Supporting Information for:

Molecular Dynamics Simulation of the Crystal Nucleation and Growth Behavior of Methane Hydrate in the Presence of the Porous Sediment Surface and Nanopore

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Table S1. Basal spacings of 1 H$_2$O layer hydrate, 3 H$_2$O layer hydrate and 6 H$_2$O layer hydrate in montmorillonite model.

<table>
<thead>
<tr>
<th>layer</th>
<th>1</th>
<th>3</th>
<th>6</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O(layer)</td>
<td>64</td>
<td>192</td>
<td>384</td>
<td>de Pablo et al.$^1$</td>
</tr>
<tr>
<td>H$_2$O(aqueous solution)</td>
<td>242</td>
<td>339</td>
<td>500</td>
<td>Boek et al.$^2$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>42</td>
<td>59</td>
<td>87</td>
<td>our work</td>
</tr>
<tr>
<td>Basal spacing(nm)</td>
<td>1.257</td>
<td>1.737</td>
<td>2.501</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.232</td>
<td>1.707</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>1.7</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

**Order parameters of simulation.** The angular order parameter (AOP) of a H$_2$O molecule as a three-body structural order parameter is used to measure deviations from the tetrahedral angle, and vanishes for any tetrahedral network. The AOP is defined as:

$$AOP_i = \sum_{j=1}^{n-1} \sum_{k=j+1}^{n} \left[ \left(\cos \theta_{ijk} \cos \theta_{ijk} \right) + \cos^2(109.47^\circ) \right]^2$$

where $\theta$ is the angle between an O atom of H$_2$O ($i$) molecules in the center and two O atoms of neighboring H$_2$O ($j$ and $k$) molecules. The summation runs over all possible $\theta_{ijk}$ of H$_2$O molecules within a spherical shell of radius 3.5 Å around the O of H$_2$O ($i$) molecules. The
average AOP of liquid, ice and hydrate structures are 0.9\(^3\), 0\(^4\) and 0.1\(^3\), respectively. Thus, the AOP of H\(_2\)O molecules is 0.4 as the location of the interface between liquid and solid hydrate\(^4\).

The four-body order parameter \((F_{4\varphi}\text{OP})\) is a function of the H-O.....O-H torsion angle between two adjacent O atoms within 3 Å and the outermost H atoms in the H\(_2\)O-H\(_2\)O pairs\(^3\)-\(^4\), which is defined as:

\[
F_{4\varphi} = \frac{1}{n} \sum_{i=1}^{n} \cos 3\varphi_i
\]

Equation S2

where \(n\) is the total number of H\(_2\)O-H\(_2\)O pairs, and \(\varphi\) is the torsion angle of H\(_2\)O-H\(_2\)O pairs. In previous research studies, the average \(F_{4\varphi}\text{OP}\) of liquid, ice and hydrate structures are -0.04, 0.4, 0.7, respectively\(^5\). The Mutually Coordinated Guest order parameter (MCGOP) is the new order parameter for tracking hydrate nucleation and growth, which is a more sensitive order parameter for detecting and quantifying the hydrate nucleation and growth\(^6\). Figure S1 shows the two-dimensional example of adjacency qualification for MCGOP. The minimum number of H\(_2\)O molecules \(N_w\) require to satisfy the following constraints: the distance of guest-guest \(R_g^{cut}\) is 9 Å, the distance of guest-water \(R_{gw}^{cut}\) is 6 Å, and the specified angle \(\varphi\) of guest-guest vector is 45°. If \(N_w\) is 5, the number of candidate guest is added to the “count” \((N_c)\). If the minimum number of \(N_c\) is 3, the candidate guest is considered as a MCG monomer.
Initial molecular configuration for System A. Figure S2 shows the snapshots of molecular configurations of System A at the $y$-$z$ plane at 0 ns at 260 K. The number of CH$_4$ molecules (yellow sphere) and H$_2$O molecules (red stick and white stick) of these molecular configurations are listed in Table S1. It can be seen from the Figure S2, in the H$_2$O-CH$_4$ bulk solution region, some CH$_4$ molecules (green sphere) and some H$_2$O molecules gather to form a bubble. Due to the two dimensional figure, some other bubbles are difficult to visible in the Figure S2.
**Influence of $x_m$ on hydrate nucleation and growth on clay system.** Figure S3 shows the molecular configurations of CH$_4$ hydrate in System A with the different $x_m$ values at the $y$-$z$ plane at 300 ns at 260 K. It can be seen from the Figure S3 the regular cages form in the bulk solution region in the systems with $x_m=0.17$ at 300 ns. In the system with $x_m=0.11$, the molecular configurations in the bulk solution region have many empty cages and irregular cages. In the system with $x_m=0.07$, few cage forms in the bulk solution region. These results present the structures of systems with the different $x_m$ are different. It implies that a significant effect of $x_m$ on the crystal growth of CH$_4$ hydrate on the clay system.

![Figure S3. Molecular configuration of CH$_4$ hydrate in System A with the different $x_m$ at the $y$-$z$ plane at 300 ns at 260 K](image)

(a) $x_m=0.07$, (b) $x_m=0.11$, (c) $x_m=0.17$. 
**Number of cages in System C.** Tung et al.\(^7\)\(^-\)\(^8\) determined the three variables to identify the three types of cages, which are: (1) the number of H\(_2\)O molecules within radius of 0.55 nm from the C atoms of CH\(_4\) molecules, \(n_w\); (2) the number of the crystal-like H\(_2\)O molecules (AOP < 0.4), \(n_h\); (3) the number of the hydrogen bonds formed from \(n_h\), \(n_b\). The three variables are determined for each of CH\(_4\) molecules in the solid phase and the liquid phase. If \(n_w = n_h = 24\) and \(n_b = 36\), the cage is an ideal complete large cage (5\(^{12}\)\(^{6}\)). If \(n_w = n_h = 20\) and \(n_b = 30\), the cage is an ideal complete small cage (5\(^{12}\)). If \(13 \geq n_h \geq 10\), CH\(_4\) molecules are enclosed in a half-complete (partial/incomplete) cage.

![Figure S4. Number of cages in System C at 260 K (a) in the bulk solution and (b) in the clay nanopore.](image)

**The sampling of several nucleation events.** Because the hydrate nucleation is a stochastic process, the several simulations under same conditions in System A, System B and System C are carried out. The run1, run2 and run3 present the sequence of repeated nucleation simulations. In
Figure S5, it can be seen that the slopes of the $F_{4p}OP$ in the same system with run1, run2 and run3 during the 200 ns period are roughly same. It indicates that the general trend of the speed of hydrate nucleation is same in the sequence of repeated simulations, though the hydrate nucleation is a stochastic process. At the same time, as shown in Figure S5, compared withing the sequence of repeated simulations in the bulk solution region and the sequence of repeated simulations in the pure water (without clay) system, these trends of the speed of hydrate nucleation are the same as those results in Figure 5. These results confirm that the hydrate nucleation and growth in these simulations, though, are insufficient to make an evaluation on the hydrate stochastic nucleation process, these simulations are adequate for qualitative elucidation of the hydrate nucleation and growth mechanism in the clay surface and nanopore.

**Molecular diffusion in the hydrate formation.** Figure S6 shows the time dependence of the number of H$_2$O molecules and CH$_4$ molecules moving in the solution and the clay pore in System C at 260 K. It can be seen from Figure S6 that the sum of CH$_4$ molecules in the bulk
solution region decreases, and the sum of CH₄ molecules in the clay nanopore increases. It indicates CH₄ molecules in the bulk solution diffuse into the clay nanopore. In the same time, it can be seen that the amount of the total CH₄ molecules in the bulk solution region is more than that in the clay nanopore. It is suggested that more CH₄ molecules diffuse in bulk rather than near the pores. After 200 ns by of the simulation, the amount of CH₄ molecules fluctuates around an average value. It means that the migrations of CH₄ molecules from the bulk solution region to the clay nanopore are slow after the hydrate formation in the bulk solution region. This low frequency for the transfer of CH₄ molecules reflects the obstruction of the hydrate crystals in the entrance of the clay nanopore and the slow hydrate growth in the clay nanopore. At the same time, the migration of H₂O molecules between the regions inside of and outside of the clay nanopore frequently occurs. During the 0-200 ns, the sum of H₂O molecules decrease in the clay nanopore due to the space occupied by the diffusion CH₄ molecules. After the 200 ns, few H₂O molecules transfer inside of and outside of the clay nanopore. In the future simulation (after 500 ns), the number of H₂O molecules in the clay nanopore layer would be change less. If no CH₄ molecule diffuses in clay nanopore (system A), it would be agree with the number of H₂O molecules of water layer hydrate systems in clay experiment⁹ and previous molecular simulation research studies of clays¹⁰⁻¹¹.
Figure S6. Time dependence of the number of (a) H$_2$O molecules and (b) CH$_4$ molecules moving in the solution and the clay nanopore in System C at 260 K.

Figure S7. Number of the hydrogen bonds of H$_2$O molecules in bulk solution and clay nanopore in System C at 260 K.

REFERENCES

(1) de Pablo, L.; Chavez, M. L.; Sum, A. K.; de Pablo, J. J. Monte Carlo Molecular Simulation of the Hydration of


