Elasticity and Stability of Clathrate Hydrate: Role of Guest Molecule Motions

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Molecular dynamic simulations were performed to determine the elastic constants of carbon dioxide (CO₂) and methane (CH₄) hydrates at one hundred pressure–temperature data points, respectively. The conditions represent marine sediments and permafrost zones where gas hydrates occur. The shear modulus and Young’s modulus of the CO₂ hydrate increase anomalously with increasing temperature, whereas those of the CH₄ hydrate decrease regularly with increase in temperature. We ascribe this anomaly to the kinetic behavior of the linear CO₂ molecule, especially those in the small cages. The cavity space of the cage limits free rotational motion of the CO₂ molecule at low temperature. With increase in temperature, the CO₂ molecule can rotate easily, and enhance the stability and rigidity of the CO₂ hydrate. Our work provides a key database for the elastic properties of gas hydrates, and molecular insights into stability changes of CO₂ hydrate from high temperature of ~5 °C to low decomposition temperature of ~−150 °C.

Gas hydrate is an ice-like, nonstoichiometric compound that consists of hydrogen-bonded water molecules that form cavities in which “guest” molecules of an appropriate size are contained (Fig. 1(a)). Hydrate forms when free gas and aqueous phases coexist under low temperature and high pressure conditions in deep marine sediments and permafrost zones. Typical “guest” molecules include methane (CH₄) (Fig. 1(b)) and carbon dioxide (CO₂) (Fig. 1(c)), which usually form a type-I clathrate structure (sI) with two types of cages: large tetrakaidecahedral 5₁₂₆ cages (L-cage) and small dodecahedron 5₁₂ cages (S-cage)¹⁻². Gas hydrates occur abundantly in nature and are considered to be future energy resource²⁻⁵. They have numerous applications including hydrogen storage, natural gas transportation, and gas separation²,³,⁶⁻⁸. Furthermore, the research on hydrate is crucial to flow assurance⁹,¹⁰ and environmental change¹¹. It is also important for astrophysics since CO₂ and CH₄ hydrates are likely to occur on Mars¹² as well as outer solar systems¹³.

The replacement of CH₄ by CO₂ in gas hydrate-bearing sediments has received great attention¹⁴⁻²² since it may enable long-term storage of CO₂, which could mitigate the influence of global warming and ocean acidification, and facilitate CH₄ recovery as a potential future energy resource. Remarkably, CO₂ hydrates have been clearly observed on the seafloor²³, implying they can be stable enough even occurring in extremely shallow marine sediments. An understanding of the elastic properties of gas hydrate-bearing sediments is important not only for monitoring their distributions (e.g. via seismic analysis) when CO₂ replaces CH₄ from gas hydrate deposits, but also for predicting the stability of their formations²⁴. CO₂ and CH₄ hydrates have been synthesized in the laboratory²⁵,²⁶. Brillouin scattering experiments⁷, compressional, and shear-wave speed measurements⁸ have been reported for CH₄ hydrate. However, the mechanical properties of CO₂ hydrate have rarely been reported, and limited information exists on the differences in mechanical properties between CO₂ and CH₄ hydrates. This stimulated our interest to investigate the mechanical properties of CO₂ hydrate in comparison with CH₄ hydrate.

CO₂ hydrate has been studied extensively experimentally in the laboratory in terms of phase change²⁷, stability¹²,³⁰⁻³², structure²⁶,³⁰,³³⁻³⁷, cage occupancy³⁶,³³⁻³⁷, and dynamics³⁸,³⁹. X-Ray, neutron diffraction, and dissociation experiments have been used to determine the occupancy of CO₂. It was found that the occupancy

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is a function of the synthesis pressure\(^{26,33-37}\). In general, higher overpressure ratio (to the phase equilibrium pressure) during synthesis produced higher occupancies\(^{36,37}\). It reaches full occupancy, when the overpressure ratio is greater than 6\(^{36,31}\). For the hydrate synthesized at the proximity of phase equilibrium pressure, the refined model show that CO\(_2\) occupied almost all (>99%) of the large cages and roughly 2/3 of small cages\(^{33,35-37}\). NMR measurements\(^{38}\) and Raman spectra\(^{39}\) have been used to describe the motions of guest molecules with increase in temperature. Clearly, the thermal effect is critical to CO\(_2\) hydrate\(^{37-39}\). CO\(_2\) hydrate will decompose at either too high or too low temperatures\(^{12,30-32}\). It is the only hydrate known to have a stability limit at low temperatures of approximately \(-150^\circ\text{C}\)^{12,30-32}. This is because the vapor pressure of dry ice is lower than the dissociation pressure of the CO\(_2\) hydrate\(^{32}\). However, there lacks of understanding for low-temperature stability limit from a mechanical point of view. For instance, the shear modulus of the CO\(_2\) hydrate may decrease as the temperature decreases, no information on this aspect has been documented yet.

Molecular dynamics (MD) simulations can provide insights on hydrates at the molecular level with linkages to macroscopic phenomena\(^{17-19,22,40-59}\), where interactions between guest and host are of particular importance. Those simulation studies provided valuable information on free energy changes for CO\(_2\) replacing CH\(_4\) from gas hydrate\(^{27-19}\), structural changes induced by various guest molecules\(^{41}\), dissociation\(^{42}\), nucleation\(^{43,44}\), thermal conductivity\(^{41,45}\), mechanical properties\(^{46-49}\), and NMR spectra\(^{46}\). Our previous work\(^{46}\) has studied the mechanical strength, and explained the underlying mechanisms of strain hardening of CH\(_4\) hydrate as against normal ice. The compressibility (i.e. the inverse of bulk modulus) has been determined on the basis of the fluctuation theorem for both CH\(_4\) and CO\(_2\) hydrates\(^2\). The elastic moduli of CH\(_4\) hydrate have also been determined at 0 K by first-principles calculations\(^{49}\) and at finite temperatures by classical MD simulations\(^{48}\). However, there is no applicable data on shear modulus and elastic constants for CO\(_2\) hydrate. We have performed MD simulations to construct pressure (P)–temperature (T) diagrams of the elastic properties of CO\(_2\) hydrate (with full and partial occupancy), CH\(_4\) hydrate (full occupancy), and hypothetical empty-cage hydrate at 100 different pressure and temperature conditions; this equates to 2,000 different non-equilibrium MD simulations for constant strain-rate deformation tests (Fig. S1). The diagrams cover a wide range of P–T conditions that represent deep marine sediments and permafrost zones. The aim of the work is to obtain a priori knowledge on the elastic properties of two different gas hydrates for the purpose of monitoring their distributions in the field during CO\(_2\) replacement of CH\(_4\) from gas hydrate deposits.

**Results**

**Diagram of elastic constants and elastic moduli.** At first, we compared the lattice constants for both hydrates. Tables S1 and SII present the data under 0.1 MPa, which are in good agreement with previous experimental\(^{30}\) and simulation results\(^{41}\). For CH\(_4\) hydrate, the deviation from experiments is less than 0.3%. For CO\(_2\) hydrate, we found that the estimated lattice constant is very close to the experimental one (the deviation is within 0.3%) if their occupancy is assumed to be the same (ca. 2/3 occupancy of small cages)\(^{35}\). Interestingly, we could reproduce that CO\(_2\) hydrate has smaller lattice constants than CH\(_4\) hydrate at low temperatures and larger lattice constants than CH\(_4\) hydrate at high temperatures with a crossover at \(-73.15^\circ\text{C}\) (200 K). Gas hydrate is a cubic system, which can be characterized by three independent elastic constants C\(_{11}\), C\(_{12}\), and C\(_{44}\). We calculated them by the stress-strain linear relationship as shown in Fig. S1. A fairly good agreement was found between our computed elastic constants of CH\(_4\) hydrate (C\(_{11}\) = 13.9, C\(_{12}\) = 8.6, and C\(_{44}\) = 3.2) and those from Brillouin scattering measurements (C\(_{11}\) = 11.9, C\(_{12}\) = 6.0, and C\(_{44}\) = 3.4)\(^{27}\) at room temperature (22.85°C and 20 MPa). We constructed P–T diagrams of the elastic constants and elastic moduli of the CH\(_4\) and CO\(_2\) hydrates. Figure 2 shows our calculated elastic constants of CH\(_4\) and CO\(_2\) hydrates with full occupancy from -40°C to 5°C in increments of 5°C and from 20 MPa to 110 MPa in increments of 10 MPa. The low and high temperatures on the diagrams represent the permafrost zones in the Arctic area and deep marine sediments under the seafloor, respectively. All the elastic constants of the CH\(_4\) hydrate are comparatively larger than those of the CO\(_2\) hydrate. C\(_{44}\) of the CH\(_4\) hydrate is nearly two times as large as that of the CO\(_2\) hydrate. Variations of C\(_{11}\) and C\(_{12}\) for CO\(_2\) and CH\(_4\) hydrates exhibit the same trend, that is, the calculated values decrease with increase in temperature and increase with increase in

*Figure 1.* Gas hydrate (sl) microstructure. (a) Bulk structure of gas hydrate. (b) Large cage (51262) and small cage (512) of CH\(_4\) hydrate. (c) Large cage (51262) and small cage (512) of CO\(_2\) hydrate. Red, cyan, and white balls represent oxygen, carbon and hydrogen atoms respectively. Green lines represent hydrogen bonds.
pressure. It is interesting to note that $C_{44}$ exhibits different trends for the two different hydrates: $C_{44}$ for the CH$_4$ decreases with increase in temperature and appears to be not dependent on pressure. In contrast, $C_{44}$ for the CO$_2$ hydrate increases with increase in temperature and decreases when the pressure increases.

Based on the results in Fig. 2, the elastic moduli of the hydrate aggregate were evaluated using the Voigt–Reuss–Hill (VRH) model shown in Fig. 3. The four elastic moduli can be divided into two groups according to different patterns. The first group is composed of the bulk modulus and Poisson's ratio, which increase with increase in pressure, and decrease with increase in temperature. The trend is as same as that of $C_{11}$ and $C_{12}$.

Figure 2. Three independently evaluated elastic constants of CH$_4$ and CO$_2$ hydrate with full occupancy from $-40^\circ$C to $5^\circ$C and 20 MPa to 110 MPa. Red represents large value of elastic constant while blue represents small value with unit of GPa.
Figure 3. Diagrams of bulk modulus, shear modulus, Young's modulus, and Poisson's ratio of CH₄ and CO₂ hydrates with full occupancy from −40 °C to 5 °C and 20 MPa to 110 MPa. Red represents large value of elastic moduli while blue represents small value with unit of GPa. Poisson's ratio has no unit.
The bulk modulus of the CH₄ hydrate is larger than that of the CO₂ hydrate, which implies that it is harder to compress; this result is consistent with those of previous research calculated using the fluctuation theorem²². In contrast, the CH₄ hydrate has a smaller Poisson's ratio compared with the CO₂ hydrate, which indicates less transferred deformation in the lateral direction perpendicular to the applied load. The second group includes shear modulus and Young's modulus. The trends coincide with those of CO₂. The computed results of the CH₄ hydrate are nearly two times as large as those of the CO₂ hydrate. The computed P-wave velocity of CH₄ hydrate is about 0.8 km/s larger than that of CO₂ hydrate which is consistent with experimental result³⁴, whereas the computed S-wave velocity of CH₄ hydrate is about 0.6 km/s larger than that of CO₂ hydrate. The shear modulus and Young's modulus signify material rigidity, which indicates that the CO₂ hydrate becomes more rigid when the temperature increases. Different potential models (refer to method section and Fig. S2) were employed for CO₂ hydrate, with regard to the crystalline materials. While this finding is on the basis of VRH model¹⁻³⁷⁻⁻⁴³, it holds for both Voigt and Reuss models, respectively. We hypothesize that this phenomenon is related to the kinetic behavior of the CO₂ molecules that reside in the cages since the only difference between the two materials is induced by the "guest" molecules. The CO₂ hydrate micro-structure in Fig. 1(c) shows that if the rotation of the guest CO₂ molecules is constrained and "locked" in a certain orientation (at low temperature), the elastic properties (related to angle variables of the crystalline cell) of this compound may present anomalous behavior. In contrast, the CH₄ molecule is more isotropic in shape, the rotational motion of the guest CH₄ molecules should not be "locked", and the mechanical properties of the whole structure may present a regular behavior of crystalline materials.

Rotational motion of CO₂ and mechanisms for thermal-enhanced stability. We show here that the different properties of CO₂ and CH₄ hydrates are attributed to the enclathrated "guest" molecules, which have limited translational motion but substantially more rotation and rattling ability within the cavities. In such a case, the linear CO₂ with comparatively large diameter would result in certain trajectories facilitating its rotation. This rotational motion has been attributed to temperature-dependent NMR line-shape anisotropy and "anomalous" large thermal expansion of CO₂ hydrate. The primitive unit cell of sl structure includes six L-cages, which are oblate in shape with equatorial planes (parallel to hexagonal faces), and two S-cages without equatorial planes. In the oblate L-cage of the gas hydrate sl, the effective cage radius is smaller in the direction of the cage axis of symmetry ("polar" direction) than that in the equatorial plane. This kind of structure provides the CO₂ molecule with greater freedom in the equatorial plane than in the "polar" direction perpendicular to this plane. Therefore, the CO₂ molecule can rotate non-uniformly towards the short symmetry axis inside the L-cage. To characterize the CO₂ rotational motion, the Cartesian coordinates of oxygen atoms of each step as predicted by MD simulations were output and used to calculate rotational correlation coefficients using a first order Legendre polynomial of the angle between oxygen–carbon–oxygen vectors of the CO₂ molecules and principal axes expressed by \( \cos \theta = \frac{\mathbf{e}_h \cdot \mathbf{e}}{||\mathbf{e}_h||} \) where \( \mathbf{e}_h \) denotes the X, Y, and Z axes, \( \mathbf{e} \) means vectors of the CO₂ molecules at each step successively during the simulation processes, \( \theta \) is the angle between vectors \( \mathbf{e}_h \) and \( \mathbf{e} \), the dot sign means the dot product, and \( || \) signifies the length of the vectors on a two-dimensional Euclidean space.

We have analyzed the rotational motions of all CO₂ molecules from one primitive unit cell. According to the orientation of equatorial planes, the L-cages can be classified into: (1) the ones with equatorial planes which are perpendicular to Y axis are termed No. 1 and 2, that is, Y axis is the polar direction; (2) the ones with equatorial planes that are perpendicular to Z axis are termed No. 3 and 4, that is, Z axis is the polar direction; and (3) those with equatorial planes which are perpendicular to X axis are termed No. 5 and 6, that is, X axis is the polar direction. The two S-cages are termed No. 7 and 8. We take No. 1 L-cage (Fig. 4(a)) and No. 7 S-cage (Fig. 4(c)) for examples, where \( \theta_h \) represents the angle between the X axis and long axis of the CO₂ molecule (red line), \( \theta_1 \) denotes the angle between the Y axis and red line, \( \theta_2 \) denotes the angle between the Z axis and red line. Figure 4(b) and (d) shows the distributions of these angles at 40 MPa with varying temperatures in the three directions respectively. In addition to the P–T conditions within the range of diagrams, an extra data point (−173.15°C, 40 MPa) is calculated to facilitate our discussions below.

Regarding No. 1 L-cage from the middle centering distributions of the cosine value of \( \theta_h \), we know that most of the angles are close to 90°, which indicates that the CO₂ molecule's long axis is easier to rotate within a confined area in the vicinity of the equatorial plane because the direction of the symmetry axis is too short for full rotational motion (Fig. 4(a)). When the temperature increases, the orientation range of CO₂ molecule is enlarged. This happens because the thermal-enhanced kinetic energy of the CO₂ molecule can overcome the restrictions induced by the aspherical cavity and enable more rotational motions near the short symmetry axis direction.

Interestingly, the angle distribution of \( \theta_h \) appears similar to that of \( \theta_1 \), which implies resembling behaviors. The CO₂ molecule rotates mainly about the short symmetry axis near the equatorial plane. The projection of the distribution probability on the X–Z plane is uniform. \( \theta_1 \) and \( \theta_h \) can be resolved into motions on the X–Y plane in conjunction with the X–Z plane and Y–Z plane in conjunction with X–Z plane, respectively. The X–Y component and Y–Z component are concentrated near the equatorial plane, which induces the same "saddle" shapes of combined motion with regard to \( \cos \theta_1 \) and \( \cos \theta_h \). In supplementary materials, the distributions of \( \theta_1 \), \( \theta_2 \), and \( \theta_h \) with regard to the other two molecules (in L-Cages of No. 3 and No. 5) from the same primitive unit cell are documented. Concerning No. 3 L-cage (Fig. S3) and No. 5 L-cage (Fig. S4) molecules, the angles between the polar direction and the long axis of CO₂ molecule are middle centering at 90° under low temperature. When the temperature increases to 5°C, the distribution of cosine values of polar angles further widen to 1 or −1 implying the rotational plane can be along the short symmetry axis of the L-cages. All distribution patterns in L-cages indicate that the molecules rotate about the short symmetry axis near the equatorial plane and the thermal effect can enable more uniform angle distributions (See Figs. 4(a) and (b), S3–S4). For the S-cages (Fig. 4(c) and (d)), the distribution of CO₂ rotational motion was "locked" within a narrow range at low temperature and become uniform as the
temperature increases. That is, the temperature significantly influenced the rotational motions of CO\textsubscript{2} molecules in S-cages. Hence these temperature-enhanced freedoms of rotational motions make the entire structure more stable and more rigid.

Besides, two parallel layers exist with the same longest radii at the equatorial plane. One is composed of upper water molecules of the zigzag structure in the middle (orange ellipse in Fig. 4); the other exists along the bottom water molecules of the zigzag structure (grey ellipse in Fig. 4). Thus, the centroid of the CO\textsubscript{2} molecule can move between the two layers to gain the largest freedom of rotational motion. Here, thermal expansion may be an important effect with temperature increasing. At 40 MPa, for example, the unit cell lengths are 1.182 nm, 1.196 nm, and 1.201 nm at –173.15 °C, –40 °C, and 5 °C respectively. As the space inside the cages increases with the increase in temperature, the CO\textsubscript{2} molecule moves more easily and rotational motion becomes easier compared with the situation at low temperature. That is, expanded cages facilitate guest CO\textsubscript{2} rotational motions, which enhance the stability of CO\textsubscript{2} hydrate. In conclusion, the thermal effect is a critical external factor that plays an important role in affecting the stability and rigidity of the CO\textsubscript{2} hydrate.

Figure 4. Kinetic behavior of CO\textsubscript{2} molecules residing in L-cage (No. 1) and S-cage (No. 7), the equatorial plane in L-cage is perpendicular to Y axis. (a,c) Schematic graph of rotational motion of CO\textsubscript{2} molecule. Red straight line represents the long axis of the CO\textsubscript{2} molecule. Blue solid circles denote water molecules on the vertices of the cage. Red solid circles (oxygen atoms) and large green solid circle (carbon atom) comprise CO\textsubscript{2} molecule. (b,d) Distribution of rotational correlation coefficients (cosθ) in different directions for CO\textsubscript{2} molecules shown in (a,c).
To corroborate that the observed anomaly indeed results from CO₂ guest molecules, we have also investigated the elastic constants of a hypothetical hydrate structure without “guest” molecules (Fig. S5). The result shows that the variation trends of \( C_{11} \) and \( C_{12} \) are same to those of CH₄ and CO₂ hydrate, however, \( C_{44} \) of empty cage structure decreases regularly (like CH₄ hydrate) with the increase in temperature. This finding further demonstrates that the anomalous behavior of \( C_{44} \) and shear modulus (as well as Young modulus) of CO₂ hydrate is due to the “entrapped” CO₂ molecule.

Previous studies have shown that mechanical properties are susceptible to the cage occupancy⁴⁰. Since the occupancy of CO₂ hydrate is likely a function of the synthesis pressure, it is interesting to discuss how the occupancy (especially, of the small cages) affects the above results (i.e. the anomalous behavior of \( C_{44} \) and shear modulus). For this purpose, 75% (both of the two S-cages are empty in the primitive unit cell) and 87.5% (one of the S-cage is empty in the primitive unit cell) occupancy were investigated by the same method, and the comparisons of elastic constants are shown in Figs S2 and S6. Elastic constant of \( C_{44} \) is nearly invariable with temperature increasing when no CO₂ molecules exist in the S-cages, and dramatically increases when half of the S-cages are occupied by CO₂ molecules. We conclude that the CO₂ molecules existing in the S-cages play a decisive role in elevating the stability and rigidity of the material with temperature increasing. For the most recent experiments, where the S-cage occupancy was found to be ~2/3⁶⁰, we anticipate that CO₂ hydrate exhibits the anomalous thermally-enhanced-stability and -rigidity phenomenon, since the occupancy is indeed larger than 87.5% occupancy case (half in terms of S-cage occupancy).

**Discussions**

In solid state physics, Born criterion⁵⁴,⁵⁵ has been widely used to address the mechanical stability of a crystalline structure⁵⁶. The violation of the Born criterion is regarded as the mechanism causing the onset of the structural transformation, including melting, polymorphism, and pressure-induced amorphization⁴⁴–⁵⁷. For a cubic system, three conditions need to be fulfilled: \( C_{44} > 0, C_{11} - C_{12} > 0, \) and \( C_{11} + 2C_{12} > 0 \). The vanishing of \( C_{44} \) and tetragonal shear \( (C_{11} - C_{12}) \) was suggested to be responsible for melting⁴⁴–⁵⁶. For normal crystalline materials, as the temperature increases, the shear modulus presents softening behavior and eventually leads to a collapse of the crystal lattice into a liquid phase (with a shear modulus equal to zero). However, we show here that the shear modulus of CO₂ hydrate increases with the temperature increasing. On the other hand, according to thermodynamic data, CO₂ hydrate decomposes into ice and CO₂ dry ice at around −150 °C¹²,³⁰–³². It is shown here that the shear modulus indeed decreases with the temperature decreasing. When the temperature is lower than −120 °C, the calculated stress-strain curves for \( C_{44} \) clearly display non-linear behaviors regardless of strain rate (Fig. S7) which implies an instability of the crystalline structure of CO₂ hydrate. We show that this instability may result from the “locked” rotational motions of CO₂ molecules, in particular, those in small cages, under low-temperature condition. When the small cages are empty, the calculated stress-strain curves for \( C_{44} \) clearly display linear again (Fig. S7). This indicates that the stability can be tuned by the occupancy of small cages. So far, the experimental evidence of CO₂ hydrate decomposition at low-temperature limit has been indirect, namely by observing the pressure hysteresis by cooling the CO₂ hydrate to −168.15 °C (105 K) and warming to around −43.15 °C (230 K)³⁰. Structural analyses⁶⁵ are needed for CO₂ hydrate (presumably with high CO₂ occupancy) to study the above-documented phase changes in detail. This study provides a new perspective on gas hydrates and new physics on temperature-enhanced stability of a crystalline material. Finally, elasticity anomaly may be anticipated in materials with the negative thermal expansion coefficient, as an example, the shear modulus was found to be increased slightly with temperature in the high-temperature β-quartz⁶⁸. The anharmonic atomistic motions are crucial to describe the high-temperature elasticity behavior, and yet to be explored.

**Methods**

**Main theory applied for mechanical properties.** The generalized Hooke’s Law⁴¹ was used to investigate the stress–strain relationships of the gas hydrate, which is a cubic system and has only three independent elastic constants, namely \( C_{11}, C_{12}, \) and \( C_{44} \). The constitutive equation could be expressed as:

\[
\begin{bmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6 \\
\end{bmatrix} =
\begin{bmatrix}
C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{44} \\
\end{bmatrix}
\begin{bmatrix}
\varepsilon_1 \\
\varepsilon_2 \\
\varepsilon_3 \\
\varepsilon_4 \\
\varepsilon_5 \\
\varepsilon_6 \\
\end{bmatrix}
\]

(1)

where \( \sigma_i \) and \( \varepsilon_i \) represent the stress and strain tensors, respectively. \( C_{ij} \) is the elasticity matrix of materials, which determines the stiffness. The subscripts \( (1, 2, 3, 4, 5, 6) \) denote different directions (XX, YY, ZZ, ZY, ZX, YX). The elastic constants are the ratio of stress to corresponding strain and can be obtained from the slope of stress–strain curves if the deformation exists in the elastic regime. It is anticipated that the microscopic method (MD simulations) reflects the experimental observations well within the elastic regime of stress–strain relationships. Once the elastic constants are derived, the bulk modulus \( K \) and shear modulus \( G \) are evaluated using the Voigt model and assuming that strain is uniform and the Reuss model⁴²,⁵⁸ by considering that the stress is uniform throughout the system.

Voigt model:
\[ K_V = \frac{1}{3} C_{11} + \frac{2}{3} C_{12} \]  
\[ G_V = \frac{1}{5} C_{11} - \frac{1}{5} C_{12} + \frac{3}{5} C_{44} \]  

Reuss model:
\[ \frac{1}{K_R} = 3S_{11} + 6S_{12} \]  
\[ \frac{1}{G_R} = \frac{4}{5} S_{11} - \frac{4}{5} S_{12} + \frac{3}{5} S_{44} \]

where \( S_{ij} \) represents the compliance matrix, which is the reverse matrix of the elasticity matrix \( C_{ij} \). Since the Voigt and Reuss models signify the maximum and minimum value of the moduli, respectively, the results are optimized by the Hill average:
\[ K = \frac{K_V + K_R}{2} \]  
\[ G = \frac{G_V + G_R}{2} \]

The results of the Hill average are used as input to evaluate Young’s modulus \( E \) and Poisson’s ratio \( \nu \) as follows:
\[ E = \frac{9KG}{3K + G} \]  
\[ \nu = \frac{3K - 2G}{2(3K + G)} \]

The P-wave velocity and S-wave velocity are calculated using bulk modulus \( K \) and shear modulus \( G \) as follows,
\[ V_P = \sqrt{\frac{K + \frac{4}{3}G}{\rho}} \]  
\[ V_S = \sqrt{\frac{G}{\rho}} \]

\( \rho \) denotes density of the system.

**Simulation details.** The GROMACS version 4.5.5\textsuperscript{59} was used to perform the equilibrium and non-equilibrium MD simulations in this study. A Nosé–Hoover thermostat\textsuperscript{60} and Parrinello–Rahman pressure coupling\textsuperscript{61} were used for temperature and pressure control, respectively. A particle mesh Ewald summation method\textsuperscript{62} was used to calculate long-range electrostatic interactions. The cutoff distance for Van der Waals interactions was set to 1.1 nm. A time step of 1 fs was set to integrate the motion equations with the leapfrog algorithm\textsuperscript{63}.

The TIP4P/Ice\textsuperscript{64, 65} OPLS-AA\textsuperscript{66, 67}, and EPM2\textsuperscript{68} models (potential parameters in the Table SIII) were used to model behaviors of water, CH\textsubscript{4}, and CO\textsubscript{2} molecules in the simulations. For CO\textsubscript{2}, TraPPE\textsuperscript{69} model was also employed to test whether the conclusion is dependent on the model that we used. While most of our results for CO\textsubscript{2} hydrate are based on EPM2 model, the result from TraPPE is presented in Fig. S2. Previous studies have shown that the models describe the liquid–solid phase transition of ice Ih, and three-phase coexistence line of CH\textsubscript{4} hydrates very well\textsuperscript{64, 65}. In addition, our preliminary studies using the same model could reproduce three-phase coexistence line of carbon dioxide hydrates. We used the proton-disordered unit cell of gas hydrate (sI) with a vanishingly small total dipole moment\textsuperscript{45, 48}. The unit cell was duplicated six times in each direction to obtain the initial configurations. This structure consists of 1728 "guest" molecules and 9936 water molecules. Initially, all configuration boxes were equilibrated in an isothermal–isobaric ensemble for 1 ns under the required temperature and pressure. To calculate the elastic constants, a constant compressive and tensile strain were applied up to 0.04 in the XX direction and shear strains (both positive and negative directions) were applied up to 0.1 in the ZX direction. We used strain rates of \( 4 \times 10^8 \text{s}^{-1} \) and \( 1 \times 10^9 \text{s}^{-1} \) for uniaxial strain and shear strain when calculating the elastic moduli, respectively. Additional studies show that the elastic constants are independent of the loading speeds within the elastic regime\textsuperscript{46}. Five independent simulation runs were performed for CO\textsubscript{2} hydrate under 40 MPa and 0 °C in order to investigate the calculation reliability, and the results are given in Table SIV. Furthermore, similar calculations were performed at 10 different temperatures under 40 MPa. Calculated \( C_{11} \), \( C_{12} \), and \( C_{44} \) were shown in Fig. S8. The standard deviation of each parameter is at least ten times less than difference
between the values of −40 °C and 5 °C with same pressure, which indicates the variation trends (as shown in Figs 2 and 3) are not affected by calculation uncertainty. This is indeed the case as presented in Fig. S8.

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Author Contributions

J.J., Y.L., T.T., S.M. and T.M. planned the research. J.J. performed all the calculations. J.J. and Y.L. prepared the figures. All authors wrote and reviewed the manuscript.

Additional information

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