

DYNAMIC LIFETIMES OF CAGELIKE WATER CLUSTERS IMMERSSED IN LIQUID WATER AND THEIR IMPLICATIONS FOR HYDRATE NUCLEATION STUDIES

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ABSTRACT

Recently, by performing molecular dynamics simulations in the methane-water system, we have measured the static lifetimes of cagelike water clusters (CLWC) immersed in bulk liquid water, during which the member-water molecules of CLWCs are not allowed to exchange with their surrounding water molecules [J. Phys. Chem. C, 2007, **111**, 2595]. In this study, we measure the dynamic lifetimes of CLWCs with permitting such water exchanges. It is found that the dynamic lifetimes of CLWCs are not less than the static lifetimes previously obtained, and their ratio increases with the lifetime values. The results strengthen that CLWCs are metastable structures in liquid water and the occurrence probability of long-lived CLWCs will increase if one uses the dynamic lifetimes instead of the static lifetimes. The implications of this study for hydrate nucleation are discussed.

Keywords: cagelike water cluster, dynamic lifetime, hydrate nucleation

INTRODUCTION

The hydrate nucleation mechanism is still an unsolved question in the hydrate research fields [1]. Several conceptual pictures of hydrate nucleation have been summarized as the labile cluster nucleation hypothesis [2-3], the nucleation at the interface hypothesis [4-5], and the local structuring nucleation hypothesis [6-7]. Recently, we propose a different model that gas molecules can aggregate through a cagelike water cluster (CLWC) adsorbing dissolved gas molecules around it — a possible step favoring hydrate nucleation [8], and predict that the face-saturated incomplete cages have the potential to act as the precursors of hydrate nucleus [9].

The model is mainly based on the lifetime studies of CLWCs by performing molecular dynamics simulations [8, 10-11]. We find the CLWCs

immersed in liquid water are metastable structures and their lifetimes obey the lognormal distribution. The CLWC lifetimes increase with lowering temperature and increasing the number of adsorbed methane molecules. The shape and the H-bond topology of CLWCs almost do not affect their lifetimes. Additionally, the CLWC filled with a methane molecule survives longer than the empty CLWC.

However, when we measure the CLWC lifetimes, the member-water molecules of CLWC are not allowed to exchange with the surrounding water molecules. Therefore, the lifetimes are measured just for the static CLWC. The case deviates from the real situations more or less because the member-water and the neighbor-water of CLWC are in fact identical and can exchange their positions each other. If a CLWC exchanges

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several member-water molecules with equal amount of neighbor-water molecules, the initial static CLWC breaks down but the updated dynamic CLWC still exists. In this study, we measure the lifetimes of such dynamic CLWCs.

METHODS

We first briefly describe the procedures to measure the CLWC lifetime used previously [10]. A rigid CLWC prepared in advance is immersed in bulk liquid water, and then the system is equilibrated for a period during which the CLWC can move as a whole while keeping the relative positions of member-water fixed. When we begin to measure its lifetime, the CLWC in the last configuration of the equilibrium stage is relaxed and its member-water molecules can move freely. We use the Lindemann index (δ) to monitor the evolution of the CLWC, and its lifetime (τ) is measured as the time when the δ value reaches 0.07. The δ is calculated by

$$\delta = \frac{2}{N(N-1)} \sum_{i < j}^N \left[\frac{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}{\langle r_{ij} \rangle^2} \right]^{1/2} \quad (1)$$

where r_{ij} is the distance between oxygen atoms in the i th and the j th water molecules, $\langle \rangle$ represents a time average, and the sum runs over all N member-water molecules of the CLWC. The Lindemann index reflects the relative root-mean-square fluctuations of interparticle distances, which can show the structural change of the CLWC sensitively. The deformation of CLWC, that is the deviation of member-water molecules from their original equilibrium positions, will cause the δ value to increase with time. When δ reaches 0.07, the deformation of CLWC is large enough to cause the CLWC breakdown (see Figure 2 in Reference [10]). Because we always regard the CLWC as being composed of the initial N member-water molecules, the CLWC is actually static in component. Correspondingly, we denoted the Lindemann index of the static CLWC as δ_s and its static lifetime as τ_s .

In order to monitor a dynamic CLWC in this study, we first built two lists of water molecules — one was for its N member-water and the other was for its M neighbor-water. In each time step, we first calculated a usual δ value, and then we let every member-water to exchange with every neighbor-

water one by one and calculated a temporary δ value for each exchange operation. The $N \times M$ temporary δ values plus the usual δ value were compared together to find the minimum δ value. Subsequently, the exchange operation corresponding to the minimum δ value was accepted to update the member-water list and the neighbor-water list. Thus, the records of the member-water list reflect a dynamic CLWC with time. It can be imagined that the dynamic CLWC attempts to maintain its initial structure as possible as it can. We denoted the Lindemann index of the dynamic CLWC as δ_d and its dynamic lifetime as τ_d . Obviously, the δ_d should be not more than the δ_s , and the τ_d should be not less than the τ_s . Each exchange between member-water and neighbor-water reduces the anticipated structural deformation of CLWC so as to prolong the lifetime of CLWC.

In this study, by re-analyzing the previous simulation data that were used to study the effect of methane adsorption on the static lifetimes of a dodecahedral water cluster (DWC), we calculated the dynamic lifetimes of the DWC. Totally, we studied seven systems $M_1 \sim M_{13}$ containing 1240 water molecules, 1 DWC, and 1 ~ 13 methane molecules. In each system, the DWC was always filled with a methane molecule, and adsorbed other methane on its different faces. The DWC contained 20 member-water molecules, and was surrounded with 22 ~ 33 neighbor-water molecules on average, which were separated from the DWC center within 7.26 Å — the distance corresponding to the first minimum of the RDF between the encaged methane in the rigid DWC and the oxygen of bulk water (see Figure 1 in Reference [8]). The lifetime measurements in each system were repeated 200 times to obtain good statistics. Other simulation details were described in our previous work [8].

RESULTS AND DISCUSSION

The dynamic lifetimes (τ_d) of DWC are listed in Table 1 together with the static lifetimes (τ_s). One can see, the τ_d is indeed not less than the τ_s as expected, and increases with the number of adsorbed methane (N_M), similar to the previous results [8]. However, from the system M_1 to the system M_{13} , the ratio of τ_d/τ_s is not a constant value but increases with the DWC lifetime (Figure 1). This phenomenon can be explained by that the

longer the DWC survives, the more opportunities of exchanging water molecules can occur between the DWC and its surroundings (see the numbers of times of water exchange, e_{total} and e_{final} , in Table 1),

and that the more stable the DWC is, the more efficiently each water exchange can prolong the DWC lifetime (see the τ_e in Table 1).

Table 1. Results of lifetime measurements of DWC in different systems*

System	M ₁	M ₃	M ₅	M ₇	M ₉	M ₁₁	M ₁₃
N_M	0	2	4	6	8	10	12
τ_s (ps)	8.2 ± 0.2	12.1 ± 0.4	17.5 ± 0.6	28.7 ± 1.0	49.8 ± 1.9	118.4 ± 4.8	314.1 ± 13.7
τ_d (ps)	8.3 ± 0.2	12.3 ± 0.4	17.7 ± 0.6	29.8 ± 1.0	52.5 ± 1.9	128.1 ± 5.2	341.8 ± 14.3
τ_d / τ_s	1.00 ± 0.00	1.02 ± 0.01	1.01 ± 0.00	1.05 ± 0.01	1.06 ± 0.01	1.12 ± 0.03	1.12 ± 0.02
e_{total}	0.6 ± 0.1	0.9 ± 0.1	2.1 ± 0.3	3.8 ± 0.4	8.5 ± 0.7	26.0 ± 1.8	83.1 ± 4.8
e_{final}	0.08 ± 0.02	0.21 ± 0.03	0.24 ± 0.03	0.42 ± 0.05	0.61 ± 0.05	1.06 ± 0.08	2.03 ± 0.11
τ_e (ps)	0.0 ± 0.0	0.1 ± 0.1	0.2 ± 0.1	1.0 ± 0.3	2.0 ± 0.4	5.0 ± 0.7	13.1 ± 1.6

* In the first column, N_M is the number of adsorbed methane molecules on the DWC faces. τ_s and τ_d are the static and dynamic lifetimes, respectively. e_{total} is the total number of times of water exchange occurring before the DWC breakdown and e_{final} is the number of times of apparent exchange counted by comparing the final member-water to the initial member-water site by site. τ_e is the prolonged lifetime per apparent exchange, calculated by $\tau_e = (\tau_d - \tau_s) / e_{\text{final}}$. Numbers before and after ± are average values and standard errors, respectively, calculated from 200 independent measurements.

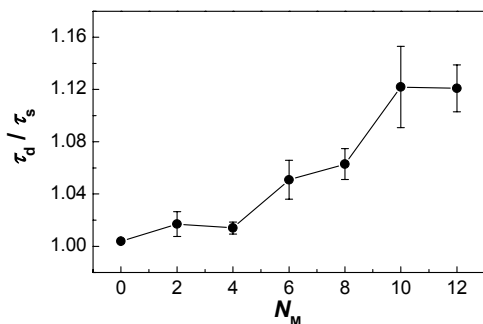


Figure 1. The ratio of τ_d / τ_s as a function of N_M .

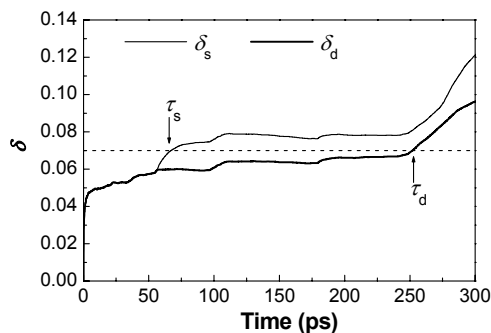


Figure 2. The evolution of δ , taking from a run in the system M₁₁. The dashed line is the lifetime criterion of CLWC, i.e., $\delta = 0.07$.

By checking the records of the member-water list or simply comparing the δ_d and δ_s curves in a run, one can easily observe the water exchanges in the DWC. Figures 2 and 3 show a typical example among these water exchanges. Generally, a water exchange can occur in either of two manners. One is sudden, meaning that a member-water and a neighbor-water exchange their positions straightforwardly and almost do not re-exchange back. The other is gradual, meaning that a member-water and a neighbor-water compete for a

vertex position of DWC continuously until a stable exchange between them accomplishes or fails completely. For the later, many times of exchanges, such as 15 or more, can be observed in the records of the member-water list while only few times of exchanges, such as 1 ~ 5, for the former exchange manner. Certainly, the member-water can leave the DWC for a while and enter back again but not occupying its initial position. In this case, two apparent exchanges are expected.

Recently, through studying the NMR spectrum of aqueous methane, Dec *et al.* [12] measure the hydrate number of aqueous methane as 20, and infer that the hydration shell of methane is dynamic and water molecules might continuously enter and leave the hydration sphere, which corresponds to the famous concept of “the labile cluster” proposed by Sloan *et al.* [1-3]. Here, we provide an unambiguous evidence (Figure 3) to support the dynamic feature of the concept. The evidence also agrees with Nada’s observation that the surface cages of methane hydrate are dynamic (see Figure 2b in Reference [13]).

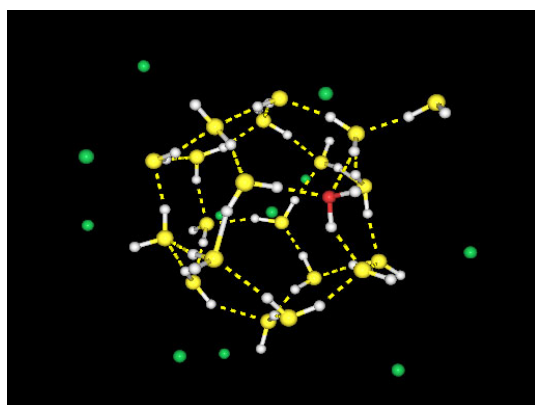


Figure 3. A snapshot taken from the run in Figure 2 at 92 ps. At the beginning, the yellow balls are the oxygen atoms of member-water of DWC, the red the oxygen of bulk water, the white the hydrogen, and the green the methane. The yellow dash lines mean the H-bonds. The figure shows a member-water and a neighbor-water of DWC have exchanged their positions each other. Other bulk water molecules are omitted for clarity.

In this study, the CLWC lifetimes are always limited even if we have considered the dynamic feature of CLWC. The fact reinforces our previous conclusion that the CLWC is a metastable structure [8]. Because the CLWC disturbs the H-bond topology network of bulk liquid water, its collapse should be a collective response to the surroundings. The present results also show that the occurrence probability of long-lived CLWCs will increase if one uses τ_d instead of τ_s . Although the water exchanges prolong the τ_s less than 12% on average (Table 1), they can actually prolong the τ_s up to 4.7 times in some individual measurements. Obviously, the longer a CLWC lives, the more opportunities it will have to adsorb

the dissolved methane molecules around it, thus favoring hydrate nucleation. In previous work [8], we have discussed that such a CLWC-methane aggregation is an autocatalytic process because the CLWC lifetime increases with the N_M (Table 1). In other words, the larger N_M , the more stable the CLWC, and thus the CLWC can exist longer time in liquid water waiting to adsorb another methane so as to prolong its lifetime again. Can the CLWC-methane aggregation further develop toward a critical nucleus of methane hydrate? If yes, how does it? More efforts are expected to answer these questions in the future.

CONCLUSIONS

As an extension of the previous study on the static lifetimes of CLWCs, we calculate the dynamic lifetimes of CLWCs with considering the possible exchanges between the member-water and the neighbor-water. The results show that the τ_d is not less than the τ_s and the ratio of τ_d/τ_s increases with the CLWC lifetime. The phenomenon is explained by that both the e_{final} and the τ_e increase with the CLWC lifetime (Table 1). The present work strengthens that the CLWCs are metastable structures in liquid water even if their dynamic features have been considered. Certainly, the occurrence probability of long-lived CLWCs will increase if one uses τ_d instead of τ_s .

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