

Supporting Information

Homogeneous nucleation rate of methane hydrate formation under experimental conditions from seeding simulations

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S1. ESTIMATION OF THE VALUES OF $\Delta\mu_{nucleation}$ BY ASSUMING CONSTANT ENTHALPY OF DISSOCIATION (EQ. 28 OF REF. 1) AS COMPARED TO THE MORE ELABORATED EQ. 18 OF REF. 1

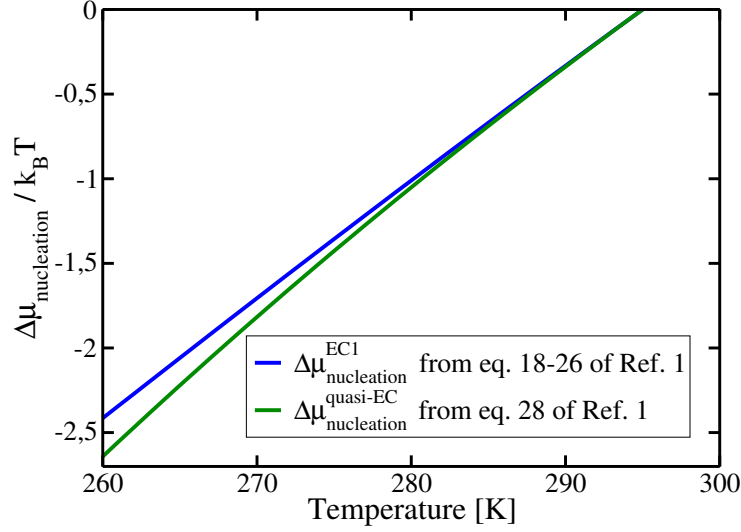


FIG. S1: Values of $\Delta\mu_{nucleation}$ as obtained from assuming a constant enthalpy of dissociation (Eq. 28 of Ref. 1) as compared to the more elaborated Eq. 18 of Ref. 1. The value of 295 K was used as T3 at 400 bar.

S2. ESTIMATION OF THE NUCLEATION RATE OF A METHANE HYDRATE USING BRUTE FORCE SIMULATIONS AND \bar{q}_3 ORDER PARAMETER

As was mentioned in the main text, the estimation of the nucleation rate of a methane hydrate from the brute force simulations should not be affected much by the choice of the order parameter used to differentiate between solid and liquid phases in the system. In order to confirm that, we repeated the calculations presented in the section III.B of the main text where we used $\bar{q}_{3scaled}$ order parameter, now using the \bar{q}_3 order parameter. It was shown in Table II of the main text that the difference between the sizes of the solid clusters obtained with \bar{q}_3 and $\bar{q}_{3scaled}$ order parameters is the largest among the parameters that were considered in the paper, therefore the comparison of the nucleation rates of a hydrate obtained using both of them should give an idea to what extent the choice of the order parameter influences the results from the brute force runs.

In Fig. S2 we presented changes in time of the size of the largest cluster of solid present in the brute force systems, obtained with the use of \bar{q}_3 order parameter. From these results, we estimated the value of $\tau_{1/2} = 1.629 \mu s$, assuming that the nucleation occurred in a particular system if the size of the cluster of a hydrate is larger than 250 molecules of water (the cluster is postcritical). Using this value, we estimated the nucleation rate of a hydrate using Eq. 10 in the main text, obtaining the value of $2.68 \cdot 10^{30} 1/(m^3 \cdot s)$. Compared with the value of $2.71 \cdot 10^{30} 1/(m^3 \cdot s)$ that we obtained using the $\bar{q}_{3scaled}$ order parameter, it is clear that the estimation of the nucleation rate is hardly affected by the choice of the order parameter.

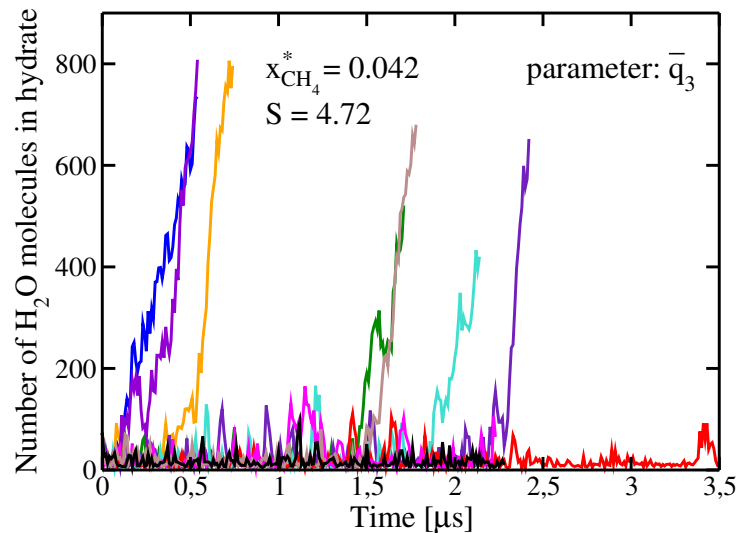


FIG. S2: Changes in time of the size of the largest cluster of methane hydrate in a brute force NpT simulations (260 K, 400 bar) of homogeneous supersaturated solution of methane in water ($S = 4.72$). The results were obtained with the use of \bar{q}_3 order parameter.

S3. RESULTS OF THE SEEDING TECHNIQUE IN A SUPERSATURATED SOLUTION ($S = 4.72$) OF METHANE IN WATER - COMPARISON OF THE RESULTS OBTAINED WITH DIFFERENT ORDER PARAMETERS

In this section we present the results of the Seeding technique used for a supersaturated solution of methane in water ($S = 4.72$, Fig. 2a in the main text). In the main text we presented only the results obtained for the system in which the size of the inserted seed was critical ($r = 0.95$ nm, see Fig. 6 in the main text), while here - in Fig. S3 - all of the results for different seeds sizes and four order parameters considered in the study are shown. Since the MCG order parameter gives the size of the cluster of hydrate as a number of molecules of methane in the solid phase, the results were scaled by a factor of 5.75 in order to obtain the number of molecules of water in the cluster. In order to estimate the size of the critical cluster firstly we conducted a crude search of the possible range in which the critical size is using only 4 or 5 trajectories. Based on these results we could already infer if the cluster was too small (seeds were melting in most of the runs) or too big (seeds were growing in most of the runs). After that we carried out additional simulations for the systems with the seeds of the sizes closer to the critical value. The size of the critical cluster was estimated for the system in which the number of growing and melting seeds inserted into liquid was around 50%.

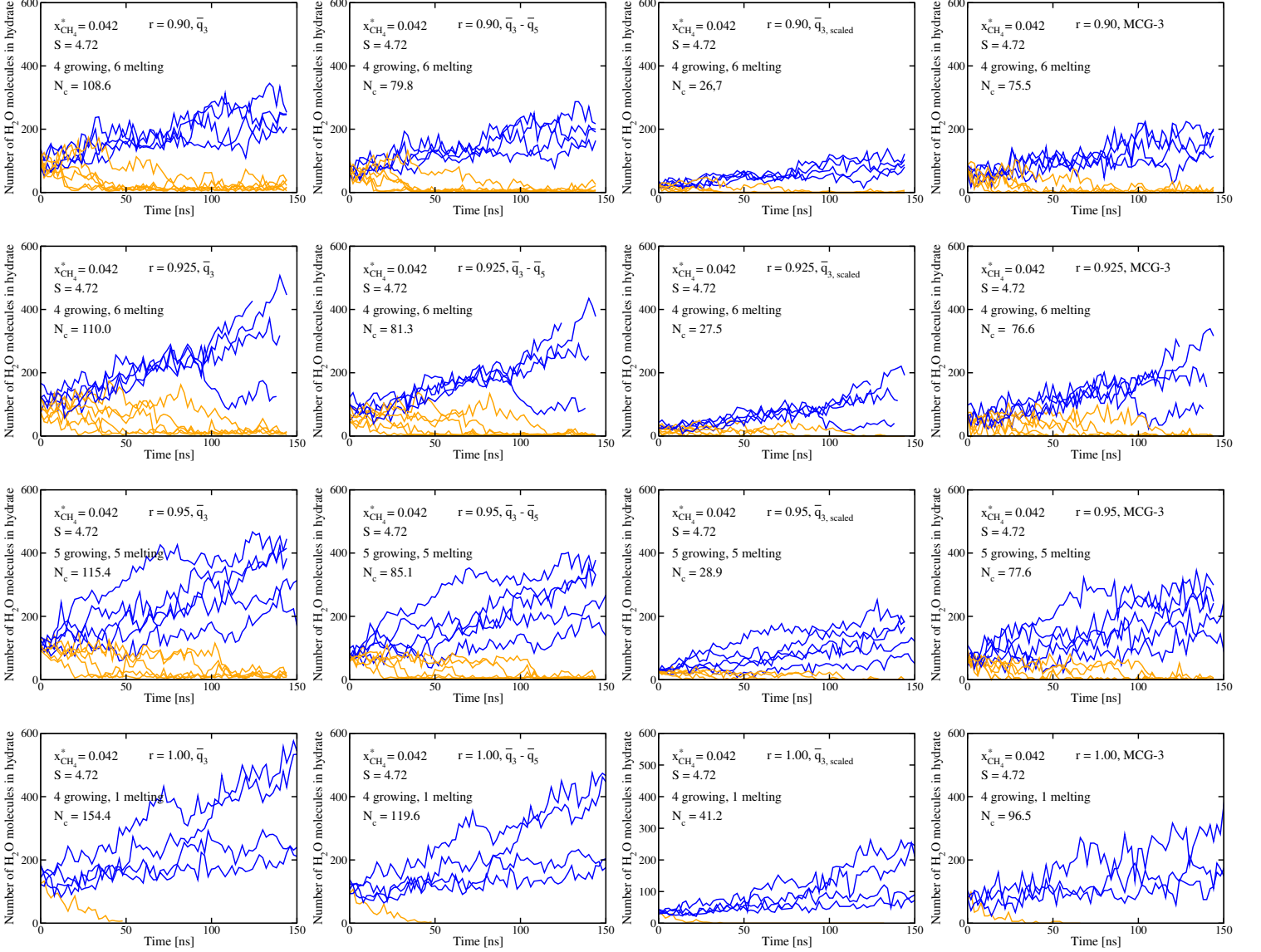


FIG. S3: Changes in time of the size of the largest cluster of methane hydrate obtained for seeding simulations (260 K, 400 bar, NpT) in a supersaturated solution of methane in water ($S = 4.72$). The results were obtained with the use of \bar{q}_3 , linear combination of the \bar{q}_3 and \bar{q}_5 , $\bar{q}_{3, scaled}$ and MCG-3 order parameters for the seeds of different sizes.

S4. RESULTS OF THE SEEDING TECHNIQUE FOR A TWO-PHASE GAS-LIQUID SYSTEM WITH $S = 1$

The results of the Seeding technique used for a solution of methane in water for which the concentration of methane was equal to the equilibrium solubility under the studied conditions of temperature and pressure - 260 K and 400 bar. The system used was two-phase gas-liquid system with a planar interface (see Fig. 2c in the main text). In Fig. S4 results obtained with the use of $\bar{q}_{3, scaled}$ parameter are presented for the seeds of different sizes. In order to estimate the size of the critical cluster firstly we conducted a crude search of the possible range in which the critical size is using only 4 trajectories. Based on these results we could already infer if the cluster was too small (seeds were melting in most of the runs) or too big (seeds were growing in most of the runs). After that we carried out additional simulations for the systems with the seed of the sizes closer to the critical value. The size of the critical cluster was estimated for the system in which the number of growing and melting seeds inserted into liquid was around 50%. For the system at $S = 1$ the size of the cluster of solid is critical for the seed radius of 1.95 nm.

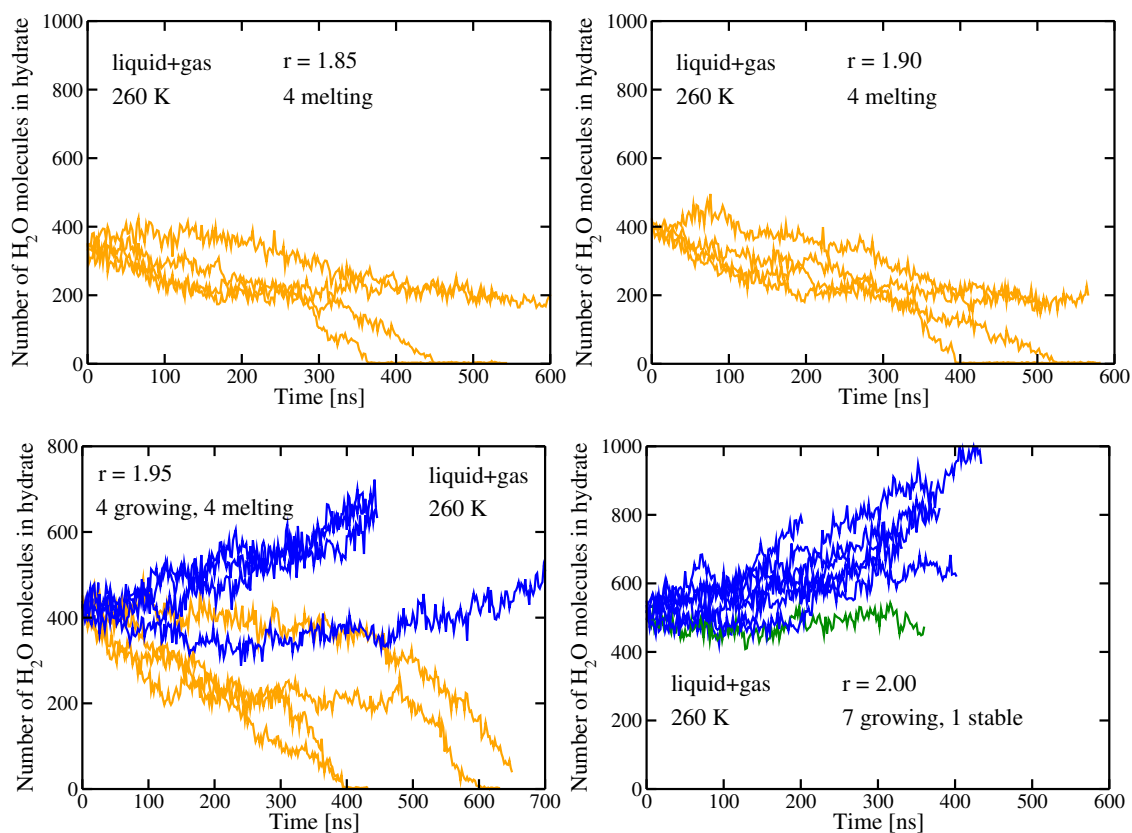


FIG. S4: changes in time of the size of the largest cluster of methane hydrate obtained for seeding simulations (260 k, 400 bar, NpT) in a solution where the concentration of methane was equal to the equilibrium solubility under the same conditions of temperature and pressure. the results were obtained with the use of $\bar{q}_{3,scaled}$ order parameter for the seeds of different sizes.

S5. NUCLEATION RATES OBTAINED WITH THE USE OF THE SEEDING TECHNIQUE FOR A TWO-PHASE GAS-LIQUID SYSTEM WITH $S = 1$

TABLE S1: Nucleation rates J in Seeding runs in a solution of methane in water (260 K, 400 bar) in which the concentration of methane was equal to the equilibrium solubility under the studied conditions of temperature and pressure, determined according to Eq. (4) from the main text, along with values of quantities that were required in the calculations. The values of the error of J were estimated based on the estimated errors of $N_c^{\text{CH}_4}$ and $\Delta\mu_{\text{nucleation}}^{\text{EC}}$ and are provided in the table as a $\log_{10}J$. The values of ΔG_c are provided in $k_B T$ units. The results obtained with the use of the \bar{q}_3 order parameter are presented as a comparison to the values obtained for the $\bar{q}_{3\text{scaled}}$ and \bar{q}_{12} order parameters presented in Table V in the main text. In the calculations also the values of $\rho_{\text{liq}}^{\text{CH}_4} = 3.03 \cdot 10^{26} \text{ 1/m}^3$, $\rho_{\text{solid}}^{\text{CH}_4} = 4.6 \cdot 10^{27} \text{ 1/m}^3$, $\Delta\mu_{\text{nucleation}}^{\text{EC}}/k_B T = 2.42$ were used.[1] The superindex EC indicates experimental conditions. Additionally, interfacial free energies γ (in mJ/m^2) obtained from seeding are provided (see Section III.E in the main text).

| | \bar{q}_3 | $\bar{q}_{3\text{scaled}}$ | \bar{q}_{12} |
|---|--------------------|----------------------------|-------------------|
| $N_C^{\text{H}_2\text{O}}$ | 722 | 479 | 418 |
| $N_C^{\text{CH}_4}$ | 126 | 83 | 73 |
| Z | 0.032 | 0.039 | 0.042 |
| ΔG | 151.9 | 100.7 | 88.0 |
| $f_{\text{CH}_4}^+$ [1/s] | $2.3 \cdot 10^9$ | $1.4 \cdot 10^9$ | $1.1 \cdot 10^9$ |
| J [1/($\text{m}^3 \cdot \text{s}$)] | $2 \cdot 10^{-32}$ | $3 \cdot 10^{-10}$ | $8 \cdot 10^{-5}$ |
| $\log_{10}J$ | -32 ± 2 | -4 | -10 |
| γ [mJ/m ²] | 37.3 | 32.5 | 31.1 |

S6. $\langle(N_c^{\text{CH}_4}(t) - N_c^{\text{CH}_4}(t_0))^2\rangle$ VS TIME FOR THE CRITICAL CLUSTER IN A SUPERSATURATED SOLUTION ($S = 4.72$) OF METHANE IN WATER OBTAINED WITH \bar{q}_3 , LINEAR COMBINATION OF \bar{q}_3 AND \bar{q}_5 AND MCG-3 ORDER PARAMETERS.

In this section we present the data used in order to determine values of attachment rates (reported in Table IV in the main text) for the supersaturated system ($S = 4.72$) for which the Seeding technique was employed, obtained with the use of \bar{q}_3 , linear combination of \bar{q}_3 and \bar{q}_5 and MCG-3 order parameters.

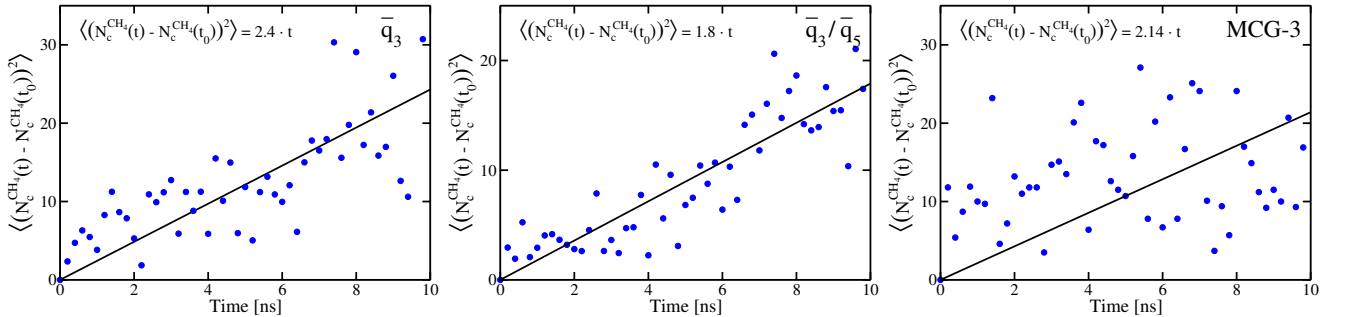


FIG. S5: $\langle(N_c^{\text{CH}_4}(t) - N_c^{\text{CH}_4}(t_0))^2\rangle$ for the critical cluster in a supersaturated solution of methane in water ($S = 4.72$) obtained with a) \bar{q}_3 , b) linear combination of \bar{q}_3 and \bar{q}_5 and c) MCG-3 order parameters. Simulations were carried out at 260 K and 400 bar. Results were obtained as an average of 10 independent runs. The attachment rate can be calculated as a half of the slope of the linear fit of the changes of $\langle(N_c^{\text{CH}_4}(t) - N_c^{\text{CH}_4}(t_0))^2\rangle$ with time. The parameters of the fits are presented in the figures.

S7. $\langle(N_c^{\text{CH}_4}(t) - N_c^{\text{CH}_4}(t_0))^2\rangle$ VS TIME FOR THE CRITICAL CLUSTER IN A TWO-PHASE GAS-LIQUID SYSTEM ($S = 1$) OBTAINED WITH \overline{q}_3 ORDER PARAMETER.

Below, the data used in order to determine values of the attachment rate (reported in Table V in the main text) for the two-phase gas-liquid system ($S = 1$) for which the Seeding technique was employed, obtained with the use of \overline{q}_3 order parameter.

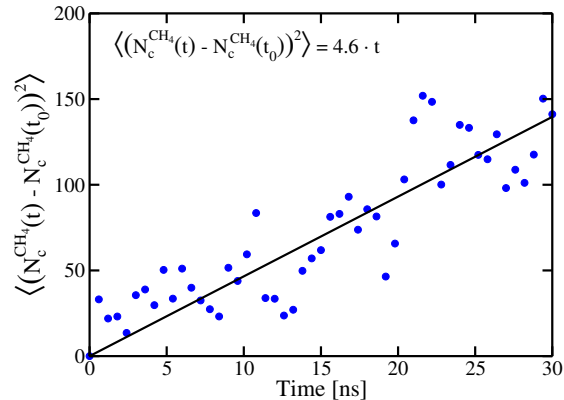


FIG. S6: $\langle(N_c^{\text{CH}_4}(t) - N_c^{\text{CH}_4}(t_0))^2\rangle$ for the critical cluster in a solution of methane in water in which the concentration of methane is equal to its equilibrium solubility at 260 K and 400 bar, obtained with the \overline{q}_3 order parameter. Simulations were carried out at 260 K and 400 bar. Results were obtained as an average of 8 independent runs. The attachment rate can be calculated as a half of the slope of the linear fit of the changes of $\langle(N_c^{\text{CH}_4}(t) - N_c^{\text{CH}_4}(t_0))^2\rangle$ with time. The equation of the fit is presented in the figure.

REFERENCES

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- [1] Grabowska, J.; Blazquez, S.; Sanz, E.; Zerón, I. M.; Algaba, J.; Míguez, J. M.; Blas, F. J.; Vega, C. Solubility of Methane in Water: Some Useful Results for Hydrate Nucleation. *J. Phys. Chem. B* **2022**, *126*, 8553.