Journal Name

ARTICLE TYPE

Cite this: DOI: 00.0000/xxxxxxxxxx

Molecular simulations on the stability and dynamics of bulk nanobubbles in aqueous environments†

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Table S1 Potential parameters of the atomistic force field.

Model	ε (kJ/mol)	σ (Å)	q_H (e)	d_{OH} (Å)	d_{OM} (Å)	∠H-O-H
TIP4P/Ice	0.8822	3.1668	0.5897	0.9572	0.1577	104.52
OPLS-UA	1.23	3.73				

Table S2 Potential parameters of the coarse-grained force field.

Model	ε (kcal/mol)	σ (Å)	λ
water	6.189	2.3925	23.15
methane	0.340	4.08	0
water-methane	0.180	4.00	0

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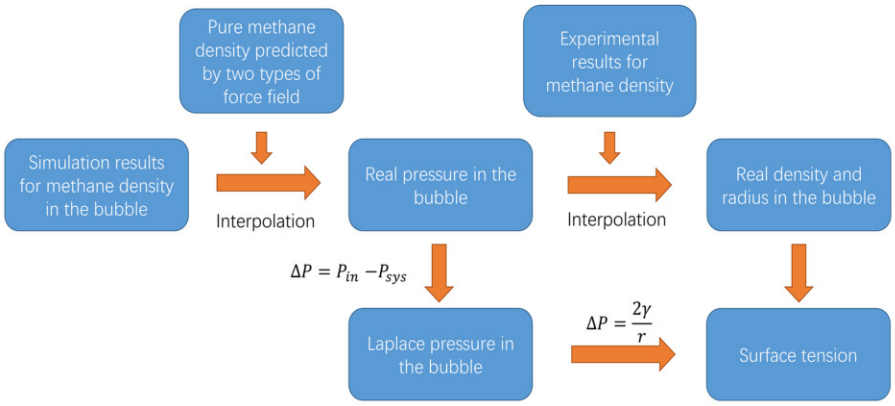

Fig. S1 A schematic diagram for obtaining the Laplace pressure and nanobubbles surface tension.

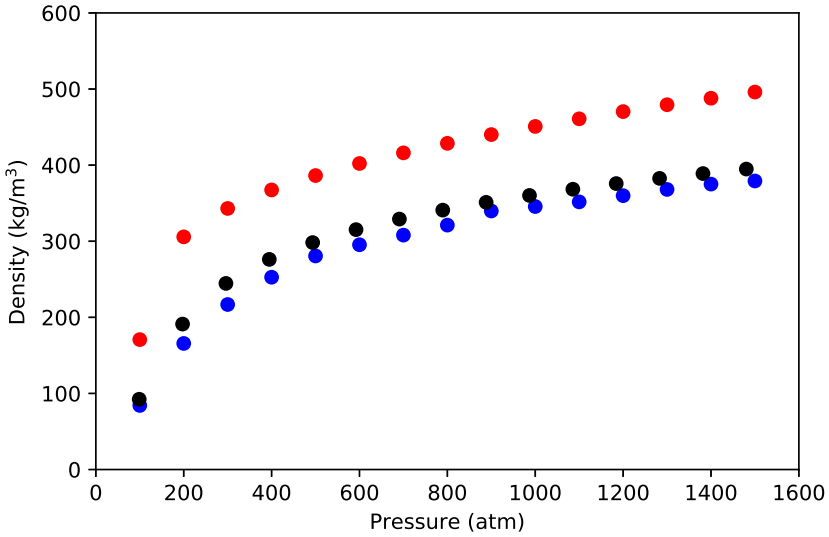

Fig. S2 Pure methane density ranging from 100 bar to 1500 bar for the two different force fields. The blue and red dots represent the methane density predicted by the atomistic and coarse-grained force field, respectively. The black dots represent the methane density from experimental results. [1]

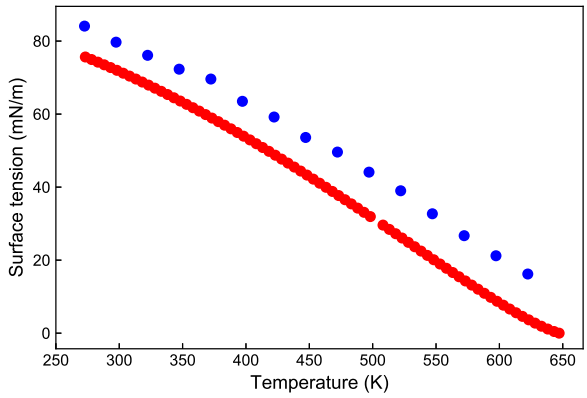

Fig. S3 Experimental surface tension[2] and TIP4P/Ice predicted surface tension.[3] The red dots represent the experimental results and the blue dots represent the TIP4P/Ice results.[4]

Table S3 Bubble diameter and methane density in nanobubble before correction for two types of force fields.

Diameter (nm)	Density (kg/m^3)	Diameter(nm)	Density (kg/m^3)
3.36 (0.10)	360.36 (26.01)	3.41 (0.03)	469.56 (12.83)
4.47 (0.06)	338.86 (13.33)	4.39 (0.03)	442.74 (9.23)
5.61 (0.07)	314.91 (10.85)	5.40 (0.03)	421.80 (8.19)
6.81 (0.06)	294.31 (7.94)	6.40 (0.03)	406.60 (6.21)
8.06 (0.05)	276.48 (5.16)	7.41 (0.03)	394.87 (5.36)
9.30 (0.06)	260.29 (4.91)	8.42 (0.03)	384.89 (4.59)
10.58 (0.06)	245.56 (3.62)	9.43 (0.03)	377.33 (4.01)

Table S4 Nanobubble size, density, inside pressure, surface tension and standard deviation results for the atomistic force field simulation.

diameter (nm)	density (kg/m^3)	solubility (%)	pressure (bar)	surface tension (mN/m)
3.29 (0.05)	361.08 (25.73)	1.95 (0.16)	1243.41 (228.29)	95.47 (13.25)
4.47 (0.06)	338.86 (13.34)	1.49 (0.05)	936.38 (121.99)	93.42 (11.75)
5.60 (0.06)	314.91 (10.85)	1.23 (0.04)	752.46 (68.10)	92.27 (7.83)
6.80 (0.06)	294.32 (7.95)	1.01 (0.03)	596.86 (49.49)	84.75 (7.46)
8.05 (0.06)	276.47 (5.17)	0.82 (0.04)	486.24 (20.54)	77.64 (4.21)
9.29 (0.05)	260.30 (4.92)	0.74 (0.03)	427.42 (16.54)	76.17 (3.19)
10.55 (0.05)	245.56 (3.62)	0.70 (0.04)	380.06 (10.13)	73.64 (2.30)

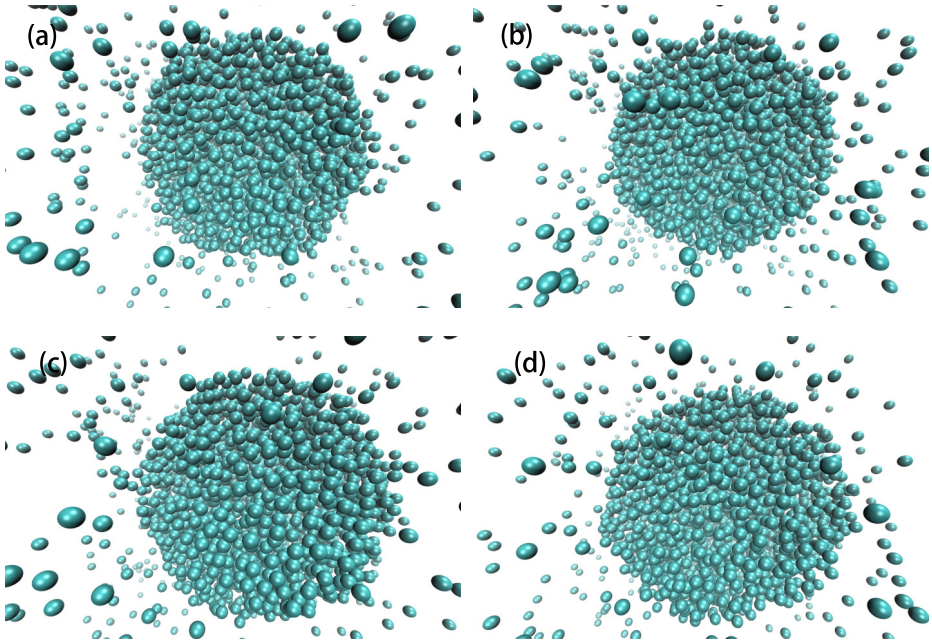

Fig. S4 The snapshots of 10 nm single-bubble system during 100-150 ns (same scale of 5 nm single-bubble system). All the snapshots were saved in the same perspective. The 10 nm bubble can maintain a better spherical shape and shake around the original position.

Table S5 Nanoubble size, density, inside pressure, surface tension and standard deviation results for the coarse-grained force field simulation.

diameter (nm)	density (kg/m^3)	solubility (%)	pressure (bar)	surface tension (mN/m)
3.68 (0.04)	376.09 (10.15)	0.68 (0.09)	1212.79 (136.43)	102.11 (11.78)
4.74 (0.04)	354.37 (7.94)	0.54 (0.05)	939.02 (85.56)	99.13 (9.41)
5.83 (0.05)	335.64 (7.70)	0.42 (0.03)	756.90 (65.51)	95.52 (8.85)
6.93 (0.05)	320.99 (6.26)	0.36 (0.03)	641.08 (43.90)	93.51 (7.02)
8.05 (0.05)	308.94 (5.67)	0.32 (0.02)	561.65 (34.61)	92.54 (6.39)
9.17 (0.05)	298.11 (5.04)	0.30 (0.01)	500.34 (26.46)	91.45 (5.55)
10.30 (0.06)	289.70 (4.64)	0.28 (0.01)	458.60 (21.51)	92.01 (5.06)

Table S6 Water density in the bulk for different nanobubble systems.

System	4 nm	5nm	6 nm	7 nm	8 nm	9 nm	10 nm
Density (kg/m^3)	997.68	997.86	997.92	997.81	997.96	998.01	998.18

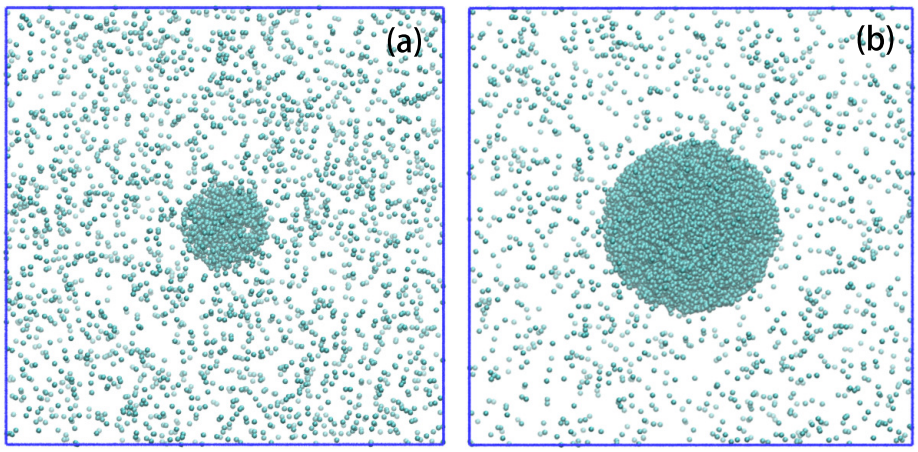

Fig. S5 The initial configurations for (a) 5 nm and (b) 10 nm nanobubble coefficient calculation. The cyan spheres represent the methane molecules. The dimensions of the boxes are both 25 nm × 25 nm × 25 nm

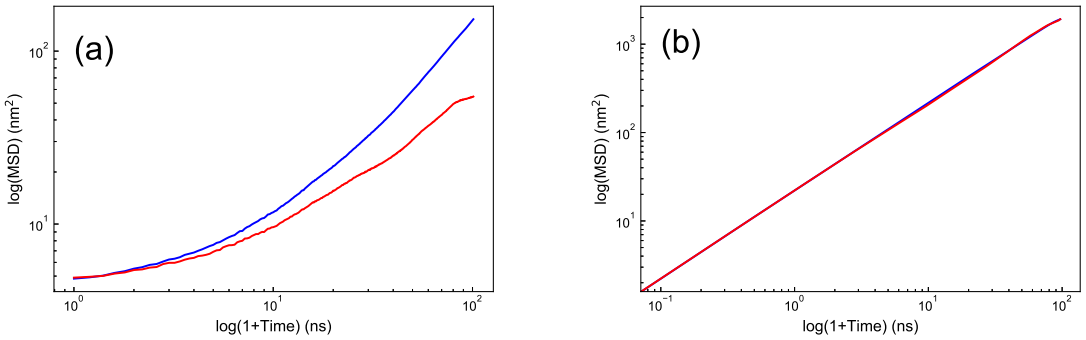

Fig. S6 log(MSD)-log(time) plot for nanobubble and methane molecules. The result for nanobubble is shown in (a) and that of methane is shown in (b). Blue and res line represent the result for 5 nm bubble system and 10 nm bubble system, respectively.

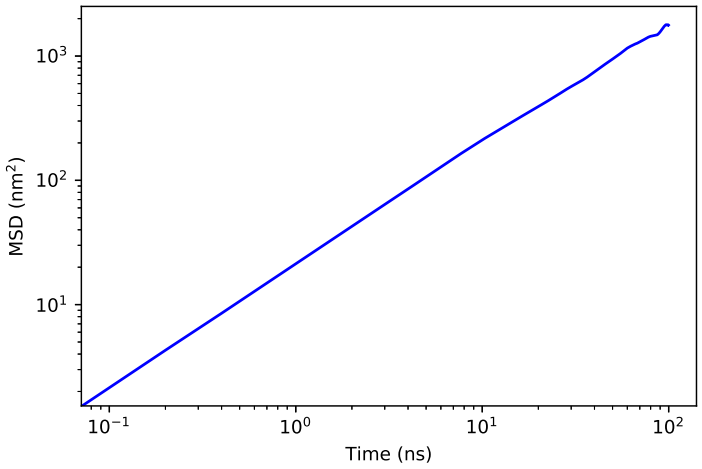

Fig. S7 log(MSD) - log(time) plot for Methane in water without nanobubble.

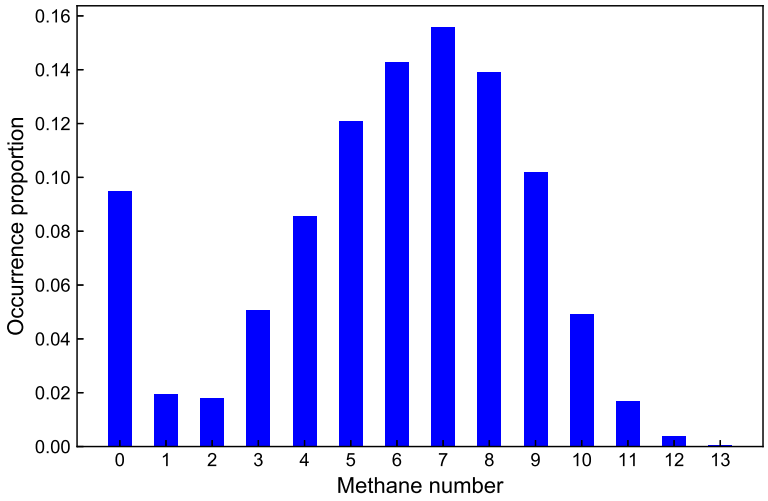

Fig. S8 Statistical data of occurrence proportion of methane molecules around tested methane.

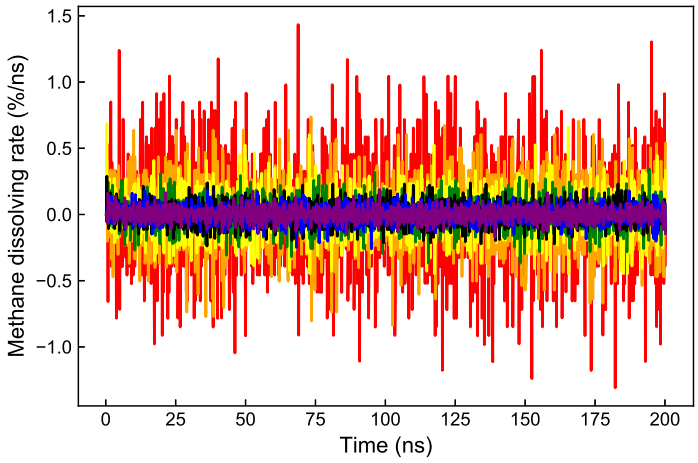

Fig. S9 Variation of methane concentration in the bulk during the simulation time. The red, orange, yellow, green, black, blue, purple represent the variation of the methane concentration in the bulk for 4-10 nm single-bubble system, respectively. The positive and negative represent the increase and decrease of concentration. The absolute value shows the variation strength.

Notes and references

1 U. Setzmann and W. Wagner, *Journal of Physical and Chemical reference data*, 1991, **20**, 1061–1155.

2 N. Vargaftik, B. Volkov and L. Voljak, *Journal of Physical and Chemical Reference Data*, 1983, **12**, 817–820.

3 R. Sakamaki, A. K. Sum, T. Narumi and K. Yasuoka, *The Journal of Chemical Physics*, 2011, **134**, 124708.

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