Supporting Information for

Formation of methane hydrate in the presence of natural and synthetic nanoparticles

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Abstract

This document contains further details of the experimental and simulation protocols used, as well as results not discussed explicitly in the main article. This includes:

- Sec. 1.1: a more detailed account of the methods used in the neutron scattering experiments, and results from further control experiments.
- Sec. 1.2: details of the samples used in the neutron scattering experiments.
- Sec. 1.3: a more detailed account of the methods used in the simulations.
- Sec. 2: an outline of how the height above the surface at which nucleation occurs is estimated in the simulations.
- Sec. 3: further simulation results, including those in the presence of the graphene sheet.
1 Methods

1.1 Neutron scattering experiments

Our neutron scattering experiments were conducted on the NIMROD\(^1\) and SANDALS\(^2\) time-of-flight neutron diffractometers at the ISIS pulsed neutron source, STFC Rutherford Appleton Laboratory (Didcot, UK). These instruments are optimized for studies of liquids and amorphous materials containing a high proportion of hydrogen (\(^1\)H), and they provide continuous access to a momentum transfer range \(0.02 < Q < 50\text{ Å}^{-1}\) where:

\[
Q = \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi}{d}
\]

(S1)

and \(\theta\) is the scattering angle, \(\lambda\) the wavelength, and \(d\) the spacing between the relevant crystal planes.

The hydrate samples were prepared \textit{in situ} on the beam-line in a cylindrical geometry null scattering titanium/zirconium alloy pressure cell, of the type originally used by Buchanan \textit{et al.}\(^3\) This cell has height 40 mm, inner diameter 15 mm and wall thickness 3 mm (see Fig. S1). The bottom of this cell has a dead-volume that contains a 10 mm steel ball bearing, and the entire cell system can be inverted with a frequency of \textit{ca.} 0.5 Hz in the neutron beam to allow mixing of the sample and the pressurizing methane gas. Temperature was controlled to within \(\pm 0.05^\circ\text{C}\) \textit{via} a circulating water-glycol heat bath. For each experiment the sealed/evacuated sample cell was first loaded with 8.3 cm\(^3\) of liquid (D\(_2\)O or D\(_2\)O + clay/silica) \textit{via} a bleed-in pipe at the cell base. Pressurized methane (CH\(_4\)) was then introduced over the liquid using a pressurized gas hand pump. Standard working conditions were 180 bar methane and 278 K. At this working pressure the sI methane hydrate is stable below 293 K.\(^3\) Methane pressure was maintained during the experiment by top-up from the hand-pump.

To ensure thorough and reproducible mixing of the methane gas and solution, we em-
ployed two agitation regimes, referred to as ‘standard’ and ‘short’. The first stage in both regimes was ‘pre-production’, which consisted of 15 min data collection, followed by 15 min shaking, then another 15 min data collection, before cooling over a 30 min interval from 298 K to 278 K. In the standard regime, we then performed the following: ‘stage 0’, 15 min data collection; ‘stage 1’, 1 shake (2 s) then 15 min data collection; ‘stage 2’, 10 shakes (20 s) then 15 min data collection; ‘stage 3’, 100 shakes (200 s) then 15 min data collection; and ‘stage 4’, 450 shakes (900 s) then 15 min data collection. We specify our time origin ($t = 0$) immediately after stage 0. We define the ‘standard agitation time’, $t_{a, st}$, as the time immediately after stage 4. Data were then collected in 15 min intervals. For the short regime, following pre-production, we performed: ‘stage 0’, 15 min data collection; ‘stage 1’, 100 shakes (200 s) then 15 min data collection. Again, we specify our time origin immediately after stage 0. The ‘short agitation time’, $t_{a, sh}$, is defined as the time immediately after stage 1. Both of these agitation regimes are shown schematically in Fig. S1.

For data correction and calibration, neutron scattering patterns were measured from each sample and also collected from: (i) the empty instrument, (ii) the empty instrument with the sample insert (but no sample container), (iii) the empty sample container, and; (iv) a 10 mm diameter cylindrical rod of vanadium that acts as a known standard scatterer. Background, multiple scattering, absorption, and normalization correction procedures were implemented by the in-house “Gudrun” suite of programs.

After corrections and normalization, the quantity that is obtained from our neutron diffraction experiment is the differential cross-section (DCS), which is defined as follows:

$$\text{DCS} = \frac{1}{N} \left[ \frac{d\sigma}{d\Omega}(Q) \right] = F(Q) + \sum_{\alpha} c_{\alpha} b_{\alpha}^2$$

where $c_{\alpha}$ and $\sigma_{\alpha} = 4\pi b_{\alpha}^2$ are, respectively, the atomic fraction and scattering cross-section of species $\alpha$, and $N$ is the number of atoms per unit volume. $F(Q)$ is the interference function.
\[ \text{INT} = F(Q) = \sum_{\alpha,\beta} c_\alpha \overline{b_\alpha} c_\beta \overline{b_\beta} [S_{\alpha\beta}(Q) - 1] \]  \tag{S3}

where \( \overline{b_\alpha} \) is the coherent scattering length of species \( \alpha \), \( S_{\alpha\beta}(Q) \) is the partial structure factor, and the sum is over all different pairs of particle types. Table S1 contains values of \( \sigma_\alpha \) and \( \overline{b_\alpha} \) for relevant nuclides. Fig. S2 illustrates the DCS and INT functions for the control CH\(_4\)-D\(_2\)O before and after agitation.

**Table S1:** Neutron scattering properties of some relevant nuclides.

| Nuclide | Total cross-section [barn] | Coherent scattering length [fm] |
|---------|----------------------------|-------------------------------|
| H       | 82.0                       | -3.7                          |
| D       | 7.6                        | +6.6                          |
| C       | 5.5                        | +6.6                          |
| O       | 4.2                        | +5.8                          |
| V       | 5.1                        | -0.3                          |
| Ti      | 4.4                        | -3.4                          |
| Zr      | 6.5                        | +7.2                          |

The DCS function oscillates about the mean scattering level, \( \sum_\alpha c_\alpha \overline{b_\alpha}^2 \), which is proportional to the average neutron scattering cross-section per atom. By reference to Table S1 we see therefore that, due to the very strong neutron scattering of hydrogen (\(^1\)H) when compared to all other nuclei in our samples, the total DCS scattering level is very sensitive to the concentration of CH\(_4\) in the system. The INT function, on the other hand, oscillates about zero. This function is the one that contains directly the structure of the sample. For crystalline materials such as the methane hydrates, the INT function includes all the normalized Bragg peaks, from which we can obtain the amount of crystal formed within the solution, again as a function of time.

The limiting DCS scattering levels, \( L_s \), were determined by averaging at high-\( Q \) (\( Q > 10 \text{ Å}^{-1} \)). As a check of our analysis procedures we confirmed that the scattering level of pure
D$_2$O (before agitation in methane) is 0.518 b sr$^{-1}$ atom$^{-1}$. In contrast, the scattering level of pure sI CH$_4$·(D$_2$O)$_{5.75}$ hydrate is approximately 1.40 b sr$^{-1}$ atom$^{-1}$. After agitation of our samples we obtained typical scattering levels of 0.7–0.8 b sr$^{-1}$ atom$^{-1}$, corresponding to a C:O ratio of around 1:20 to 1:25, meaning that on completion around one quarter of the cell volume would be occupied by sI hydrate crystals. Repeat runs on the same samples gave fluctuations in the average DCS scattering level of the order ±10% after agitation. The increase in the scattering level, $\Delta L_s(t) \equiv L_s(t) - L_s(0)$, is proportional to the dissolved methane concentration.

The INT Bragg peak areas for the (110), (200), (210) and (211) reflections from the sI methane hydrate structure were fitted to Pearson-IV (NIMROD) or pseudo-Voigt (SANDALS) line shapes as illustrated in Fig. S3. The positions of these peaks confirm that sI is the only crystal phase present, as expected, and the total area of these peaks is then directly proportional to the amount of hydrate present. While some hydrate forms during the initial stages of agitation, the growth to equilibrium after agitation takes several hours as shown in Figs. 1 and 2. A constraint here is the resolution of the instruments, which in all of our systems limits the peak width to 0.025 Å$^{-1}$, equivalent to peak broadening from a crystallite size of around 250 Å. Particles smaller than this would have caused the measured Bragg peaks to broaden further, but this effect was not observed in our data. As mentioned in the main article, all of the systems are low-viscosity liquids, with the exception of 2 wt% Laponite® B which is a strong gel former, and 2 wt% Laponite® RD which forms a thixotropic gel over ca. 6 hours. In the case of Laponite® RD and Laponite® B, increasing the concentration of nanoparticles to 2 wt % leads to the formation of a gel phase, in which the clay particles are fully dispersed due to interparticle electrostatic double-layer repulsion. For Laponite® RD this process takes place over several hours, and so we were able to compare hydrate formation in the liquid and gel phases, whereas for Laponite® B the gel forms over minutes. Fig. S4 shows that the presence of a gel phase strongly inhibits the formation of hydrate. Indeed, in the case of 2 wt % Laponite® B, only trace amounts of hydrate were formed even after
very extended agitation (4 hours of total agitation). This observation is consistent with an
excluded volume for hydrate around each clay particle, which is maximized in the gel-phase
due to the more uniform distribution of particles than in the liquid. We note from Table 1
that the average particle-particle separation is around 25 nm at this concentration, which
would imply that methane hydrate formation is inhibited up to a distance of at least 10 nm
from each particle.

1.2 Neutron scattering samples

The aim of this study is to understand the effects on methane hydrate formation of the
presence of clay and silica particles of varying hydrophilicity/hydrophobicity and at varying
concentrations. The samples studied are summarized in Table 1.

The clays we used are in the 2:1 family, for which the end members are talc and pyrophyl-
lite (uncharged, hydrophobic) and mica (highly charged, hydrophilic). To ensure dispersion
of the clays we typically prepared them in sodium substituted form, with the exception of
the high charge vermiculite which was prepared with propylammonium ($C_3H_9NH_3^+$).

Two synthetic clays were studied, Laponite® RD hectorite with dry formula unit: 6

$$\text{(Mg}_{5.5}\text{Li}_{0.3})\text{(Si}_8\text{)}\text{O}_{20}(\text{OD})_4 : \text{Na}_{0.7} \quad (S4)$$

and Laponite® B fluorohectorite with dry formula unit:

$$\text{(Mg}_{5.5}\text{Li}_{0.3})\text{(Si}_8\text{)}\text{O}_{20}\text{F}_4 : \text{Na}_{0.7} \quad (S5)$$

These synthetic clays have disc-like particles of thickness 0.92 nm and average diameter
25 nm. The surface charge density of these materials is $-0.12 \text{ C m}^{-2}$ giving $\zeta$-potentials of
around 40 mV.

We also studied two natural clays. Wyoming montmorillonite (SWy-2) was prepared in
its sodium exchanged form to give dry formula unit:

\[
(\text{Al}_{3.01}\text{Fe(III)}_{0.41}\text{Mn}_{0.01}\text{Mg}_{0.54}\text{Ti}_{0.02})(\text{Si}_{7.8}\text{Al}_{0.02})\text{O}_{20}(\text{OD})_{4} : \text{Na}^{+}_{0.61} \tag{S6}
\]

This clay has typical particle size of 0.92 nm thickness and lateral dimensions around 1–2 \(\mu\)m. The layer charge density is 0.10 C\(\text{m}^{-2}\) and \(\zeta\)-potential around \(-37\) mV. This natural clay has greater particle-to-particle compositional variations than the synthetic Laponites, including the possibility of more hydrophobic regions. Secondly of the natural clays we prepared high charge Eucatex vermiculite with interlayer propylammonium ions of composition:

\[
(\text{Mg}_{5.44}\text{Fe(III)}_{0.5}\text{Ti}_{0.13}\text{Ca}_{0.13}\text{Cr}_{0.01}\text{K}_{0.01})(\text{Si}_{6.13}\text{Al}_{1.87})\text{O}_{20}(\text{OD})_{4} : (\text{C}_{3}\text{H}_{7}\text{NH}_{3}^{+})_{1.29} \tag{S7}
\]

This material occurs naturally as macroscopic flakes, and it was exfoliated by exchanging with propylammonium counterions, dried and ground in a rotary mill to give typical particle size 10 \(\mu\)m. The surface charge density of this material is \(-0.21\) C\(\text{m}^{-2}\). Spherical silica nanospheres of 20 nm and 80 nm diameter were supplied unfunctionalized by Nanocomposix (http://nanocomposix.com/). These particles have \(\zeta\)-potentials of \(-45.3\) and \(-33.7\) mV respectively.

All measurements were made in heavy water \(\text{D}_2\text{O}\) as this provides a strong coherent signal and avoids the high background resulting from incoherent scattering from \(\text{H}_2\text{O}\). In the case 2 wt % Laponite\textsuperscript{R} B we conducted agitation over around 4 hours in total, with data collection of around an hour after each step. The lack of hydrate Bragg peaks after this extended regime pointed strongly towards hydrate inhibition around the solid particles. In the case of 2 wt % Laponite\textsuperscript{R} RD we conducted two complete cycles of agitation. In cycle \#1 we observed Bragg peak formation after the usual 15 minutes final agitation. The hydrate crystals were then melted at 298 K. After this aging, allowing a gel to form, the process was repeated in cycle \#2. As shown in Fig. S4, this second cycle showed much reduced Bragg
peak intensities.

In addition, to examine the effect of possible impurities and cell surfaces, particularly after initial mixing, we also conducted experiments on the following samples, using the ‘short’ agitation regime: control (no additives), 0.5 wt % Laponite® RD, excess 360 mesh Fe powder (Sigma Aldrich), 0.5 wt % graphene oxide (prepared by standard Hummer’s method), and 5 wt % C_{12}E_{6} hexaethylene glycol monododecyl ether surfactant (Sigma). Results are shown in Fig. S5 and show no positive effect on the growth or rate of hydrate formation.

1.3 Molecular dynamics simulations

Coarse grained MD simulations contained 6846 water and 1154 methane molecules. Water was modeled using the mW model,\textsuperscript{7} which represents a water molecule as a single site that interacts with its neighbors through both two- and three-body potentials. Despite its simplicity, mW gives a good description of water’s structural and thermodynamic quantities,\textsuperscript{7} and has been successfully applied in studies of heterogeneous ice nucleation (see e.g. Refs. 8–12). It has also been used in studies of homogeneous hydrate nucleation.\textsuperscript{13,14} Methane-methane and methane-water interactions were described by the potential outlined by Jacobson and Molinero,\textsuperscript{15} but using the reparametrization given by Knott et al.,\textsuperscript{14} which improves the solubility of methane at higher pressures.

A fcc slab was produced by cleaving a fcc crystal with lattice constant 0.390 nm along its (111) direction. The slab consisted of 2640 atoms, had a depth of 5 atomic layers, and was approximately $6.1 \times 5.7 \, \text{nm}^2$ in surface area. As described in Refs. 10 and 11, the water and methane interacted with the surface sites via the 12-6 Lennard-Jones potential:

\begin{equation}
U(r) = 4\epsilon_{SX} \left[ (\sigma_{SX}/r)^{12} - (\sigma_{SX}/r)^{6} \right]
\end{equation}

where ‘S’ indicates a surface interaction site, and ‘X’ indicates either a water (‘W’) or methane (‘M’) molecule. For all simulations involving the fcc slab, $\epsilon_{SM} = 0.72 \, \text{kcal/mol}$,
$\sigma_{SM} = 0.251$ nm and $\sigma_{SW} = 0.234$ nm. Values of $\epsilon_{SW} = 0.18, 1.17, 1.76, 2.82, 3.40$ and 4.42 kcal/mol were used, giving rise to monomer adsorption energies to the surface of 0.82, 5.32, 8.01, 12.83, 15.47 and 20.11 kcal/mol, respectively. For the graphene simulations, a single sheet of 1392 carbon atoms with C–C bond length 0.142 nm was generated. The dimensions of the sheet were $6.2 \times 5.9$ nm$^2$. As in Refs. 8,9,11,12, the water and methane molecules interacted with the graphene carbon atoms via the two-body part of the Stillinger-Weber potential (upon which the mW model is based):

$$\phi_{2B}(r) = A \epsilon'_{SX} \left[ B \left( \frac{\sigma'_{SX}}{r} \right)^4 - 1 \right] \exp \left[ - \frac{\sigma'_{SX}}{r - a \sigma'_{SX}} \right]$$

(S9)

where $A$, $B$ and $a$ are constants given in Ref. 7. For all simulations involving graphene, we used $\epsilon'_{SM} = 0.27$ kcal/mol, $\sigma'_{SM} = 0.390$ nm, and $\sigma'_{SW} = 0.320$ nm. Values of $\epsilon'_{SW} = 0.06, 0.67$ and 1.31 kcal/mol were used, giving rise to monomer adsorption energies of 0.80, 8.94 and 17.48 kcal/mol, respectively.

All simulations involving mW used the LAMMPS simulation package. The velocity Verlet algorithm was used to propagate the equations of motion of the water molecules, using a 10 fs time step. (The equations of motion for the fcc slab and graphene sheet were not integrated.) Temperature was maintained using the Nosé-Hoover thermostat (with a chain length of 10) with relaxation times of 1 ps. An anisotropic barostat with relaxation time 5 ps was employed along the $z$ dimension of the simulation cell i.e. the $x$ and $y$ dimensions remained fixed. Periodic boundary conditions in all three dimensions were used. For each surface hydrophilicity, a 100 ns isothermal-isobaric simulation was performed at 250 K and 900 atm, which resulted in a phase separated mixture of methane and water. To quantify the amount of dissolved methane, we considered the largest cluster of connected methane molecules (using a neighbor cutoff of 0.5 nm) to be the gas phase. Methane molecules not part of this cluster were considered to be in solution. Typical initial water-to-methane ratios for the fcc surface varied from 25:1 to 41:1, significantly higher than 6:1 that one obtains
by only considering the total number of methane molecules in the simulation. Five initial configurations were selected from the second half of this trajectory, and the velocities were randomized according to the Maxwell-Boltzmann distribution for a temperature of 250 K, and the target temperature of the thermostat was decreased at a rate of 0.1 K/ns. The equations of motion were integrated until nucleation was observed, which took on the order of 100 ns. We note that although these conditions result in a high driving force for nucleation, similar protocols have been used previously to successfully investigate heterogeneous ice nucleation. This suggests that if the surfaces were to act as catalysts for methane hydrate formation, then this would be observed with the simulation techniques used in this study.

We have also conducted simulations with an all-atom model of methane, water and the clay mineral kaolinite. The force field of Tse, Klein and McDonald was used to describe the methane, TIP4P/ICE was used for the water and the CLAYFF potential was used for the kaolinite. The total number of water and methane molecules was 2944 and 512, respectively, and the surface area of the kaolinite was approximately 4.6×5.4 nm². The water and methane were constrained using the SHAKE algorithm. Particle-mesh Ewald with a grid-spacing of 0.1 nm and an interpolation order of 4 was used to treat the long-range electrostatics. A cut-off of 0.9 nm was used for the real-space interactions. Dynamics were propagated with a leap-frog integrator as implemented in the GROMACS 4.5.5 simulation package with a time step of 2 fs. The system was prepared by melting a hydrate crystal at 425 K and 400 bar (394.8 atm) for 20 ns, resulting in a phase separated system with the methane at the silicate terminated face, and a planar interface separating the methane and water. Initial configurations were then drawn from this trajectory, with the velocities randomized with a target temperature of 245 K. The temperature was maintained with a Nosè-Hoover chain (length 10) and pressure of 500 bar was maintained using a Parrinello-Rahman barostat, allowing the direction normal to the kaolinite surface to fluctuate.
2 Evaluating the height from the surface at which nucleation occurs

The gray shaded regions in Fig. 5 provide estimates for the range of heights above the surface at which nucleation was observed. To provide this estimate, we first identified which water molecules were ‘hydrate-like’ according to the CHILL+ algorithm. By using a depth first search algorithm, we then identified the largest connected cluster of hydrate-like molecules, and measured the average height of the water molecules in the cluster from the surface. (Due to the periodic boundary conditions applied in our simulations, there are two distances to the surface, and we are interested in the minimum distance to the surface.) The height of nucleation was then specified as the average height of the largest cluster as it passed a size of 50 molecules in the simulation. (Although the largest cluster could decrease in size once reaching a size of 50, it was not observed that the cluster ever fully dissolved once the largest cluster exceeded 50.)

3 Results from the MD simulations

In Figs. S6 and S7 we present snapshots and density profiles, respectively, from the remaining two fcc surfaces not presented in the main article. The results are in good agreement with those presented in the main paper. In Figs. S8 and S9 we show respectively the snapshots and density profiles above the graphene sheets. Again, the results are in good agreement with those from the fcc surface. We note however, that at the surface with adsorption energy 8.94 kcal/mol (panel (b) in Figs. S8 and S9), only one simulation resulted in hydrate nucleation; in the other four simulations heterogeneous ice nucleation was observed.

In Table S2 we show the measured non-equilibrium freezing temperatures $T_f$ (temperatures at which nucleation of gas hydrate was observed). Especially at the fcc surfaces, it is clear that there is some variability in $T_f$, and it appears that as the surface hydrophilicity
increases, so too does $T_f$. While one might interpret this as evidence of the surface promoting nucleation, inspection of Figs. 5, S7 and S9 shows that this increase in $T_f$ appears to be correlated with an increase in the concentration of dissolved methane. The number densities of methane in the bulk regions are also given in Table S2. In fact, as the hydrophilicity of the surface increases, there is a driving force for more water to bind to the surface; this causes the curvature of the methane-water interface to increase, which in turn increases the amount of dissolved methane in solution (due to Laplace pressure effects). For an in-depth discussion of the effects of methane-water interfacial curvature on hydrate nucleation see Ref. 18. Due to the finite size of our simulations, it is difficult to evaluate how the surfaces investigated would affect the dissolved methane concentration in the thermodynamic limit. We can conclude from this analysis, however, that the presence of particles can affect the rate of hydrate nucleation indirectly, if they have a significant effect on uptake of methane into solution.

Table S2: Measured non-equilibrium freezing temperatures (in Kelvin) of gas hydrate in the presence of different surfaces ($T_{f,i}$ is the freezing temperature of simulation $i$, $T_{f,avg}$ is the average). The numbers in parentheses are the adsorption energies of a water molecule to the surface (in kcal/mol). The average methane number density in the bulk region $\bar{\rho}_M$ is also given (nm$^{-3}$).

| System   | $T_{f,1}$ | $T_{f,2}$ | $T_{f,3}$ | $T_{f,4}$ | $T_{f,5}$ | $T_{f,avg}$ | $\bar{\rho}_M$ |
|----------|-----------|-----------|-----------|-----------|-----------|-------------|------------|
| fcc (0.82) | 220       | 223       | 221       | 220       | 217       | 220         | 0.62       |
| fcc (5.32) | 228       | 227       | 227       | 229       | 227       | 227         | 0.83       |
| fcc (8.01) | 231       | 227       | 233       | 229       | 231       | 230         | 0.94       |
| fcc (12.82) | 232      | 231       | 231       | 233       | 229       | 231         | 1.09       |
| fcc (15.46) | 238      | 239       | 236       | 240       | 243       | 239         | 1.40       |
| fcc (20.11) | 246      | 240       | 241       | 242       | 242       | 242         | 1.74       |
| graphene (0.80) | 224   | 226       | 226       | 224       | 229       | 226         | 0.76       |
| graphene (8.94) | 236 | -         | -         | -         | -         | -           | 0.68       |
| graphene (17.48) | 227 | 224       | 223       | 226       | 225       | 225         | 0.68       |
Figure S1: Schematic of the ‘standard’ and ‘short’ agitation regimes used in the neutron scattering experiments. The ‘pre-production’ stage consisted of: 15 min data collection, then 15 min shaking, followed by another 15 min data collection. This was done at a temperature of 298 K. The sample was then cooled to 278 K over 30 min. We then followed either the ‘standard’ or ‘short’ agitation regime, as outlined in the schematic. We define $t = 0$ immediately after stage 0 in both regimes. The “standard agitation time”, $t_{a,st}$, is the time elapsed after stage 4 in the standard regime. Similarly, the “short agitation time”, $t_{a,sh}$ is the time elapsed after stage 1 in the short regime. After the agitation time, data was collected in 15 min intervals. The pressure was 180 bar CH$_4$ throughout, for both agitation regimes. The inset (bottom right) shows a picture of the shaker cell used, along with a schematic of the rocking motion.
Figure S2: DCS and INT scattering functions (Eqs. S2 and S3) from the control sample, measured before (stage 0) and after (stage 4) shaking, using the standard agitation regime (see Fig. S1). Note that the DCS function oscillates about the mean scattering level, which is proportional to the average neutron scattering cross-section per atom. The level of the DCS increases as methane CH\textsubscript{4} is dissolved in the D\textsubscript{2}O. The INT function, on the other hand, oscillates about zero. This function is the one that contains directly the structure of the sample. The increase in the scattering level, \( \Delta L_s(t_{a, st}) \equiv L_s(t_{a, st}) - L_s(0) \), is shown schematically by the arrows.
Figure S3: Example fits to the (110), (200), (210) and (211) reflections from the sI methane hydrate, obtained from the control sample after the final 15 minutes agitation. Data were fitted to (a) Pearson-IV (NIMROD) or (b) pseudo-Voigt (SANDALS) peak shapes.
Figure S4: Methane hydrate formation as studied by neutron diffraction from solutions of CH$_4$ + D$_2$O at 180 bar and 278 K, showing inhibition of hydrate formation in gel systems containing 2 wt % Laponite® RD and Laponite® B. The data show the interference functions (INT, Eq. S3) after agitation, compared to that of the control of CH$_4$ + D$_2$O. In the case of Laponite® RD, hydrate forms after the first cycle of agitation in the liquid phase, but is strongly inhibited after the second cycle of agitation and gel formation. In the case of the Laponite® B fluoro-clay sample, gel formation is rapid and hydrate formation is strongly inhibited even after more than 5 hours in the first cycle (the sample was agitated for 4 hours in total). These data are strong evidence for an excluded volume to hydrate formation around each of the clay particles.
Figure S5: Methane hydrate formation as studied by neutron diffraction from solutions of CH$_4$ + D$_2$O at 180 bar and 278 K using the ‘short’ agitation regime, showing the effects of possible contaminant and cell surface materials on the formation of sI hydrate. The blue shaded region shows the time over which agitation was performed. (a) $A_{\text{Bragg}}(t)/\Delta L_s(t_{a,\text{sh}})$, where $t_{a,\text{sh}} = 18 \text{ min } 20 \text{ s}$. (b) $A_{\text{Bragg}}(t)/A_{\text{Bragg}}(t_{f,\text{sh}})$ (filled symbols) and $\Delta L_s(t)/\Delta L_s(t_{f,\text{sh}})$ (empty symbols), where $t_{f,\text{sh}} = 360 \text{ min}$. This plot demonstrates that while the uptake of methane into solution reaches its final value relatively quickly, the growth of sI hydrate is relatively slow.
Figure S6: Snapshots of gas hydrate nucleation obtained from MD simulations in the presence of the fcc surface. The adsorption energy of a single water molecule to the surface is (in kcal/mol): (a) 5.32 and (b) 12.83. The large light-gray spheres show the surface atoms, the small dark-gray spheres show methane molecules and bonds between hydrate-like water molecules are shown by red lines. (For clarity, the remaining water molecules are not shown.) As in Figs. 3 and 4, nucleation is seen away from the surface.

Figure S7: Number densities of water $\rho_W(h)$ (blue) and methane $\rho_M(h)$ (red) vs distance $h$ from the fcc surfaces shown in Fig S6. (The labels (a) and (b) are the same as Fig. S6.) The shaded gray areas span the range of $h$ at which nucleation was observed: in all cases, $h > 1$ nm. The first peak in the methane density profile in (a) corresponds to approximately nine molecules at the $6.1 \times 5.7$ nm$^2$ surface.
Figure S8: Snapshots of gas hydrate nucleation obtained from MD simulations in the presence of the graphene surface. The adsorption energy of a single water molecule to the surface is (in kcal/mol): (a) 0.80, (b) 8.94 and (c) 17.48. The large light-gray spheres show the graphene carbon atoms, the small dark-gray spheres show methane molecules and bonds between hydrate-like water molecules are shown by red lines. (For clarity, the remaining water molecules are not shown.) As in Figs. 3, 4 and S6, nucleation is seen away from the surface.

Figure S9: Number densities of water $\rho_W(h)$ (blue) and methane $\rho_M(h)$ (red) vs distance $h$ from the graphene surfaces shown in Fig S8. (The labels (a), (b) and (c) are the same as Fig. S8.) The shaded gray areas span the range of $h$ at which nucleation was observed: in all cases, $h > 1$ nm.
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