavities, \( y = N_i / N \).

Difference from Wan-der-Waals–Platteeuw theory consists in that \( F_1 \) take into account the influence of guest molecules on the host lattice and guest molecules interactions with each other. In this case no need to do any suggestions about thermodynamic stability of these hydrate structure. By substituting (3) in (2), we obtain:

\[ F = F_1(N_i, y) + kTN \ln y + (1 - y) \ln (1 - y). \]  
(4)

This formulae simple generalize on cases when some types of cavities and guest molecules exist and a cavity can hold more than one guest molecule:

\[ F = kT \left[ V, T, y_{11}, \ldots, y_{mm} \right] + kT \sum_{t=1}^{m} \ln \left[ 1 - \sum_{i=1}^{k} \sum_{l=1}^{n} y_{il} \right] + kT \sum_{i=1}^{k} \sum_{l=1}^{n} y_{li} \ln y_{il}, \]  
(5)

where \( y_{il} = N_{il} / N_t \) - the degree of filling of \( t \)-type cavities by \( i \) cluster of \( l \)-type guest molecules; \( N_t \) – number of \( t \)-type cavities; \( N_{il} \) – number of \( l \)-type guest molecules which located on \( t \)-type cavities and united in \( i \)-clusters.

At given arrangement \( \{y_{11}, \ldots, y_{mm}\} \) of the clusters of guest molecules in the cavities the free energy \( F \left[ V, T, y_{11}, \ldots, y_{mm} \right] \) of crystal can calculated within the framework of lattice dynamics approach in the quasiharmonic approximation (QLD) [9], [10] as
\[ F_1(V, T, y_{1,1}, \ldots, y_{n,m}) = U + F_{vib} \quad (6) \]

where \( U \) is the potential energy, \( F_{vib} \) is the vibrational contribution:

\[ F_{vib} = \frac{1}{2} \sum_{j} \hbar \omega_j (\vec{q}) + k_B T \sum_{j} \ln[1 - e^{-\hbar \omega_j (\vec{q}) / k_B T}] \quad (7) \]

where \( \omega_j (\vec{q}) \) is the \( j \)-th frequency of crystal vibration and \( \vec{q} \) is the wave vector.

### 3. Model of calculation

Our model based on possibility of calculation of free energy with accounted energy of interaction of guest molecules and the host lattice. Equation of state can found by numerical differentiation of free energy:

\[ P(V, T) = -\left( \frac{\partial F(V, T, y_{1,1}, \ldots, y_{n,m})}{\partial V} \right)_0; \quad (8) \]

The “zero” index mean constancy of all thermodynamic parameters except the one which differentiation execute. After reception the free energy values we can calculate \( \mu_i^l \) – the chemical potentials of \( i \)-clusters of \( l \)-type guest molecules which located on \( t \)-type cavities and \( \mu_Q \) – the chemical potential of host molecules:

\[ \mu_i^l (P, T, y_{1,1}, \ldots, y_{n,m}) = \left( \frac{\partial F(V(P), T, y_{1,1}, \ldots, y_{n,m})}{\partial N_{i}^{t}} \right)_0 + kT \ln \frac{y_{il}}{1 - \sum_{j} y_{jt}} \quad (9) \]

\[ \mu_Q (P, T, y_{1,1}, \ldots, y_{n,m}) = \frac{1}{N_Q} \left[ F(V(P), T, y_{1,1}, \ldots, y_{n,m}) + PV(P) \right] - \sum_{i=1}^{k} \sum_{j=1}^{n} N_{il}^{t} \mu_i^l + \frac{1}{N_Q} F(V(P), T, y_{1,1}, \ldots, y_{n,m}) - \frac{1}{N_Q} \sum_{i=1}^{m} \sum_{j=1}^{n} N_{il}^{t} \frac{\partial F(V(P), T, y_{1,1}, \ldots, y_{n,m})}{\partial N_{il}^{t}} + kT \sum_{i=1}^{m} \ln \left( 1 - \sum_{j=1}^{n} y_{il} \right) \quad (10) \]

where \( N_{il}^{t} n_{il}^h \) is part number of clusters of guest molecules removed from clathrate hydrate and the derivative can be found by numerical calculation using the following approximation:

\[ \left( \frac{\partial F(V(P), T, y_{1,1}, \ldots, y_{n,m})}{\partial N_{il}^{t}} \right)_0 \approx \frac{F_1(V(P), T, N_{il}^{t} n_{il}^h, N_{il}^{h} \ldots N_{nn}^{k}) - F_1(V(P), T, N_{il}^{t} n_{il}^h, N_{il}^{h} \ldots N_{nn}^{k})}{N_{il}^{t} n_{il}^h} \]

**Phase equilibria**

We are concerned with the monovariant equilibria of the gas phase, ice and clathrate hydrate. The curve \( P(T) \) of monovariant equilibrium can be found from the equality of the chemical potentials of the system components in the phases:

\[ \mu_i^l (P, T, y_{1,1}, \ldots, y_{n,m}) = \mu_i^{gas} (P, T), \quad (11) \]

\[ \mu_Q (P, T, y_{1,1}, \ldots, y_{n,m}) = \mu_Q^{ice} (P, T). \quad (12) \]

The curve \( P(T) \) of divariant equilibria can be found at the fixed degree of filling \( y_{il} \) from equation (12). We shall assume that the ideal gas laws govern the gas phase, and then the expressions for chemical potentials of mixture components will be as following:
\[ \mu_i^{\text{gas}}(P, T) = kT \ln[x_i P / kT \Phi_i] = kT \ln\left[x_i \frac{P}{kT} \left( \frac{2\pi \hbar^2}{m_i kT} \right)^{3/2} \right], \] (13)

where \( x_i \) is the mole fraction of the \( i \)-type guest in the gas phase. In addition, we neglect the water vapor pressure.

4. Example of calculation

Here we shall deal with clathrate hydrate which has two type of cavity and one type of guest and a cavity can hold one guest molecule only. The curve \( P(T) \) of monovariant equilibrium described by the following equations (11-12) govern:

\[ \mu_0(P, T, y_1, y_2) \equiv +F(V(P), T, y_1, y_2)/N_0 - \frac{\partial F(V(P), T, y_1, y_2)}{N_0 \partial y_1} - \frac{\partial F(V(P), T, y_1, y_2)}{N_0 \partial y_2} + \]

\[ + \frac{PV(P)}{N_0} + kT \ln(1 - y_1) + kT \ln(1 - y_2) = \mu_0^{\text{gas}}(P, T) \]

\[ y_1 = [1 + \exp\left(\frac{F(V(P), T, y_1, y_2) - F(V(P), T, y_1(1-n_1), y_2)}{N_1 y_1 n_1 kT}\right) - \mu^{\text{gas}}(P, T)/kT]^{-1} \]

\[ y_2 = [1 + \exp\left(\frac{F(V(P), T, y_1, y_2) - F(V(P), T, y_1, y_2(1-n_2))}{N_2 y_2 n_2 kT}\right) - \mu^{\text{gas}}(P, T)/kT]^{-1} \]

where \( y_1, y_2 \) describes the degree of filling the 1 and 2 types cavities of clathrate hydrate.

6. Computational details

Considering ice Ih, methane hydrate phases, we used modified SPCE water–water interaction potential. The parameters describing short-range interaction between the oxygen atoms \( \sigma = 3.17 \text{ Å} \) and the energy parameter \( \epsilon = 0.64977 \text{ kJ mol}^{-1} \) of Lennard-Jones potential of SPCE potential [11] were changed and was taken \( \sigma = 3.1556 \text{ Å}; \epsilon = 0.65063 \text{ kJ mol}^{-1} \). The charges on hydrogen \( q_H = +0.4238|e| \) and on oxygen \( q_O = -0.8476|e| \) of SPCE model were not changed. The modified SPCE potential significantly improves the agreement between the calculated cell parameters for ice Ih and methane hydrate with the experimental values.

The protons have been placed according to the Bernal–Fowler rule and the water molecules have been oriented so that total dipole moments of the unit cells of ice Ih and hydrates were equal to zero. The long-range electrostatic interactions have been computed by the Ewald method.

QLD calculations have been performed on a 64 water molecules supercell of ice Ih. The structure of this model has been obtained by optimizing with a conjugate-gradient method employing a modified SPCE potential for water. The free energy and the derivatives of free energy have been calculated using 2x2x2 k-points inside the Brillouin zone.

For clathrate hydrate of CS-I, the initial configuration for QLD calculations was a single unit cell with 46 water molecules and 8 methane or xenon molecules in both large and small cavities. Analogously for clathrate hydrate of CS-II, the initial configuration for QLD calculations was a single unit cell with 136 water molecules and 24 argon molecules in both large and small cavities. The initial positions of the oxygen atoms and the guests have been taken from the X-ray analysis of ethylene oxide hydrate of CS-I [12]. The orientations of water molecules and the positions of the oxygen atoms and guests have been determined by the conjugate-gradient method at each concerned lattice parameters of the unit cell. The guests are considered as spherically symmetric Lennard–Jones particles. The potential parameters
for the methane–methane and xenon-xenon interaction \( \sigma = 3.81 \text{Å}; \ \epsilon = 1.18558 \text{kJ/mol} \) and \( \sigma = 4.047 \text{Å}; \ \epsilon = 1.9205 \text{kJ/mol} \) respectively, and for argon-argon interaction \( \sigma = 3.408 \text{Å}; \ \epsilon = 0.9936 \) are taken from [13,14]. The guest–host interaction potential is also represented in the Lennard–Jones form with relevant parameters estimated from the usual combination rules.

7. Results of calculation

Computation of chemical potentials of water and guest molecules and of degree of cavity filling was performed using the above written formulae (6), (7), (8), (14) and (15). In the first approximation calculation of free energy without the entropic contribution \( F_1 \) in the quasiharmonic approximation using formulae (6),(7), the clathrates have been assumed fully occupied, i.e. the degrees of cavity filling were accepted equal to 1. The calculated pressure dependence of the chemical potentials of water molecules of Ice Ih, empty host lattice of structure I hydrate, methane (Fig.1) and xenon (Fig.2) hydrate of cubic structure I (CS-I) and argon (Fig.3) hydrate CS-II with and without entropy term (last terms of the equations 9,10) at temperature \( T=273 \text{ K} \) are displayed in Figures.
As seen from Figures changes of chemical potentials of empty host lattice under influence of guest molecules are significant. There is an increase of difference $\Delta\mu = \mu_{\text{ice}} - \mu_{\text{Q}}$ between chemical potentials of ice and host lattice reaching values close to those that are used in construction of phase diagrams within framework of the van der Waals and Platteeuw theory. Intersection of chemical potential curves of Ice Ih and of host lattice with the account of entropic contribution defines the pressure of monovariant equilibrium at a given temperature. The calculated pressure dependence of the chemical potentials of argon atoms $\mu_{1,2}$ in the small and large cavities of structure II hydrate at $T=273$ K are displayed in Fig. 4. Frequencies of argon atoms in large cavities acquired complex values what means translational motion of these atoms. We neglect the contribution of these motions in calculations of the clathrate free energy but it will be accounted in computations of chemical potentials of argon atoms in large cavities.

Figure 5. the degree of filling of the small and large cavities of Xe hydrate CS I

Figure 6. the degree of filling the small and large cavities of Ar hydrate CS II

Experimental data was taken from [15].

Figure 7. Curve P(T) of monovariant equilibrium of the gas phase, ice Ih and Xe hydrate.

Figure 8. Curve P(T) of monovariant equilibrium of the gas phase, ice Ih and Ar hydrate
The calculated pressure dependence of the filling degree of the small and large cavities of Xe and Ar hydrate are shown in Figs. 5 and 6, respectively. As follows from the results of calculations, filling degrees differ notably from unity at low pressure and approaches closely unit value at pressure increasing already for pressures higher 50 bar for the Xe hydrate of structure I and for the Ar hydrate of structure II. This reflects, as seen from the Fig. 4, the fact that chemical potentials of Ar atoms in the gas phase and in large cavities do not differ significantly. For more exact description of thermodynamic functions of clathrates it is necessary to choose on each step of free energy calculations the values of degrees of cavity filling obtained in the preceding step of calculations and to continue this procedure till self-consistent results will be obtained.

The calculated curves P(T) of monovariant equilibrium of the gas phase, ice Ih, and Xe or Ar hydrate are displayed in Figs. 7 and 8, respectively. The calculated curves for the Xe hydrate agree well with the experiment.

8. Conclusion

The molecular model of inclusion compounds is developed which permits to calculate thermodynamic functions of inclusion compounds starting from known potentials of intermolecular interactions. In distinction from the well-known theory of van der Waals and Platteeuw the suggested model accounts for the influence of guest molecules on the host lattice and guest-guest interaction. The model is applicable to other inclusion compounds with the same type of composition (zeolites, inclusion compounds of semiconductor elements, etc.). On the molecular level the curves of monovariant equilibrium for Xe and Ar clathrate hydrates in a wide range of pressure temperature have been determined. The calculated curves of monovariant equilibrium agree well with the experiment.

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