Supporting Information for

"Size Dependence of the Dissociation Process of Spherical Hydrate Particles via Microsecond Molecular Dynamics Simulations"

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Computational setup and melting simulations

The TIP4P/ice model¹ was used to represent water, whereas methane, ethane, propane and dodecane were modeled with TraPPE-UA.² All simulations were carried out using the GRO-MACS MD simulation package (version 2018.3).^{3–6} We employed the isothermal-isobaric (NPT) ensemble for all simulations, applying the Berendsen⁷ temperature and pressure coupling schemes with time constants of 0.5 ps (during equilibration the time constant for the pressure coupling was sometimes chosen larger to avoid abrupt changes of the cell volume). The pressure was set to 100 bar, whereas the target temperature depended on the specific run. The leap-frog integration algorithm was employed with a time step of 2 fs and periodic boundary conditions were applied in all directions. Electrostatic and Lennard-Jones interactions were evaluated with the particle mesh Ewald (PME) method,^{8,9} with a cutoff of 1.2 nm and a grid spacing of 0.15 nm.

The systems for the melting simulations consisted of a spherical hydrate particle solvated in a hydrocarbon phase. The spherical hydrate particles were carved out from bulk sII hydrate, with all small cages being filled with methane molecules and all large cages with propane molecules. The positions of the water molecules were taken from Takeuchi *et al.*¹⁰ No molecules were cut during the carving process; rather we included the entire molecule if one of its atoms was within the spherical cutoff distance. We performed simulations for five different sizes of the spherical hydrate particles, namely with radii of 1.5 nm, 2.5 nm, 3.5 nm, 4.5 nm and 5.5 nm. We note that, based on the number of water molecules, the spherical hydrate particles have slightly larger effective radii r_{eff} of 1.53 nm, 2.55 nm, 3.54 nm, 4.54 nmand 5.54 nm, respectively. The spherical hydrate particles were placed in the center of a cubic box with side lengths 9 nm, 11 nm, 13 nm, 15 nm and 17 nm, respectively, and solvated with the hydrocarbon phase, consisting of 50 mol% dodecane, 4 mol% propane, 6 mol% ethane and 40 mol% methane. This molar composition corresponds to the equilibrium of a simulation where pure dodecane was put in contact with simplified Green Canyon gas.¹¹ The exact composition of the five systems is shown in Table S1, and as an illustrative example we show in Figure S1 the initial system with a spherical hydrate particle of radius 3.5 nm.

System (radius)	$r_{ m eff}$	Hydrate particle			Hydrocarbon phase			
		Water	Methane	Propane	Dodecane	Propane	Ethane	Methane
$1.5\mathrm{nm}$	$1.53\mathrm{nm}$	396	40	30	1150	92	178	920
$2.5\mathrm{nm}$	$2.55\mathrm{nm}$	1826	188	111	2125	170	443	1700
$3.5\mathrm{nm}$	$3.54\mathrm{nm}$	4867	560	291	3525	282	983	2820
$4.5\mathrm{nm}$	$4.54\mathrm{nm}$	10259	1176	610	5375	430	1821	4300
$5.5\mathrm{nm}$	$5.54\mathrm{nm}$	18680	2140	1103	7725	618	3067	6180

Table S1: Number of molecules of the investigated systems.



Figure S1: Illustration¹² of the spherical hydrate particle with radius 3.5 nm (left), and the particle embedded in the hydrocarbon mixture (right).

For all systems, the simulations started with an energy minimization to relax any unfavorable initial placements of the molecules. Subsequently, a 2 ns NPT equilibration was performed to relax the box volume and to obtain the target pressure. During this equilibration process, the positions of the oxygen atoms, the methane atoms and the central propane atoms of the hydrate were kept fixed. Finally, the production runs were launched without any position constraints. These production runs were carried out for a time period of 10 µs, or until the hydrate particles had melted completely.

The melting process was characterized using two parameters, monitored along the sim-

ulations. The first one followed the evolution of the potential energy of the system, and was directly based on the energy values calculated by GROMACS. The second parameter consisted in evaluating the amount of hydrate transformed into liquid water. To this end, the number of small (dodecahedron; 5^{12}) and large (hexakaidecahedron; $5^{12}6^4$) cages that constitute the sII hydrate was determined using the algorithm by Jacobson $et \ al.$ ¹³ Based on these numbers and the volume of the small and large cages, the amount of hydrate that was still intact could be calculated, and subtracting this value from the initial hydrate volume yielded the amount that had melted. To make the analysis more intuitive, the melted volume was transformed into an equivalent surface layer of uniform thickness, even though the melting process was not perfectly uniform, as can been seen from Figure 2 of the main text. In order to estimate the volumes of the small and large hydrate cages, the average hydrogen bond length of the pentagons in the initial structure from Takeuchi et al.¹⁰ was determined, giving a value of s = 2.7854 Å. The volume of the dodecahedrons could then be calculated as $V_{5^{12}} = \frac{1}{4}(15 + 7\sqrt{5})s^3 = 165.603 \text{ Å}^3$. Subsequently, the volume of the hexakaidecahedrons could be determined by subtracting the dodecahedron volume from the overall sII unit cell volume reported by Takeuchi *et al.*¹⁰ ($V_{sII} = 5186.7 \text{ Å}^3$). Since the unit cell contains 16 dodecahedrons and 8 hexakaidecahedrons, the result is given by $V_{5^{12}6^4} = \frac{1}{8}(V_{sII} - 16V_{5^{12}}) = 317.132 \text{ Å}^3.$

In Figure S2 (radius 1.5 nm), Figure S3 (radius 2.5 nm), Figure S4 (radius 3.5 nm), Figure S5 (radius 4.5 nm) and Figure S6 (radius 5.5 nm) we show the potential energy and the liquid layer thickness for all the executed simulations, up to a simulation time of 10 µs. If the hydrate particles had melted completely before this time, the simulation was stopped earlier. Note that complete melting was reached if the thickness of the liquid water layer was equal to the radius of the initial hydrate particle. Based on these plots we tried to estimate the melting temperature for each particle size, as discussed in the main text.



Figure S2: Potential energy (left) and liquid layer thickness (right) for various temperatures, for the hydrate sphere of radius 1.5 nm.



Figure S3: Potential energy (left) and liquid layer thickness (right) for various temperatures, for the hydrate sphere of radius 2.5 nm.



Figure S4: Potential energy (left) and liquid layer thickness (right) for various temperatures, for the hydrate sphere of radius 3.5 nm.



Figure S5: Potential energy (left) and liquid layer thickness (right) for various temperatures, for the hydrate sphere of radius 4.5 nm.



Figure S6: Potential energy (left) and liquid layer thickness (right) for various temperatures, for the hydrate sphere of radius 5.5 nm.

Particle density distribution

In order to analyze the spacial distribution of the four hydrocarbon species present in the systems (methane, ethane, propane, and dodecane), we calculated two-dimensional particle density maps for the xy, xz and yz planes intersecting the center of the hydrate-water sphere. In more detail, the density map for the x - y plane was calculated as a twodimensional histogram with bin size 0.1 nm, taking into account all atoms whose z-coordinate was within $0.5 \,\mathrm{nm}$ of the z-coordinate of the sphere center. The other planes are defined in an analogous way. We calculated these planes for all particle sizes and for two temperatures, namely the maximum temperature for which each particle is clearly stable $(T_{\text{stable}}^{\max})$ and the minimum temperature for which it has clearly melted completely (T_{melt}^{\min}) ; these values have been presented in the main text. We normalized the values of each hydrocarbon species by dividing by the maximum bin count throughout all planes and both temperatures. The resulting plots for the xy plane are shown in Figure S7 (r = 1.5 nm), Figure S8 (r = 2.5 nm), Figure S9 ($r = 3.5 \,\mathrm{nm}$), Figure S10 ($r = 4.5 \,\mathrm{nm}$) and Figure S11 ($r = 5.5 \,\mathrm{nm}$). Due to the isotropic nature of the systems the other planes are very similar and are therefore omitted for sake of brevity. We can clearly identify the spherical hydrate-water particle in the center, surrounded by the hydrocarbon phase. First of all, we see that the results for the smallest particle are completely different from the other ones. Whereas for all systems with $r \ge 2.5 \,\mathrm{nm}$ we observe a uniform distribution of the outer hydrocarbon phase, there are considerable inhomogeneities for the smallest particle. We attribute this behavior to the small temperatures that are used (T = 223 K and T = 224 K), which are clearly below the experimental melting point of dodecane (263.46 K at atmospheric pressure and 268.2 K at $274 \,\mathrm{bar}^{14}$). Indeed it seems that the dodecane phase has solidified, as can be seen from the snapshot shown in Figure S12a. This system will therefore be excluded from the subsequent analysis.

For all other systems, we can draw many interesting conclusions from these density maps:

- For temperatures below the melting point we can clearly identify the regular (and relatively dense) presence of methane and propane within the hydrate particle. As expected, no ethane and dodecane is present within the solid hydrate crystal.
- For temperatures above the melting point, the methane and propane molecules have almost completely moved away from the (now liquid) hydrate particle and are dissolved within the hydrocarbon phase. This is to be expected, as the solubility of these hydrocarbon species in liquid water is very low. Note that we now have small traces of ethane within the sphere; in contrast to the case of the solid hydrate crystal, the liquid water phase allowed them to enter within the limited solubility range.
- This low solubility of hydrocarbons within water also allows to easily detect the QLL, which can be identified as the shell of low methane/propane density between the hydrate core and the bulk hydrocarbon.
- For all systems we observe a uniform distribution of the hydrocarbon phase. This is in particular important for the higher temperatures, where the expulsion of methane and propane from the spherical hydrate particles might lead to an oversaturation of the hydrocarbon phase and consequently to the formation of gas bubbles. Even though the present analysis is only performed for planes intersecting the particle center, the absence of inhomogeneities throughout all systems and temperatures indicates that no such bubbles form, and that the melting of the hydrate does not oversaturate the surrounding liquid phase.
- Apart from the absence of hydrocarbon species within the QLL, we do not observe any modifications of the hydrocarbon phase close to the hydrate-water surface. This fact is also visible from Figure S12b, showing a representative snapshot of the particle surface and the surrounding hydrocarbon phase. A recent study by Naeiji *et al.*¹⁵ has shown that the distribution of a gaseous hydrocarbon mixture (methane, ethane and propane) close to a water surface can be significantly different from the values in the

gas phase. However, they studied a water-gas interface (i.e. liquid-gaseous), whereas the present study investigates a (solid-)liquid-liquid interface. Therefore, we do not think that there is any contradiction between their results and ours.



Figure S7: Density map for the particle with size r = 1.5 nm (indicated by the green line).



Figure S8: Density map for the particle with size r = 2.5 nm (indicated by the green line).



Figure S9: Density map for the particle with size r = 3.5 nm (indicated by the green line).



Figure S10: Density map for the particle with size r = 4.5 nm (indicated by the green line). Since the hydrate has not melted completely within the simulation time, we still observe an intact inner core even for the high temperature.



Figure S11: Density map for the particle with size r = 5.5 nm (indicated by the green line). Since the hydrate has not melted completely within the simulation time, we still observe an intact inner core even for the high temperature.





(a) System with radius 1.5 nm at 223 K. The blue frame indicates the simulation box.

(b) System with radius $5.5 \,\mathrm{nm}$ at $271 \,\mathrm{K}$. Only a subset of the simulation box is shown.

Figure S12: Final configuration after 10 µs of simulation. The hydrocarbon species are represented in yellow (methane), cyan (ethane), green (propane) and orange (dodecane), whereas the atoms of the water molecules are shown in red (oxygen) and white (hydrogen).

Additional parameters of the Gibbs-Thomson equation

In order to calculate the surface tension γ from the Gibbs-Thomson constant K_{GT} , three additional parameters need to be determined, namely the bulk melting temperature T_m^{bulk} , the molar volume v, and the bulk enthalpy of dissociation ΔH_m .

The determination of T_m^{bulk} was already discussed in detail in the main text. In what follows we will provide additional details and discussion regarding the calculation of the bulk enthalpy of dissociation, the hydrate molar volume, and the surface tension.

Enthalpy of hydrate dissociation from MD simulations

The calculation of the enthalpy of hydrate dissociation, ΔH_m , was performed following an approach similar to the one outlined by Tsimpanogiannis *et al.*¹⁶ for the case of pure sI methane hydrates. Note that in the current study the method had to be slightly adapted due to the presence of mixed methane-propane hydrate. Normalized with respect to methane, the enthalpy of dissociation (with units $\left(\frac{kJ}{mol\,met}\right)$) is given by:

$$\Delta H_m = H_{met} + n_{pro}H_{pro} + n_{wat}H_{wat} - n_{hyd}H_{hyd}, \qquad (1)$$

where H_{met} , H_{pro} , H_{wat} and H_{hyd} are, respectively, the enthalpies of pure methane, propane, water and hydrate (unit cell), and $n_{pro} = 1/2$, $n_{wat} = 8.5$, and $n_{hyd} = 1/16$ are stoichiometric correction factors (i.e. the number of propane/water/hydrate molecules per methane molecule) for a fully occupied sII hydrate crystal). The enthalpies of the individual components were calculated with additional simulations with GROMACS, using 8000 molecules (methane and propane), 4138 molecules (water), and a 3x3x3 unit cell (hydrate). ΔH_m is thus calculated as

$$\Delta H_m = \frac{H_{met(8000)}}{8000} + n_{pro} \frac{H_{pro(8000)}}{8000} + n_{wat} \frac{H_{wat(4138)}}{4138} - n_{hyd} \frac{H_{hyd(3x3x3)}}{27} , \qquad (2)$$

where $H_{met(8000)}$, $H_{pro(8000)}$, $H_{wat(4138)}$ and $H_{hyd(3x3x3)}$ are the enthalpies obtained from these individual simulations.

To calculate the enthalpies for the individual components, a three-step equilibration process was performed, consisting of an energy minimization, a 50 ps NVT equilibration, and an NPT equilibration of 50 ns (hydrate and water) or 100 ns (methane and propane). Subsequently, the NPT production simulation to determine the enthalpy was run for 20 ns. The temperature was maintained at 277 K using the velocity-rescaling thermostat¹⁷ with a time constant of 0.05 ps (NVT equilibration) and 0.5 ps (NPT equilibration and NPT production). The pressure was maintained at 100 bar using the Berendsen barostat⁷ with a time constant of 0.5 ps. From these simulations the following values were obtained:

- $H_{met(8000)} = (31\,094.4 \pm 7.3) \,\text{kJ/mol}$
- $H_{pro(8000)} = (3019.6 \pm 12.0) \, \text{kJ/mol}$
- $H_{wat(4138)} = (-200\,666.0 \pm 5.8) \,\mathrm{kJ/mol}$
- $H_{hyd(3x3x3)} = (-208\,241.0\pm2.0)\,\text{kJ/mol}$

Inserting these values into Eq. (2) yields a value of $\Delta H_m = (73.92 \pm 0.04) \,\text{kJ/mol}$.

It should be noted that Handa¹⁸ reported experimental measurements for the enthalpy of dissociation of pure methane $((54.19 \pm 0.28) \text{ kJ/mol})$ and propane $((129.2 \pm 0.4) \text{ kJ/mol})$ hydrates. Additional discussion and comparison between the hydrate dissociation value calculated in the current study and other literature values or calculations using alternative approaches (*e.g.* Clausius-Clapeyron equation) can be found in the following subsections.

Enthalpy of hydrate dissociation from the Clausius-Clapeyron equation

The Clausius-Clapeyron equation is a simplified version of the Clapeyron equation and is given as follows (see also the detailed discussion in Tsimpanogiannis *et al.*¹⁶):

$$\frac{\mathrm{d}\ln(P)}{\mathrm{d}(1/T)} = -\frac{\Delta H_m}{zR},\tag{3}$$

where R is the universal gas constant, z is the compressibility factor of the gas phase and P and T are the equilibrium pressure and temperature, respectively, at three-phase equilibrium conditions. Therefore, three-phase equilibrium measurements can be used in order to calculate the enthalpy of hydrate dissociation, ΔH_m , from the slope of the Clausius-Clapeyron equation. To this purpose, we used here the experimental data of Verma *et al.*¹⁹ for a gas mixture with a composition of methane (65.1%) and propane (34.9%). In the neighborhood of 106 bar and 298.2 K, which is the closest to the conditions we are interested in the current study, we calculated (using the Abbot correlation for the second virial coefficient, as described in Smith *et al.*²⁰) that z = 0.422, which results in a value of $\Delta H_m = 70.9$. This result is very close to the value that was calculated through the MD simulations in the previous subsection.

Hydrate molar volume from MD simulations

To determine the molar volume v, we again take methane as reference; v is then simply given by the volume of the hydrate crystal per mol of methane. Assuming that all small cages are fully occupied by methane, the unit cell contains 16 methane molecules, and the molar volume is therefore $v = \frac{N_A}{16}V$, with N_A being Avogado's number and V the sII unit cell volume. Relying on the calculation done for the determination of the enthalpy of dissociation $(3 \times 3 \times 3$ supercell at 277 K and 100 bar), the hydrate unit cell volume was determined to be $V = 5.2372 \text{ nm}^3$, resulting thus in a molar volume equal to $v = 1.971 \times 10^{23} \text{ nm}^3$. Our calculations are in very good agreement with the sII unit cell volume reported by Takeuchi et al.,¹⁰ namely $V = 5.1867 \text{ nm}^3$, which in turn yields $v = 1.952 \times 10^{23} \text{ nm}^3$.

Surface tension from the Gibbs-Thomson equation

As indicated in the main text, there are no experimental measurements for conditions similar to the ones used in the current study to verify our calculated value of the surface tension ($\gamma = 64.28 \text{ mJ/m}^2$). Therefore, we can only compare the current results with systems reported in the literature that are similar.^{21–25} In these studies, for various mixed methane/propane hydrate-water systems, values in the range of 72–129 kJ/mol and 42–60 mJ/m² have been reported for ΔH_m and γ , respectively. Therefore, the literature values are in reasonable agreement with the current calculations.

In particular, Uchida *et al.*²¹ reported three-phase hydrate equilibrium measurements under confinement in porous glass for a gas mixture containing propane (91.2%), methane (6.7%) and ethane (2.1%). By using a value for the enthalpy of dissociation, ΔH_m , equal to 129.2 kJ/mol, a value of (50 ± 2) mJ/m² can be calculated for γ using the Gibbs-Thompson equation.

Lee *et al.*²³ reported three-phase hydrate equilibrium measurements under confinement in silica gel pores for a gas mixture containing methane (90%), ethane (7%) and propane (3%). By using a value for the enthalpy of dissociation, ΔH_m , equal to 79.2 kJ/mol, a value of (47 ± 4) mJ/m² was reported for γ using the Gibbs-Thompson equation.

Lee and Seo²² reported three-phase hydrate equilibrium measurements under confinement in silica gel pores for a gas mixture containing methane (90%) and propane (10%). The authors calculated the enthalpy of dissociation using experimental data and the Clausius-Clapeyron equation. They reported a value for ΔH_m equal to 79.2 kJ/mol. Thus, by using the Gibbs-Thompson equation they calculated a value of (42 ± 3) mJ/m² for γ . The authors further reported NMR measurements and confirmed the formation of sII hydrate structure.

Kang and Lee²⁴ reported three-phase hydrate equilibrium measurements under confine-

ment in silica gel pores for a natural gas mixture containing methane (89.86%), ethane (6.4%), propane (2.71%), while the remaining (1%) consisted of isobutene, n-butane, n-pentane and nitrogen. By using a value for the enthalpy of dissociation, ΔH_m , equal to 72.498 kJ/mol, a value of (59.74 ± 2.00) mJ/m² was reported for γ using the Gibbs-Thompson equation.

Finally, in a similar coarse grained study of sI hydrates, for a hydrate-former with properties between methane and carbon dioxide a value for the surface tension equal to $(36 \pm 2) \text{ mJ/m}^2$ was obtained.²⁵

References

- Abascal, J. L. F.; Sanz, E.; García Fernández, R.; Vega, C. A potential model for the study of ices and amorphous water: TIP4P/Ice. *The Journal of Chemical Physics* 2005, 122, 234511.
- (2) Potoff, J. J.; Siepmann, J. I. Vapor-liquid equilibria of mixtures containing alkanes, carbon dioxide, and nitrogen. AIChE Journal 2001, 47, 1676–1682.
- (3) Van Der Spoel, D.; Lindahl, E.; Hess, B.; Groenhof, G.; Mark, A. E.; Berendsen, H. J. C. GROMACS: Fast, flexible, and free. *Journal of Computational Chemistry* 2005, 26, 1701–1718.
- (4) Hess, B.; Kutzner, C.; van der Spoel, D.; Lindahl, E. GROMACS 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation. *Journal of Chemical Theory and Computation* **2008**, *4*, 435–447.
- (5) Pronk, S.; Páll, S.; Schulz, R.; Larsson, P.; Bjelkmar, P.; Apostolov, R.; Shirts, M. R.; Smith, J. C.; Kasson, P. M.; van der Spoel, D. *et al.* GROMACS 4.5: a high-throughput and highly parallel open source molecular simulation toolkit. *Bioinformatics* 2013, 29, 845–854.

- (6) Abraham, M. J.; Murtola, T.; Schulz, R.; Páll, S.; Smith, J. C.; Hess, B.; Lindahl, E. GROMACS: High performance molecular simulations through multi-level parallelism from laptops to supercomputers. *SoftwareX* 2015, 1-2, 19–25.
- (7) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A.; Haak, J. R. Molecular dynamics with coupling to an external bath. *The Journal of Chemical Physics* 1984, *81*, 3684–3690.
- (8) Darden, T.; York, D.; Pedersen, L. Particle mesh Ewald: An N log(N) method for Ewald sums in large systems. *The Journal of Chemical Physics* **1993**, *98*, 10089–10092.
- (9) Essmann, U.; Perera, L.; Berkowitz, M. L.; Darden, T.; Lee, H.; Pedersen, L. G. A smooth particle mesh Ewald method. *The Journal of Chemical Physics* **1995**, *103*, 8577–8593.
- (10) Takeuchi, F.; Hiratsuka, M.; Ohmura, R.; Alavi, S.; Sum, A. K.; Yasuoka, K. Water proton configurations in structures I, II, and H clathrate hydrate unit cells. *The Journal* of Chemical Physics **2013**, 138, 124504.
- (11) Mohr, S.; Hoevelmann, F.; Wylde, J.; Schelero, N.; Sarria, J.; Purkayastha, N.; Ward, Z.; Navarro Acero, P.; Michalis, V. K. Ranking the Efficiency of Gas Hydrate Anti-agglomerants through Molecular Dynamic Simulations. *The Journal of Physical Chemistry B* 2021, 125, 1487–1502.
- (12) Humphrey, W.; Dalke, A.; Schulten, K. VMD Visual Molecular Dynamics. Journal of Molecular Graphics 1996, 14, 33–38.
- (13) Jacobson, L. C.; Hujo, W.; Molinero, V. Thermodynamic Stability and Growth of Guest-Free Clathrate Hydrates: A Low-Density Crystal Phase of Water. *The Journal* of Physical Chemistry B 2009, 113, 10298–10307.

- (14) Yang, M.; Narita, T.; Tanaka, Y.; Sotani, T.; Matsuo, S. Solid–liquid phase equilibria in binary (1-octanol + n-alkane) mixtures under high-pressure: Part 2. (1-Octanol + n-octane, n-dodecane) systems. *Fluid Phase Equilibria* 2003, 204, 55–64.
- (15) Naeiji, P.; Woo, T. K.; Alavi, S.; Varaminian, F.; Ohmura, R. Interfacial properties of hydrocarbon/water systems predicted by molecular dynamic simulations. *The Journal* of Chemical Physics **2019**, 150, 114703.
- (16) Tsimpanogiannis, I. N.; Michalis, V. K.; Economou, I. G. Enthalpy of dissociation of methane hydrates at a wide pressure and temperature range. *Fluid Phase Equilibria* 2019, 489, 30–40.
- (17) Bussi, G.; Donadio, D.; Parrinello, M. Canonical sampling through velocity rescaling. *The Journal of Chemical Physics* 2007, 126, 014101.
- (18) Handa, Y. P. Compositions, enthalpies of dissociation, and heat capacities in the range 85 to 270 K for clathrate hydrates of methane, ethane, and propane, and enthalpy of dissociation of isobutane hydrate, as determined by a heat-flow calorimeter. *The Journal of Chemical Thermodynamics* **1986**, *18*, 915–921.
- (19) Verma, Y. K.; Hand, J. H.; Katz, D. L. Gas hydrates from liquid hydrocarbons methanepropane-water system. GVC/AIChE Joint Meeting. Munich, 1975; p 10.
- (20) Smith, J. M. Introduction to chemical engineering thermodynamics; McGraw-Hill Education: New York, NY, 2018.
- (21) Uchida, T.; Ebinuma, T.; Takeya, S.; Nagao, J.; Narita, H. Effects of pore sizes on dissociation temperatures and pressures of methane, carbon dioxide, and propane hydrates in porous media. *Journal of Physical Chemistry B* 2002, *106*, 820–826.
- (22) Lee, S.; Seo, Y. Experimental measurement and thermodynamic modeling of the mixed

 $CH_4 + C_3H_8$ clathrate hydrate equilibria in silica gel pores: Effects of pore size and salinity. *Langmuir* 9742–9748.

- (23) Lee, S.; Cha, I.; Seo, Y. Phase behavior and 13C NMR spectroscopic analysis of the mixed methane + ethane + propane hydrates in mesoporous silica gels. *Journal of Physical Chemistry B* **2010**, *114*, 15079–15084.
- (24) Kang, S.-P.; Lee, J.-W. Formation Characteristics of Synthesized Natural Gas Hydrates in Meso- and Macroporous Silica Gels. *The Journal of Physical Chemistry B* 2010, 114, 6973–6978.
- (25) Jacobson, L. C.; Molinero, V. Can Amorphous Nuclei Grow Crystalline Clathrates? The Size and Crystallinity of Critical Clathrate Nuclei. *Journal of the American Chemical Society* 2011, 133, 6458–6463.