Elastic Moduli and Absolute Stability Limits of Clathrate Hydrates of Structure I at Positive and Negative Pressures

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The behavior of clathrate hydrate of structure I with and without enclathrated methane and xenon guests has been investigated at high pressure and wide temperature range using the quasi-harmonic lattice dynamics approach up to absolute stability limits. The mechanical stability boundaries of the clathrate hydrate of structure I have been determined from the Born stability criteria via the calculations of the elastic constants at positive and negative pressures. For comparison the spinodals of the clathrate hydrates are calculated. It is found that in spite of weakness of interaction the enclathrated guests with host lattice the guest molecules contribute greatly to the stability of the hydrate framework structure.

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1. Introduction

The hydrogen bonded ice-like network of the host water molecules forming cages surrounding guest molecules determines stability of clathrate hydrates. The guest molecules stabilize the cages but their interaction with guest molecules is very weak. Therefore, it would be possible to expect that stability of clathrate hydrates is close to stability of ice. However, on phase \( P-T \) diagram the field of stability of hydrates is much wider than the field of stability of ice.

There is correlation between size of the guest molecule and the host lattice structure.² The hydrates of structure I are formed by molecules with maximum van der Waals diameters up to 0.58 nm while hydrates of structure II are formed by larger molecules up to about 0.79 nm in size with the exception of the four smallest molecules argon, krypton, oxygen, and nitrogen, which also form hydrates of structure II.² At higher pressure a general rule for determining hydrate structure is not established.² A number of structural transitions have been observed at sufficiently high temperature and increased pressure in the case of the guest molecule size comparable or larger than the host lattice cavity one.² High-pressure transition have been observed in the hydrates of neon,⁷ argon,⁸ nitrogen,⁹ and methane.¹⁰

When at low temperature clathrate hydrates are compressed by high pressure, the crystalline structures collapsed into high-density phases. The nature of the phase transition has been postulated to be related to the onset of mechanical instability by the analogy with the amorphization of ice under pressure.¹³ The volume-pressure behavior near the phase transition is found to be different for hydrates with different enclathrated guests. For example, the experiments show a very sharp transition at \( P = 1.3 \) GPa for tetrahydrofuran (THF) hydrate; a much smoother volume decrease at \( P = 1.58 \) GPa for SF₆ hydrate and the absence of sudden volume change for Xe hydrate pressed up to 1.8 GPa.¹³ Now we have evidence that the hydrate behaves just like ice \( Ih \). That is at low temperature it will undergo amorphization but at high temperature it transforms into high-pressure crystalline forms.

The experimental results raise the problem of model construction of phase diagram of hydrates. In theory the curves of phase equilibria in the system can be obtained from condition of equality of chemical potentials of the components of the systems. However, at crossing of curves of phase equilibria the change of phases (the thermodynamic transition) cannot happen at once, that is a problem for experimental definition of the phase diagrams. The realization of this phase transition depends on the initiation nucleation mechanism. Thus, from the results of the molecular dynamics study of silicon crystal melting¹⁴-¹⁷ it has been concluded that thermodynamic melting could take place only for crystal with defects, but the perfect crystal could be stable right up to the mechanical stability boundary. Crystal undergoes the mechanical melting outside this limit. There is the distinction between thermodynamic melting, which occurs heterogeneously at extrinsic lattice defects, and melting due to a mechanical instability, which is a homogeneous process. Thermodynamic melting is the process occurring at high atomic mobility, mechanical melting is the process occurring in the absence of the defects or at low atomic mobility. For determination of the thermodynamic melting point it is necessary to know free energies of two phases but for the mechanical melting point that is enough to know the properties of the solid phase only. At low temperature the mechanical stability boundary and the thermodynamic limit of metastability of crystal (spinodal: \( dP/dV = 0 \)) are the important properties of crystal and those can be used to construct the absolute stability limits of clathrate hydrates.

The phase transition can take place also at negative pressure that corresponds to a stretch of the crystal lattice. In this case it is possible to obtain the limits of mechanical and thermodynamic stability too. The spinodal lines for ices, quartz and perovskites has been founded for positive and negative pressures by the molecular dynamics and the universality of equation of state for such different compounds has been es-
tablished. In clathrate compounds the guest molecules can compress or expand the host lattice in dependence on their size and it is possible to consider the empty host lattice as being under external positive or negative pressure. It has been shown that methane molecules owing to the van der Waals interaction between themselves squeeze the host lattice up to the high temperature.\(^\text{19}\)

In order to investigate the mechanism of phase transformations, the quasiharmonic lattice dynamics method\(^\text{20-25}\) and a new geometry optimization scheme\(^\text{26}\) have been used. In this approach for the examination of the mechanical stability boundary the elastic constants are computed and the thermodynamic limit of metastability of crystal (spinodal) as the absolute stability boundary is obtained for clathrate hydrates of structure \(I\) at positive and negative pressures. For comparison, ice \(Ih\), methane, xenon hydrates, and a hypothetical empty structure of hydrate \(I\) are investigated.

The organization of this paper is as follows. The mathematical framework of the structure optimization scheme for the molecular crystals will be briefly discussed in the next two sections. Some calculation details will be presented in Sec. 4. The calculation results at the negative and positive pressure and the effects of the guest enthalration on the empty cage hydrate structure will be discussed in Sec. 5. The paper concludes with a summary of the main results.

2. Elastic Moduli and Born Criteria

At fixed temperature (entropy) in accordance with the generalized Born stability criteria all determinants \(D_k\) of principal minors \(C_{ij}\) (\(i, j = 1, \ldots, k\)) of isothermic (adiabatic) elastic moduli matrix \(C_{ijkl}\) (\(i, j = 1, \ldots, 6\)) written in Voight notation must be positive. Therefore, the study of the crystal stability under pressure can be defined as the calculation of the relevant elastic constants.

Theoretical calculation of the elastic constants of solids under different thermodynamic conditions can be approached in a number of ways. The adiabatic elastic constants under pressure can be obtained by molecular dynamics (MD) calculations.\(^\text{27}\) This method has been applied to the calculation of the elastic constants of solid argon\(^\text{28}\) and ice \(Ih\)\(^\text{29}\) with very satisfactory results. A serious drawback of this approach is the large statistical error and very long simulation time that is required for high accuracy.\(^\text{28,29}\) An alternative approach employs lattice dynamics in the quasiharmonic approximation where the free energy of a given system \(F_{\text{th}}\) is given as:

\[
F_{\text{th}} = U + F_{\text{vib}}
\]

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

\[
F_{\text{vib}} = \frac{1}{2} \sum_{\mathbf{q}} \hbar \omega (\mathbf{q}) + k_B T \sum_{\mathbf{q}} \ln(1 - e^{-\hbar \omega (\mathbf{q}) / k_B T}),
\]

where \(\omega (\mathbf{q})\) are the lattice vibrational frequencies.

In the quasiharmonic approximation the free energy for a given crystal structure is taken to be that resulting from the harmonic approximation, but the anharmonicity causes mode frequency dependence of the structural parameters, making the vibrational free energy part a function of these parameters as well as of temperature.

The expressions for the elastic constants, for example for the isothermal constants, can be subdivided into two parts:\(^\text{20}\)

\[
C^{i\alpha \beta}_{\text{th}} = C^0_{\text{th}} + C^{i\alpha \beta}_{\text{th}},
\]

where

\[
C^0_{\text{th}} = \frac{1}{V_0} \left( \frac{\partial^2 U}{\partial \eta_{\alpha \beta} \partial \eta_{\alpha \beta}} \right)_0,
\]

and in case of isotropic compression, \(C^{i\alpha \beta}_{\text{th}}\) takes the form:

\[
C^{i\alpha \beta}_{\text{th}} = \frac{1}{V_0} \left( \frac{\partial^2 F_{\text{vib}}}{\partial \eta_{\alpha \beta} \partial \eta_{\alpha \beta}} \right)_0 - P (\delta_{\alpha \theta} \delta_{\alpha \gamma} + \delta_{\alpha \gamma} \delta_{\gamma \beta} - \delta_{\alpha \beta} \delta_{\gamma \theta}),
\]

where \(\eta_{\alpha \beta}\) is the strain tensor. The \(C^0_{\text{th}}\) has the form as in the harmonic approximation but it is dependent on the temperature \(T\) and the pressure \(P\) to account for the change of the equilibrium configuration of the system. For molecular crystal, when the approximation of “rigid” molecules is used, expression for \(C^0_{\text{th}}\) has been obtained.\(^\text{19,25}\)

The expressions for the elastic constants involve calculating the derivatives of the frequencies of the phonon spectrum with respect to the strain. The derivatives are computed numerically with the help of the algorithms given previously,\(^\text{30}\) which result in a guaranteed precision for the frequencies for any configuration.

3. Molecular Crystal Geometry Optimization

Geometry optimization schemes were well developed for ionic crystals,\(^\text{23,24}\) within the conventional LD approach. For molecular crystals, where the rigid molecule approximation is often invoked, the optimization procedure is more complex due to additional rotational degrees of freedom. In this case, the dynamical matrix of the crystal includes translational, rotational and mixed terms. A unique feature of the present approach is that all structural parameters are optimized in conjunction with the calculation of the dynamical matrix and elastic constants.\(^\text{26}\) This approach gives the opportunity to study both the stability and structure variation of complex compounds with much reduced computational effort.

At a finite temperature \(T\) under an applied stress \(\sigma_{\alpha \beta}\) the equilibrium shape of the crystal unit cell (external coordinates) is determined by the equation of state:

\[
\frac{1}{V_0} \left( \frac{\partial F_{\text{th}}}{\partial \eta_{\alpha \beta}} \right)_0 = \sigma_{\alpha \beta}.
\]

The derivatives in eq. (20) with respect to \(\eta_{\alpha \beta}\) are calculated for the reference (equilibrium) configuration and \(V_0\) is the corresponding volume. From general thermodynamic consideration, the variation of the equilibrium strain tensor under small change of the stress tensor or temperature can be obtained: \(^\text{25}\)

\[
\Delta \eta_{\alpha \beta} = \frac{1}{V_0} \sum_{i} C^{i\alpha \beta}_{\text{th}} F_{\gamma \delta \tau} \Delta T + \sum_{i} C^{i\alpha \beta}_{\text{th}} \Delta \sigma_{\gamma \delta}\]

\[
\Delta \eta_{\alpha \beta} \Delta \eta_{\gamma \delta} = \frac{1}{V_0} \sum_{i} C^{i\alpha \beta}_{\text{th}} F_{\gamma \delta \tau} \Delta T + \sum_{i} C^{i\alpha \beta}_{\text{th}} \Delta \sigma_{\gamma \delta},
\]
where

\[ F_{T,\sigma}^{\text{vb}} = \left( \frac{\partial^2 F_{\text{vb}}}{\partial T \partial \eta_{\sigma}} \right)_0 \]  

(8)

and \( \sigma^{-1}_{\alpha\beta\sigma\tau} \) is the inverse of isothermal elastic matrix \( \sigma^{(i)}_{\alpha\beta\sigma\tau} \).

The equilibrium deformation \( \Delta \eta^{eq}_{\sigma\tau} \) is found at the change of pressure \( \Delta P \) (\( \Delta \sigma_{\sigma\tau} = -\Delta P \delta_{\sigma\tau} \) corresponds to an ambient external pressure) or temperature \( \Delta T \) by using expression (7). From eq. (6) at new unit cell parameters the strain tensor \( \sigma_{\alpha\beta} \) is calculated and, if it has non-diagonal form the correction of the equilibrium unit cell form is carried out on the value of \( \Delta \eta^{cor}_{\sigma\tau} \) that calculated from eq. (7) by using the expression for correction tensor \( \Delta \sigma^{cor}_{\alpha\beta} \),

\[ \Delta \sigma^{cor}_{\alpha\beta} = -P_0 \delta_{\alpha\beta} - \sigma_{\alpha\beta} \]  

(9)

where

\[ P_0 = -\frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33}). \]  

(10)

For corrected unit cell the strain tensor is calculated. If this tensor takes the diagonal form \(-P_0 \delta_{\alpha\beta}\) the unit cell is equilibrium for fixed isotropic external pressure \(P_0\). If the tensor takes the non-diagonal form \(\sigma'_{\alpha\beta}\), the procedure is repeated. For calculation of new correction tensor it is necessary to substitute in eqs. (9), (10) the non-diagonal tensor \(\sigma'_{\alpha\beta}\). The procedure of diagonalization must be repeated until the value of non-diagonal tensor elements become less then some fixed value that determines the accuracy of calculation.

For the optimization of internal coordinates, the Newton-Raphson method is used. In this case for each molecule the internal coordinates are the positions of center of mass and three rotation variables. Taking into account of the large number of water molecules in the unit cell, the zero static internal stress approximation (ZSISA) is employed. In this approximation the contribution of the vibrational part of free energy is ignored for internal coordinates optimization and, therefore, the optimization problem reduces to minimization of potential energy with respect to internal coordinates.

The method details are presented in.\textsuperscript{26}

4. Computational Details

The interactions between the water molecules in ice \(Ih\) and hydrate are described by the modified empirical TIP4P potential.\textsuperscript{28} The TIP4P potential\textsuperscript{33} can be improved by scaling the interaction parameters by a constant \(K = 1.0066\). Scaling factor for the effective charges is \(K^{-2}\). The parameter describing short-range interaction between the oxygen atoms, \(\sigma\), is scaled by \(K^{-1}\) and the energy parameter, \(\varepsilon\), by \(K^{-3}\). Finally, all distances between the interacting centers on the water molecule are scaled by \(K^{-1}\). By this scaling, the modified TIP4P potential improves significantly the agreement between the calculated cell parameters for ice \(Ih\) with the experimental values without deteriorating the other calculated quantities. The protons have been placed according to the Bernal-Fowler rule\textsuperscript{34} and the water molecules have been oriented such that the dipole moment in the unit cells of ice \(Ih\) and hydrates is equal to zero. The long-range electrostatic interactions have been computed with the Ewald method. The quasiharmonic lattice dynamics (QLD) calculations have been performed on a 64 water molecules supercell of ice \(Ih\). The free energy and the derivatives of free energy have been calculated using \(2 \times 2 \times 2\) k-points inside the Brillouin zone. The vibrational part of free energy has been defined in this process.

The initial configuration for the QLD calculations is a single unit cell of structure \(I\) clathrate hydrate containing 46 water molecules and 8 methane or xenon molecules, with lattice parameter \(a = 1.182\) nm at \(T = 10\) K. The positions of the oxygen atoms and the guests have been taken from the X-ray analysis of ethylene oxide hydrate by McMullan and co-workers.\textsuperscript{35} The guests (xenon and methane molecules) are considered as spherically symmetric Lennard-Jones particles. The potential parameters for the methane-methane and xenon-xenon interactions are taken from another investigations.\textsuperscript{36,37}

Starting from the initial configuration, the calculations have been performed in compliance with optimization procedure described in Sec. 3. First, the reference structure has been obtained by optimizing the host water and guest positions at the fixed lattice parameter. After that, the stress tensor and the elastic constants have been computed. The optimization of cell shape has been carried out if the calculated stress tensor contains non-isotropic components. In the ensuing step a new shape of the unit cell under the variation of \(T\) or \(P\) has been determined according to the formula (7). Thereupon, the optimization procedure has been repeated for the internal and external coordinates. In this way, the evolution of hydrate structure as the function of temperature or pressure can be modeled.

To test the correct work of internal coordinates optimization scheme, the potential energy of crystal is calculated at any iteration step of optimization. Our experience shows that the Newton-Raphson method demonstrates the fast convergence during 2–3 first iteration steps in the calculation and using of 5 steps only is enough for accurate optimization. At all calculated \(T\), \(P\) points the principal minors \(D_2, D_3, D_4, D_5, D_6\) of elastic constants matrix have been calculated for testing of mechanical stability according to the Born criteria. The elastic moduli of ice \(Ih\) at pressures up to 300 MPa at 80 K have been calculated\textsuperscript{38} to access the accuracy of the quasiharmonic lattice dynamics (LD) method using empirical TIP4P potential. To access the lattice dynamics (LD) method using modified empirical TIP4P potential, we have computed the elastic moduli at the pressures up to 350 MPa at 238 K and the mechanical stability boundary and the thermodynamic limit of metastability of crystal (spinal) of ice \(Ih\). Using the modified TIP4P potentials, the calculated elastic moduli are compared with experimental measurements.\textsuperscript{39} These results are shown in Fig. 1. As seen from Fig. 1, the relative position and slopes of moduli curves reproduce well the experimental data.

5. Results and Discussion

Like in the ices, in the clathrate hydrates each oxygen atom is connected by the hydrogen bonds with four nearest oxygen atoms and form ice-like structure (host lattice). In contrast to the ice structures in these crystals there are cavities,
which could include single atoms or molecules (guests). The clathrate hydrates of cubic structure I can be considered as a structure composed of pentagonal dodecahedra forming the small cavities. In Fig. 2 the unit cell of the host lattice of the structure I is presented. It consists of 2 dodecahedra and 6 additional water molecules. The vertices of dodecahedron are formed by oxygen atoms. Between the nearest oxygen atoms on the edge of the dodecahedron there are hydrogen atoms which form the hydrogen bonds. The centers of the dodecahedra form two primitive cubic sublattices which are displaced relatively each other along the vector \(0.5a, 0.5a, 0.5a\) where \(a\) is the lattice parameter. The distance between the centers of neighboring dodecahedra from the same sublattice equals to \(a\). The distance between the centers of neighboring dodecahedra from different sublattices is equals to \(\sqrt{3}/2a\). The dodecahedra are held together by hydrogen bonding with the remaining water molecules (six in the unit cell of hydrate of structure I) which do not belong to the dodecahedra (Fig. 3).

At positive and negative pressures the mechanical stability of empty hydrate of structure I has been studied. In calculations, the negative pressures can be modeled by proportional increasing of the unit cell from some starting value. Physically, it means that, if crystal is expanded homogeneously, there is possible a structural phase transition into an expanded-volume phase with cavities which can include single atoms or molecules. Free energy, Gibbs function and elastic moduli have been calculated. After that, the spinodals and the boundaries of mechanical stability have been determined for the empty structure I (Fig. 4). For comparison the spinodals of ice Ih calculated by the methods of LD and MD at negative and positive pressures are also shown in Fig. 4. The boundaries of mechanical stability and spinodals calculated in the framework of the LD method coincide at negative as well as at positive pressures. Figure 4 shows that the absolute stability boundaries of ice Ih calculated by MD and LD methods are close.

The stability boundary at positive pressures shows two characteristic types of behavior with temperature growth: initially the crystal stability increases, then diminish. This could be related with temperature dependencies of the unit cell parameters and the elastic moduli. At heating of the crystal the
lattice expands and, in order to reach the stability boundary, it is necessary to apply higher pressures. Besides, with increase of temperature the relationships between the elastic moduli change, leading to decreasing of the stability boundary. These two effects determine the behavior of the absolute stability boundary of the crystal. At negative pressures the crystal expansion at temperature rise leads to lowering of the crystal stability.

The region of existence of the empty hydrate of structure I lies within the stability region of the ice Ih. The calculations show that empty host lattices can exist at positive pressures, but only as a metastable phase relative to ice, and they become stable only at negative pressures. In Fig. 4 the calculated equilibrium line of the first order phase transition ice Ih-empty hydrate of structure I is shown. In the area I empty hydrate is stable and ice Ih is metastable, while in the area II, vice versa, ice Ih is stable and empty hydrate is metastable.

We have calculated elastic constants for the xenon and methane hydrates at temperature 80 K and pressure up to 350 MPa. The pressure variation of the $C_{11}, C_{12}, C_{44}$ component of the adiabatic elastic constants of xenon and methane hydrates are shown in Fig. 5. The calculated pressure coefficients ($dC_{ij}/dP$) in the case of $C_{11}$ are found to be about 6.3 for xenon and methane hydrates, in the case of $C_{12}$, about 7.45 for xenon and 8.09 for methane hydrates. In contrast $C_{44}$ increases slowly with pressure ($dC_{44}/dP \approx 0.245$) for xenon hydrate, and decreases slowly and gives a negative pressure coefficient $\approx -0.328$ for methane hydrate.

The pressure variation of $C_{ij}$ components of adiabatic elastic matrix for xenon hydrate at temperature 80 K near the mechanical stability boundaries are depicted in Figs. 6(a) and 6(b). The variation of the calculated elastic constants with pressure confirms also the different structure variation of hydrate cell as well as loosing of cubic symmetry with the pressure increasing. Near the stability boundaries $C_{ij}$ components of the adiabatic elastic matrix decrease slowly at positive pressures (Fig. 6(a)), while the principal minors ($D_2, D_3, D_4, D_5, D_6$) of elastic constants matrix tend to zero, as shown in Fig. 7(a). At negative pressures near the stability boundary both the minors (Fig. 7(a)) and $C_{ij}$ (Fig. 6(b)) are strongly changed.

The mechanical stability boundaries for the xenon and methane hydrates, as well as spinodals for the xenon hydrate have been determined and are shown in Fig. 8 and Fig. 9. The mechanical stability boundary and spinodal for the xenon hydrate coincide at negative pressures. At positive pressures the mechanical stability boundary starts from 2.5 GPa, while the spinodal starts from the higher pressure 6.3 GPa. For crystals only the mechanical stability boundary has physical meaning. In most cases, as shown by the calculations, the mechanical stability boundary and spinodal coincide. However, the some cases exist where these boundaries do not coincide and, therefore, for the calculation of the absolute stability boundary of the crystal it is necessary to use the Born criteria, but not the $dP/dV = 0$ condition. As seen from Fig. 9, the stability boundary for the methane hydrate lies between the stability boundaries of the empty hydrate of structure I and the xenon hydrate. At negative pressure the stability boundaries of the empty and the xenon hydrates of structure I are close to each other.

6. Conclusions

Lattice dynamics calculations employing the modified empirical TIP4P potential for water have been used to study the mechanical stability of the methane and xenon hydrates.
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Fig. 7 A principal minors variation of xenon hydrate versus \( P \) at \( T = 80 \) K at positive (a) and negative (b) pressures.

Fig. 8 The experimental xenon hydrate decomposition line (●)\(^{40}\), mechanical stability boundaries (■), and spinodals (▲) of xenon hydrate of structure I. At the negative pressure the spinodal is identical to the mechanical stability limit but at the positive pressure in contrast to a case of ice Ih (Fig. 4) these limits are different.

For solving of stability problem, the calculations of elastic constants, optimization of molecular positions and cell shape at different \( P, T \) points have been performed in quasiharmonic approximation. The mechanical stability boundaries and spinodals of the methane and xenon clathrate hydrate of structure I have been calculated. With the increase of the guest size the stability region of hydrates is widened.

The calculated pressures at the onset of mechanical instability for the methane and xenon hydrates are in the same range as observed experimentally for other hydrates.\(^{13}\) The line on \( P, T \) phase diagram of the first order phase transition ice Ih-empty hydrate of structure I has been determined. This line is situated in the negative pressure range. Ice Ih is the stable phase at the right of this line, while empty structure I hydrate is metastable phase. At the left of this line, empty structure I hydrate becomes the stable phase, while ice Ih is metastable. Physically, it means that when ice crystal is expanded homogeneously, there is possible a structural phase transition into more expanded-volume phase with cavities, which could include only single atoms or molecules (guests). Such structure is unstable thermodynamically at positive pressures, it can be made stable only with cavities filled by atoms of suitable size.

The present investigation has been performed for crystals with hydrogen bonds, but one may suggest that analogous phase transitions can be expected also for other crystals. Performing experiments at negative pressures (homogeneous expansion of, e.g., crystals with high enough concentration of guest atoms) can permit to obtain new crystals of clathrate type with the stability region considerably wider than for pure crystal.

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