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Effects of cage type and adsorption face on the cage–methane adsorption interaction: Implications for hydrate nucleation studies

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ABSTRACT

The adsorption interaction between a water cage and a methane molecule, shown by the cage–methane PMF (potential of mean force), is key to understanding hydrate formation mechanisms. We investigate how the cage type and adsorption face affect the PMF. The PMF is found to depend on the face size rather than the cage type, and the adsorption interaction becomes stronger as the face size increases. However, once the face becomes 7-membered, it no longer adsorbs methane but allows methane crossing it to enter the cage. The results suggest that a preferential direction may exist during hydrate nucleation and growth.

1. Introduction

Gas hydrates are crystalline compounds consisting of a hydrogen-bonded network of polyhedral water cavities (the hosts) that encage small gas molecules (the guests), and methane hydrate is a prototype. Because methane hydrate is abundant in permafrost regions and the seafloor of continental margins, it is considered to be a potential energy resource [1,2]. Methane hydrate is also important for flow assurance in the oil and gas industry and in the environment for global warming. In hydrate research fields, the molecular mechanism of methane hydrate formation is a fundamental issue relating to many still open topics, such as stochastic nucleation [1,3–4], the memory effect [5,6], and structural transition [7,8]. Early studies on the hydrate nucleation mechanism mainly include the labile cluster hypothesis (LCH) proposed by Sloan and co-workers [1,9], which emphasized the aggregation of cage-like water clusters, and the local structuring hypothesis (LSH) proposed by Radhakrishnan and Trout [10], which emphasized the adjustment of water molecules around a local, ordered arrangement of gas molecules. Recently, Guo and co-workers [11] proposed the cage adsorption hypothesis (CAH), in which the cage–methane adsorption interaction is the inherent driving force controlling hydrate formation. The CAH also predicts that an intermediate amorphous hydrate phase should occur before the final crystalline hydrate forms, which is supported by the MD simulations of methane hydrate formation [12,13], and by the two-step mechanisms of hydrate formation [14,15].

In this Letter, we focus on the adsorption interaction between a water cage and a methane molecule. Given a water cage formed in a methane aqueous solution, when a dissolved methane molecule approaches the cage, the cage will adsorb the methane on one of its faces. This is considered to be a favorable step in triggering a hydrate nucleation event because the adsorbed methane can prolong the cage's lifetime and induce a new cage to form around it [16]. If the cage is located on the hydrate surface in contact with the methane solution, the step will also favor the crystal growth for the same reason. In our previous work [11], we studied the cage–methane adsorption interaction by calculating the potential of mean force (PMF) between a dodecahedral cage (5^{12}) and a methane molecule, and considered three influencing factors: the rigidity, filling status, and orientation of the cage. The main finding was that the strength of the attractive interaction between the cage and methane was comparable to the strength of hydrogen bonds. A rigid cage led to a slightly stronger adsorption interaction than a soft cage, while the filled cage with a methane molecule was no different from an empty cage. Additionally, the cage's adsorption interaction showed a kind of directionality, with the strongest interaction points oriented toward the center of the adsorption face and perpendicular to this face.

However, because just the 5^{12} cage, which has only pentagonal faces, was used in the previous work, the effects of cage type and face size on the cage–methane adsorption interaction could not be studied. These two factors are very important and should be examined carefully. Regarding the former, thousands of types of cages can occur during hydrate formation [17], and hydrate nuclei need not develop only from the 5^{12} cage initially. Regarding the latter, the size of the cage faces determines whether the methane is adsorbed on one of the cage faces or enters the cage through the face. Although it is taken for granted that a methane molecule can passage a heptagonal (or larger) face but not a hexagonal (or smaller) face, no direct evidence exists in the literature. This point is also of significance for studies on the inter-cage diffusion of guests in hydrate, especially in amorphous-phase hydrate that

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can occur during the intermediate stage of hydrate formation [14–15,17], and the structural transition of hydrate caused by high pressure [18,19]. Therefore, in this work we study how the cage type and the size of the adsorption face affect the cage–methane adsorption interaction.

2. Method

All molecular dynamics simulations were carried out using the GROMACS package [20,21]. The system was designed as a cuboid of $45 \times 30 \times 30$ Å ($x \times y \times z$), consisting of one cage, two methane molecules, and 1240 water molecules. The water molecules were described by the TIP4P/2005 potential model [22] and the methane by the OPLS-UA potential [23]. The cross interactions between water and methane were calculated according to the modified Lorentz–Berthelot combining rules (with $\chi = 1.07$) [24]. The Nosé–Hoover thermostat and Parrinello–Rahman barostat, with a period of 0.8 ps for both, were used to obtain the NPT ensemble with a temperature of 258.5 K and a pressure of 30 MPa, with a state point located in the methane hydrate phase region for the above potential models [25]. The cutoff distance was 10 Å for the Lennard–Jones potential. Periodic boundary conditions were used in all directions and the long-range interaction was calculated using the particle mesh Ewald method with a real space cutoff of 10 Å, spline order of 4, and Fourier spacing of 1.2 Å. In total, eight representative cages containing five types of faces (Figure 1) were used to check the effects of the cage type and the face size on the cage–methane adsorption interaction. The cages were all extracted from the MD trajectories for hydrate formation reported by Walsh et al. [13] using our face-saturated incomplete cage analysis [17]. The edge length of these cages was set as 2.82 Å (i.e., the average length of H-bonds), which is slightly larger than the previously used value of 2.75 Å [11].

To study the cage–methane adsorption interaction, similar to the method used in our previous work [11] we used constrained molecular dynamics simulations to calculate the potential of mean force (PMF) between a cage and a methane molecule. It is possible to constrain the distance between the cage and the methane at r_c during simulations, and then calculate the constraint mean force $F(r_c)$ exerted on them. Thus, the cage–methane PMF is equal to the integration of $F(r_c)$; that is,

$$\mathrm{PMF}(r_2) - \mathrm{PMF}(r_1) = -\int_{r_1}^{r_2} F(r_c)dr_c, \tag{1}$$

where r_1 is the constrained distance of the reference state and r_2 is an arbitrary constrained distance. For convenience, r_1 often takes a value large enough so that $\mathrm{PMF}(r_1)$ reaches zero. Therefore, the PMF can be calculated from

$$\mathrm{PMF}(r_2) = -\int_{r_1}^{r_2} F(r_c)dr_c. \tag{2}$$

In addition, because of the above constraint condition, the rotation of the combination of cage and methane will produce an entropy contribution to the PMF [21]. This should be corrected by subtracting $2k_BT/r_c$ from the original output of $F(r_c)$ in GROMACS [11]. According to the above definition, the cage–methane PMF is actually the free energy along the reaction coordinate, r_c. Using it, we can obtain the radial distribution function (RDF) by

$$\mathrm{RDF}(r) = e^{-\mathrm{PMF}(r)/k_BT}, \tag{3}$$

where k_B is the Boltzmann constant and T is the system temperature. It is not possible to calculate the cage–methane RDF directly from the MD simulations due to the problem of poor sampling, and the relevant discussion can be found elsewhere [11].

To perform the constrained MD simulations, we first defined two groups – the adsorption face and the dissolved methane. The definition of the first group differs from that in our previous work, in which the whole cage was defined as a group. The current definition removes the influence of different distances from the cage center to the different face centers on the PMF, thus enabling us to conveniently compare different PMF curves. Nevertheless, because the present definition shifts the origin of r_c from the cage center to the face center by Δr_c (= 3.1 Å for the 5^{12} cage), the difference must be considered when comparing the present and the previous PMF. Then, we placed the two groups on the x-axis in the middle of the simulation box, with the adsorption face of the cage perpendicular to the x-axis. During the simulation, the two groups could move freely but their separation was fixed at r_c. To ensure the cage face was always perpendicular to the straight line linking the face center and the dissolved methane, we additionally constrained all N_v numbers of distances between every face vertex and the dissolved methane to be equal, where N_v is the number

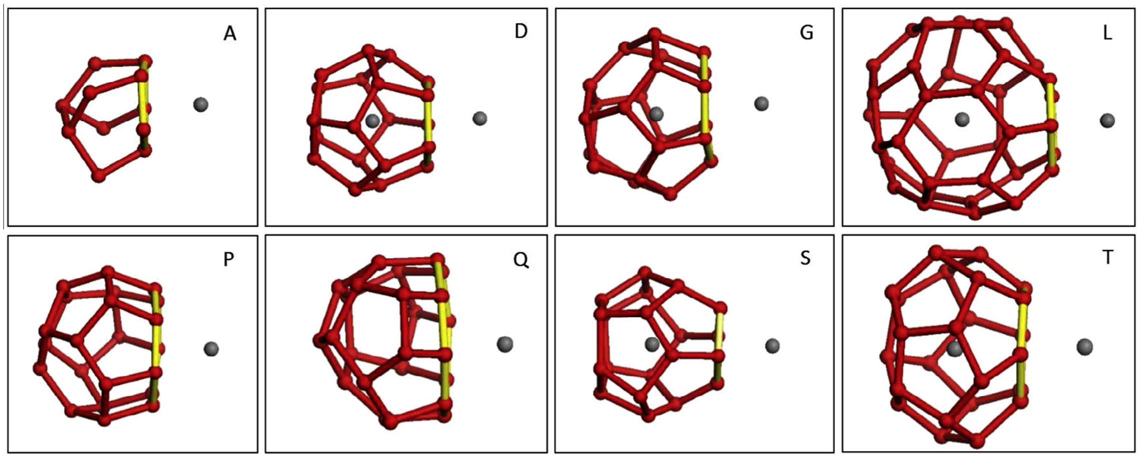

Figure 1. The different cages used in this work. The red balls are water oxygen and the gray balls are methane. The sticks are H-bonds, in which the yellow sticks indicate the adsorption face to the dissolved methane. The cage names are shown in the top right corners, respectively, and are described as follows. (A) $[5^26^3]_5$ cage, the most abundant cage in the methane solution prior to hydrate nucleation [17]. According to our previous notation, $[\ ]_5$ indicates that it is an incomplete cage with five vertices with only two shared edges for each. (D) 5^{12} cage, the most common cage in hydrates. (G) $4^15^{10}6^2$ cage, which contains 4-, 5-, and 6-membered faces and is very abundant during hydrate nucleation. (L) $5^{12}6^8$ cage, an example of a large cage. (P) $4^35^76^27^1$ cage containing a 7-membered face. (Q) $4^45^66^38^1$ cage containing an 8-membered face. (S) $4^35^66^3$ cage, a small cage containing 4-, 5-, and 6-membered faces. (T) $5^{12}6^2$ cage, the main cage in the sI hydrate.