Supporting information for

Bridging Solution Properties to Gas Hydrate Nucleation through Guest Dynamics

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Simulation details: In this study, the Gromacs package was used to perform all simulations.¹ The force field models used in this work are given in Table S1. The crossinteractions between atoms were obtained according to the Lorentz-Berthelot combining rules, except those between water and carbon dioxide were from Duan and Zhang.⁸ The simulations were performed under NPT conditions at 50 MPa, and 250 and 273.15 K. Hereafter, only temperature is specified for each simulation. Pressure and temperature were held constant by using the Parrinello-Rahman barostat (with a time constant of 4 ps) and the Nosé-Hoover thermostat (with a time constant of 2 ps), respectively. Each simulation system contains 2944 water molecules and varying numbers of a specific guest species (with an interval of 25 guest molecules), where the guest molecules were randomly placed in the liquid phase. Fig. S1 shows a typical initial configuration with a guest concentration of 0.085 mol fraction. To obtain solution properties, each system was firstly equilibrated at target condition for 3 ns. Then, 5 nslong simulation for each system was performed to generate data for hydration properties. Six parallel simulations with different initial velocities for all molecules were used to evaluate the error. To observe the hydrate nucleation events, 80 ns or 400 ns long simulations were performed. Details of these runs can be found in Table S2. Note that we did not observe gas bubble formation in any of our simulations, except the propane system at 273.15 K. The solubility data of guests in water at 273.15 K and 50 MPa are summarized in Table S3.

Molecule	Atom/site	$\sigma(nm)$	ε (KJ/mol)	q (e)	Geometric parameters
TIP4P-Ice water ²	0	0.316680	0.882170	0.0000	$l_{\rm OH} = 0.09572 \ nm$
	Н	0.000000	0.000000	0.5897	\angle HOH = 104.52°
	М	0.000000	0.000000	-1.1794	
Methane ³	CH ₄	0.373000	1.230096	0.0000	
Carbon dioxide ⁴	С	0.279180	0.239832	0.5888	$l_{\rm CO} = 0.1163 \ nm$
	Ο	0.300000	0.687244	-0.2944	$\angle \text{OCO} = 180.00^{\circ}$
Argon ⁵	Ar	0.354200	0.775744	0.0000	
Krypton ⁵	Kr	0.365500	1.487466	0.0000	
Xenon ⁵	Xe	0.404700	1.920652	0.0000	
Radon ⁶	Rn	0.414500	2.427822	0.0000	
Propane ⁷	C1 (CH ₂)	0.396000	0.465584	0.0000	$l_{\rm C1C2} = 0.1540 \ nm$
	C2 (CH ₃)	0.376000	0.897912	0.0000	$\angle C2C1C2 = 109.47^{\circ}$

Table S1 Details of the models used in the present molecular simulations.



Fig. S1. A typical initial configuration which contains 2944 water molecules and 275 methane molecules. Water molecules are in red. Methane molecules are in cyan. The image was generated with VESTA-3.⁹

T (K)	Guest	Concentration range	Total runs*	Total simulation time (ns)
273.15	CH_4	0.033 - 0.120	60A+18B	1920
	Kr	0.033 - 0.120	60A+18B	1920
	Xe	0.033 - 0.092	36A+18B	1728
	Rn	0.017 - 0.064	24A+18B	1632
	C_3H_8	0.017 - 0.064	24A+18B	1632
	CH_4	0.017 - 0.078	42A+12C	5136
250	CO_2	0.033 - 0.120	66A+12C	5328
	Ar	0.048 - 0.092	30A+12C	5040
	Kr	0.033 - 0.064	18A+12C	4944
	Xe	0.017 - 0.041	12A+12C	4896
	Rn	0.017 - 0.048	12A+18C	7296
	C_3H_8	0.017 - 0.048	12A+18C	7296

Table S2 List of all simulations in this study

*A: 8 ns-long simulations; B: 80 ns-long simulations; C: 400 ns-long simulations. The A simulations and the first 8 ns of B and C simulations were used to get the solution properties. The B and C simulations were used to evaluate the induction time for gas hydrate nucleation.

Guest	Solubility (10 ⁻³ mole fraction)	Reference
CH_4	6.5	10
C_3H_8	0.2	11
CO_2	43.5	12
Ar	21	13
Kr	45	13
Xe	91	13
Rn	-	

Table S3 The solubility of guests in water at 273.15 K and 50 MPa.^a

^{*a*} The solubility data for CH₄, C_3H_8 , and CO₂ are from the thermodynamics models (Refs. 10, 11, 12). Values for noble gases were obtained by using the Henry's constant from Ref. 13.

Estimating the entropy change: Previous studies have shown that the pair correlation entropy can give a reasonable estimate of the entropy change when spherical solutes are inserted in water.¹⁴ Therefore, we assume that the pair correlation entropy can give a reasonable estimate for the relative change in the system entropy with increasing guest concentration. The pair correlation entropy can be determined from the atom-atom radial distribution functions for a binary system with:¹⁴⁻¹⁵

$$S/Nk_B = 2\pi\rho \sum_{\alpha,\beta} x_{\alpha} x_{\beta} \int_0^\infty \{g_{\alpha\beta}(r) \ln g_{\alpha\beta}(r) - [g_{\alpha\beta}(r) - 1]\} r^2 dr$$
(1)

where $g_{\alpha\beta}(r)$ is the pair correlation function between particles of type α and type β , x_{α} is the mole fraction of particles of type α , N is the total number of particles and $k_{\rm B}$ is the Boltzmann constant. In this study, we only use the radial distribution functions between the centers of mass. This means that we have ignored all orientational contributions to the pair correlation entropy. In this sense, we underestimate the total entropy change with increasing guest concentration, but expect relative changes are successfully captured.



Fig. S2. (A) The change of the average $F_{4\phi}$ with increasing methane concentration for the water molecules within 0.54 nm of methane molecules at 250 K. (B) The change in the pair correlation entropy and methane-methane, methane-water, and water-water contributions with increasing methane concentration at 250 K.



Fig. S3. The same as Fig. S2 but for carbon dioxide at 250 K.



Fig. S4. (A) Methane-methane radial distribution functions (RDF) for different solution concentrations, and (B) the change in of the coordinate number of methane molecules in the first (contact pairs) and second shell (solvent-separated pairs) of methane molecules with the increasing concentration at 250 K.



Fig. S5. The same as Fig. S4 but for carbon-carbon of carbon dioxide at 250 K.

Critical concentration and self-diffusion coefficient of guest molecules: We first determined the critical concentrations for those systems with the guest concentration around the previous reported critical concentrations (methane hydrate, ~0.08 mol% at 275 K;¹⁶ methane hydrate, ~0.04 mol% at 250 K;¹⁷ carbon dioxide hydrate, 0.088-0.092 mol%.¹⁸). Simulations were performed for 80 ns at 273.15 K and 400 ns at 250 K. We tracked the nucleation events with the FSICA method,¹⁹ and defined the critical concentration as the smallest guest concentration where the averaged induction times for hydrate nucleation are within 30 ns at 273.15 K and 300 ns at 250 K. These values were chosen based on three considerations: 1) the hydrate forms via a nucleation process and not spinodal decomposition (we also need to evaluate the solution properties within the waiting time); 2) the hydrate nucleates within reasonable simulation time; 3) the systems at 250 K were allowed more time for cage rearrangement due to the slower molecular dynamics. Here, the induction time of hydrate nucleation is defined as the average time required for the appearance of the largest cage cluster (consisting of at least two face saturated cages) that does not disappear. A summary of the induction times is provided in Table S4. We found results similar to those of previous studies¹⁶⁻¹⁸ except for slight difference for methane hydrate nucleation at 273.15 K and carbon dioxide nucleation at 250 K because of somewhat different force-field parameters (see Table S5). Accordingly, the self-diffusion coefficient of guest molecules at these critical concentrations can be obtained (Table S6). Interestingly, a common critical value of the self-diffusion coefficient of different guest molecules is identified. Then, two or three sets of long simulations were performed for other guests with concentrations close to the critical one to examine nucleation behavior and self-diffusion coefficients. Gas hydrate nucleation was not observed for argon and carbon dioxide at 273.15 K with the concentrations considered in this work. Additionally, we have shown only the results for krypton at 273.15 K in Fig. 3 because krypton and methane gave very similar results (see Fig. 3A and Table S6). It should be noted that at high concentration, propane solutions degas readily, therefore we were unable to determine the critical concentration within 80 ns.

T (K)	Guest	Mole fraction	Induction time (ns)	Average induction
		0.071	43 10 78 26 80* 20 08 46 42 20 34	
(CU	0.071	45.10, 78.20, 80, 20.08, 40.42, 20.54	20
	CH4	0.078	19.76, 13.94, 10.30, 23.20, 23.30, 28.62	20
		0.085	6.02, 9.94, 14.12, 7.74, 3.40, 17.10	10
	17	0.071	38.38, 31.14, 80*, 26.06, 51.72, 49.82	>46
	Kr	0.078	16.78, 16.76, 21.56, 28.34, 13.2, 25.92	20
		0.085	11.62, 13.00, 4.74, 8.94, 18.08, 13.10	12
		0.041	80*, 80*, 80*, 71.46, 72.36, 80*	>///
070 15	Xe	0.048	29.44, 34.60, 18.76, 13.70, 36.86, 45.16	29
273.15		0.056	17.52, 21.02, 24.84, 20.46, 16.64, 12.86	19
		0.041	62.58, 34.02, 28.60, 55.14, 49.46, 15.82	41
	Rn	0.048	42.46, 25.44, 39.8, 33.56, 15.56, 27.32	31
		0.056	16.32, 10.20, 12.96, 5.72, 8.50, 20.82	12
		0.041	No nucleation event	>80
	C ₂ H ₂	0.048	80*, 80*, 80*, 62.38, 80*, 80*	>77
	0,118	0.056	degas, 41.52, degas, 49.70, degas, 49.60	-
		0.064	degas, degas, degas, degas, degas, degas	-
CH ₄ CO ₂ Ar	СЦ	0.041	288.70, 400*, 400*, 122.58, 400*, 250.88	>310
	CH4	0.048	209.26, 300.32, 327.40, 202.08, 148.64, 390.76	263
	CO	0.092	400*, 400*, 400*, 235, 400*, 400*	>373
	CO_2	0.099	70.64, 109.10, 8.60, 340.82, 287.74, 328.76	191
	A	0.064	400*, 400*, 400*, 400*, 400*, 400*	>400
	Ar	0.071	400*, 284.06, 224.3, 277.34, 143.16, 375.18	>284
	V	0.041	400*, 257.26, 400*, 367.84, 400*, 400*	>371
	Kr	0.048	155.98, 133.32, 389.40, 147.12, 65.2, 296.62	198
250		0.025	400*, 400*, 400*, 304.26, 400*, 400*	>384
-	Xe	0.033	356.56, 371.68, 309.56, 145.68, 291.64, 226.52	284
		0.041	93.92, 201.80, 122.20, 122.08, 161.16, 246.28	158
		0.025	332.30, 400*, 400*, 182.28, 400*, 328.36	>340
	Rn	0.033	400*, 389.80,166.98, 113.86, 253.26, 338.14	277
		0.041	182.44, 115.78, 110.80, 189.78, 286.36, 162.54	174
		0.033	400*, 400*, 400*, 400*, 400*, 400*	>400
	C3H8	0.041	356.66, 162.60, 153.44, 201.18, 160.40, 161.08	199
	50	0.048	63.88, 104.86, 131.10, 91.56, 146.96, 76.38	102

Table S4 Summary of the induction time for hydrate nucleation

* indicates that hydrate did not nucleate within our simulation time. Degas means that a gas bubble of guest molecules nucleates.

Model	Atom/site	$\sigma(nm)$	ε (KJ/mol)	q (e)		Critical concentration
CH4 (Jiménez-Ángeles and	CIL	0 27200	1 212000	0.0000		~0.08 mol fraction
Firoozabadi ¹⁶)	CI14	0.37200	1.518000	0.0000		(275 K)
CH4 (this work)	CU	0 27200	1 220006	230096 0.0000 0.08		0.0831 ± 0.0072 mol fraction
	CI14	0.37300	1.230090		(273.15 K)	
CO ₂ (this work)	С	0.27918	0.239832	0.5888	$l_{\rm CO} = 0.1163 \ nm$	0.0959 ± 0.0035 mol fraction
(Z D)	0	0.30000	0.687244	-0.2944	$\angle OCO = 180.00^{\circ}$	(250 K)
CO ₂ He <i>et al.</i> $(I)^{18}$	С	0.27570	0.233865	0.6512	$l_{\rm CO} = 0.1149 \ nm$	0.088 mol fraction
(EMP2)	0	0.30330	0.669335	-0.3256	$\angle OCO = 180.00^{\circ}$	(250 K)
CO_2 He <i>et al.</i> (II) ¹⁸	С	0.28000	0.224478	0.7000	$l_{\rm CO} = 0.116 \ nm$	0.092 mol fraction
(TraPPE)	0	0.30500	0.656806	-0.3500	$\angle OCO = 180.00^{\circ}$	(250 K)

Table S5 Model parameters used in this work and by previous studies. ^{ab}

a. The parameters used for CH₄ combing with TIP4P/ICE water model reasonably predict the phase equilibria of methane hydrate.²⁰ *b*. The interaction parameters for CO₂ and H₂O used in this work²¹ predict the solubility of CO₂ better than those used by He *et al.*¹⁸

Temperature (K)	Molecule	Critical x_g (mol fraction)	Critical D_g (10 ⁻⁵ cm ² /s)
273.15	CH_4	0.075 ± 0.004	0.083 ± 0.007
	Kr	0.075 ± 0.004	0.080 ± 0.013
	Xe	0.045 ± 0.004	0.079 ± 0.010
	Rn	0.052 ± 0.004	0.044 ± 0.006
	C_3H_8	-	-
250.00	CH_4	0.045 ± 0.004	0.020 ± 0.001
	Kr	0.045 ± 0.004	0.020 ± 0.003
	Ar	0.067 ± 0.004	0.022 ± 0.001
	CO_2	0.096 ± 0.004	0.021 ± 0.001
	Xe	0.029 ± 0.004	0.019 ± 0.002
	Rn	0.029 ± 0.004	0.015 ± 0.003
	C_3H_8	0.037 ± 0.004	0.010 ± 0.002

Table S6. The critical concentration and the corresponding critical self-diffusion

coefficient of guest species.^a

^{*a*} the lines between Xe and Rn are to separate of sI and sII formers.

The self-diffusion coefficient of water: We have investigated the relationship between guest and water mobilities. According to the Stokes-Einstein relation,²²

$$D_g = kT/6\pi\eta R_g \tag{2}$$

where k is Boltzmann constant, T is the temperature, η is the viscosity of the solvent, and R_g is the hydrodynamics radius. When Eqn. (2) is valid, then the ratio D_w/D_g should be proportional to the value R_g/R_w independent of the temperature and viscosity of water. Such behavior is demonstrated in Fig. S6 for the present methane solutions. Since different guest species have different R_g and these guests, except radon and propane, have essentially the same critical values for D_g , the corresponding critical values of D_w are not constant. Therefore, the value of D_w is apparently not appropriate as an indicator for hydrate nucleation.



Fig. S6. Plot of the self-diffusion coefficient of water (D_w) vs that of methane (D_g) for the methane concentrations considered in this work at 273.15 K. The linear-regression fitted line is in red, and its slope defines the ratio of hydrodynamic radii between methane and water.

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