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Molecular Insights into Factors Affecting the Generation Behaviors, Dynamic Properties, and Interfacial Structures of Methane Gas Bubbles

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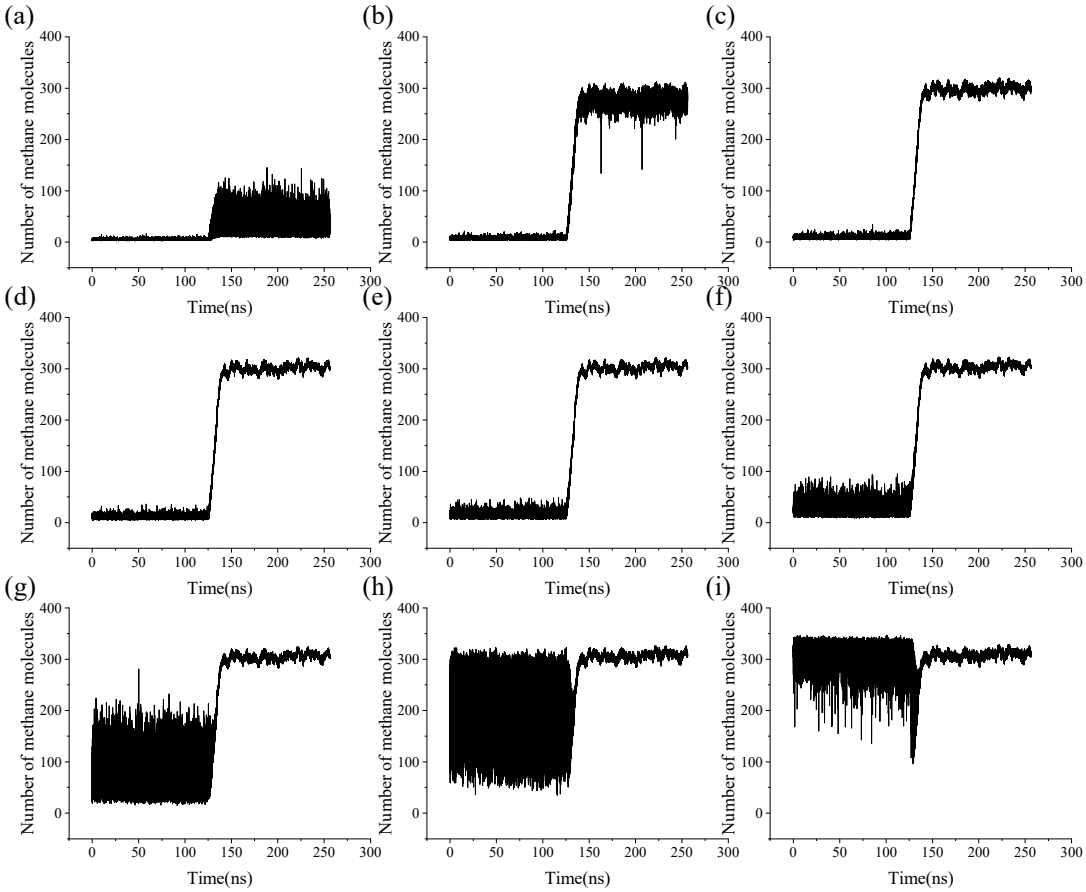

Figure S1. Time evolutions of $N_{methane}$ in the largest methane cluster in Sys3_5MPa calculated by cluster analysis method with cutoff lengths of (**a**) 0.4 nm, (**b**) 0.45 nm, (**c**) 0.5 nm, (**d**) 0.55 nm, (**e**) 0.6 nm, (**f**) 0.65 nm, (**g**) 0.7 nm, (**h**) 0.75 nm and (**i**) 0.8 nm.

Computation details of independent simulations to obtain inner pressures of methane gas bubbles.

Methane molecules were randomly placed in cubic boxes with the size of 6.0 × 6.0 × 6.0 nm, with the number of methane molecules present in Table S1. NVT simulations were carried out for each system for 20 ns, and the temperatures set for each system were present in Table S1. The pressure of each system was obtained by averaging the pressure every 10 ps.

All the simulations were performed in GROMACS 2019.3 [48]. The TraPPE model [42] was used for methane molecules. Equations of motion were integrated with a time step of 2 fs. Periodic boundary conditions were applied in all the three Cartesian directions [44]. V-rescale thermostat [45] were used to control the temperature of the systems with time constants of 0.2 ps. The van der Waals interactions were calculated with a cutoff of 1.2 nm.

Table S1. Details of number density of methane molecules, number of methane molecules and the temperature set in the simulation.

Number density (nm^{-3})	Number of methane	Temperature (K)
11.11	2399	293.15
10.94	2363	298.15
10.74	2321	303.15
10.54	2276	308.15
10.35	2235	313.15
10.46	2259	313.15
10.64	2299	313.15
10.90	2353	313.15
11.07	2392	313.15
11.20	2420	313.15
11.05	2387	313.15
10.79	2331	313.15
10.46	2260	313.15

Steps for identifying outermost methane and water molecules in bubble-solution systems. [35–40]

i) Identify the largest methane cluster in the system by cluster method with a cutoff length of 0.53 nm.
ii) Determine the geometric center of the largest methane cluster.
iii) Translate the origin to the geometric center of the largest methane cluster.

iv) For a given methane molecule, a spherical probe with a radius of 0.373 nm is translated from origin at a direction from origin toward this methane molecules. After the probe has just crossed this methane molecules, the probe moves with a step = 0.05 nm.
v) Counting of the number (N_m) of methane molecules which come in contact with the probe after the probe has crossed the methane molecule considered in step **iv**.
vi) Terminate the movement of probe once the probe has moved 60 step (1.5 nm).
vii) Identify the methane molecule considered in step **iv**, as one of the outermost methane molecules, if $N_m = 0$.

viii) The positions of oxygen atoms are used to represent the positions of water molecules. For a given water molecule, a spherical probe with a radius of 0.31668 nm is translated from this water molecule at a direction from this water molecule toward origin. After the probe has just crossed this water molecules, the probe moves with a step = 0.05 nm.
ix) Counting of the number (N_w) of water molecules which come in contact with the probe after the probe has crossed the water molecule considered in step **viii**.
x) Terminate the movement of probe once the probe has moved 60 step (1.5 nm).
xi) Identify the water molecule considered in step **viii**, as one of the outermost water molecules, if $N_w = 0$.