Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic supplementary information for

Using the face-saturated incomplete cage analysis to quantify the cage compositions and cage linking structures of amorphous phase hydrates

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This file includes some FSICA results for T2μs and T5μs, including Fig. S1-S8 and Tables S1-S3.

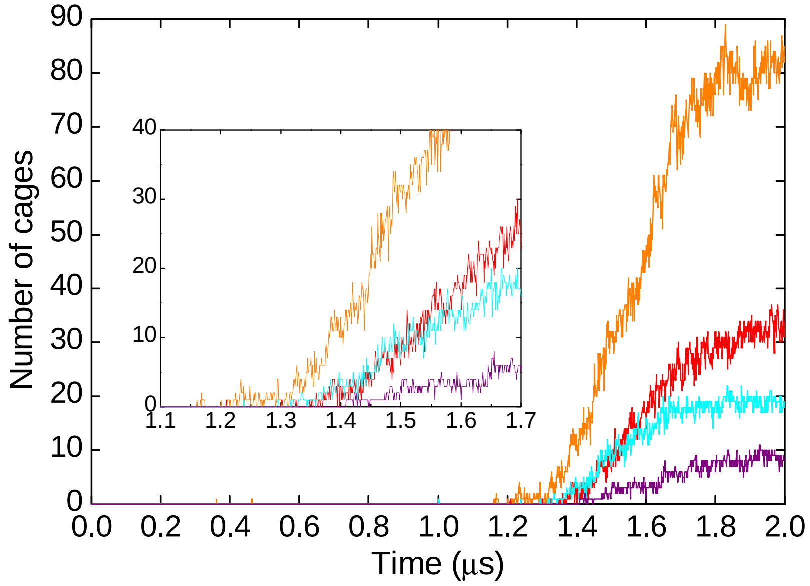

Fig. S1 Evolution of selected CCs in T2μs, including 5^{12} (orange), $5^{12}6^{2}$ (red), $5^{12}6^{3}$ (cyan), and $5^{12}6^{4}$ (purple). The inset is an enlargement for the initial nucleation stage. Note: Although the slight differences between this figure and Figure 3 of Walsh *et al*. (Ref. 6) for the first three cage types can be attributed to different H-bond definitions, the number of $5^{12}6^{4}$ cages is systematically larger in our analysis because the FSICA identifies another sub-type of $5^{12}6^{4}$ (see Fig. 1E) besides the standard one in the sII hydrate. After removing the non-standard $5^{12}6^{4}$ sub-type, our results are consistent with theirs (not shown here but shown in Fig. S2 for T5μs).

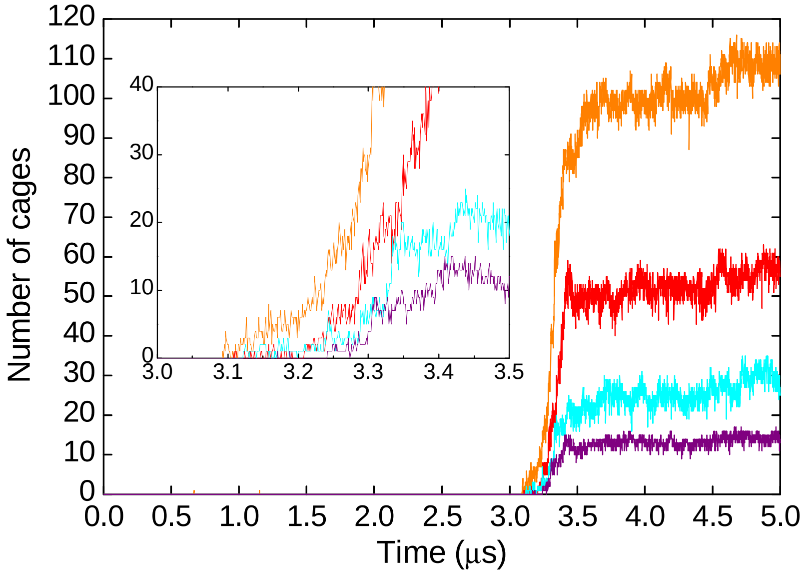

Fig. S2 The same as Fig. S1 but for T5μs. Note: The non-standard $5^{12}6^{4}$ sub-type has been removed in this figure, and so results for all four cage types agree well with those of Walsh *et al.* (see Figure S3 in Ref. 6).

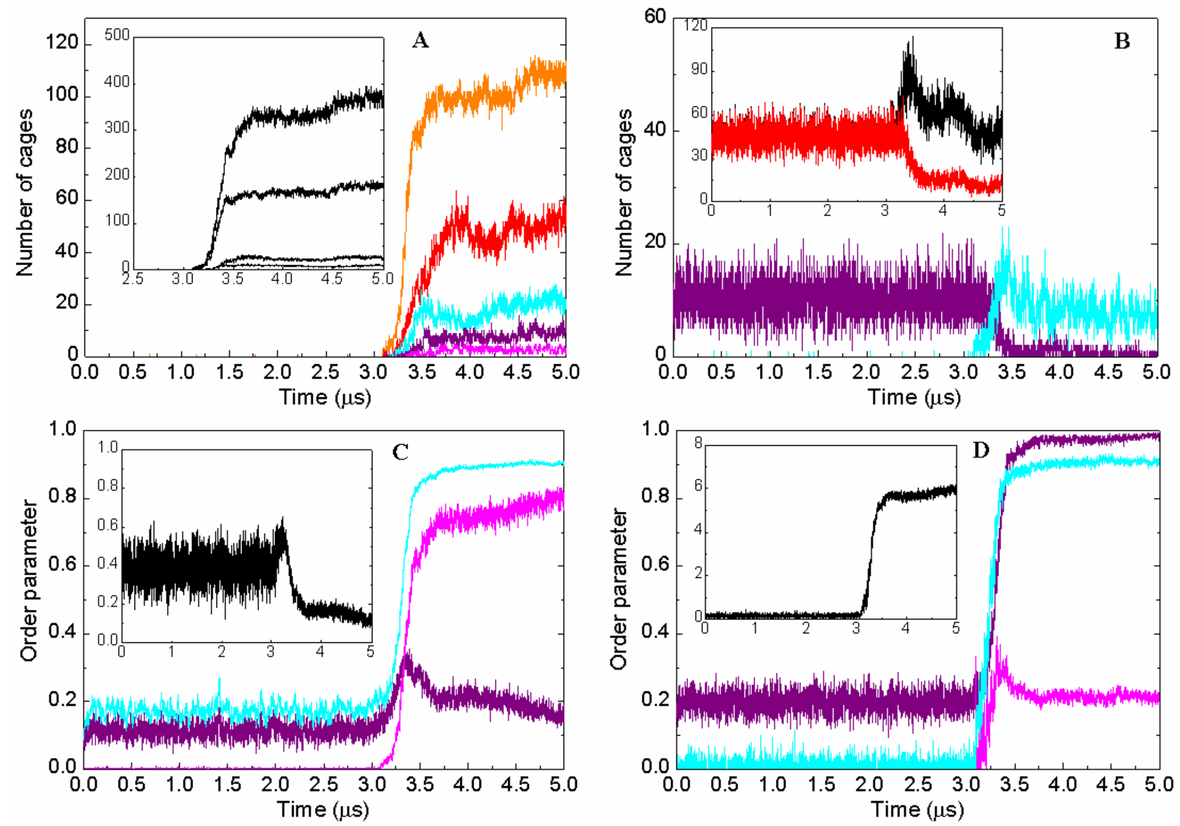

Fig. S3 (**A**) Evolution of selected CCs, including 5^{12} (orange), $4^15^{10}6^2$ (red), $4^15^{10}6^3$ (cyan), $4^25^86^2$ (purple), and $4^35^66^3$ (magenta). The four black lines in the inset, from the top down, are for CCs, standard hydrate cages, empty CCs, and empty standard hydrate cages. (**B**) Evolution of selected FSICs, including $[5^26^3]_5$ (purple) and $[5^{10}6^2]_1$ (cyan). In the inset, the black and red lines refer to FSICs and empty FSICs, respectively. (**C**) Evolution of several order parameters, including fractions of different types of methane to total methane, *i.e.*, the aqueous methane (cyan), the guest methane (magenta), and the adsorbed methane (purple). The inset shows the fraction of the adsorbed aqueous methane to total aqueous methane. In this study, a methane molecule is classified as aqueous if it has 16 or more hydration water molecules, otherwise it belongs to the gaseous class. The radius of the hydration shell of a methane molecule is set at 5.4 Å. Note: the peak at ~3.3 μs in the curve for adsorbed methane actually results from using the periodic boundary conditions (PBCs). During the growth of a cage cluster, the surface of cluster will reduce and some adsorbed methanes have to change to guest methanes when the cage cluster spans the simulation box. (**D**) Evolution of several order parameters, including the cage occupancy (cyan) which is the fraction of occupied cages to total cages, the fraction of cage water to total water (purple), and the hydrate crystallinity (magenta) which is the ratio of the number of standard hydrate cage links (including sI, sII, and sH) to total cage links. In the inset, the black line represents the links per cage, *i.e.*, the ratio of total cage links to total cages, and so measures the aggregate degree of cages. Note: There is an unusual peak at ~3.3 μs in the curve of hydrate crystallinity. We infer that it is probably caused by the PBC mentioned above because the cages induced by the PBC may disturb the natural growth of the cage cluster, but we know little about how the hydrate crystallinity really changes with time if the PBC can be removed.

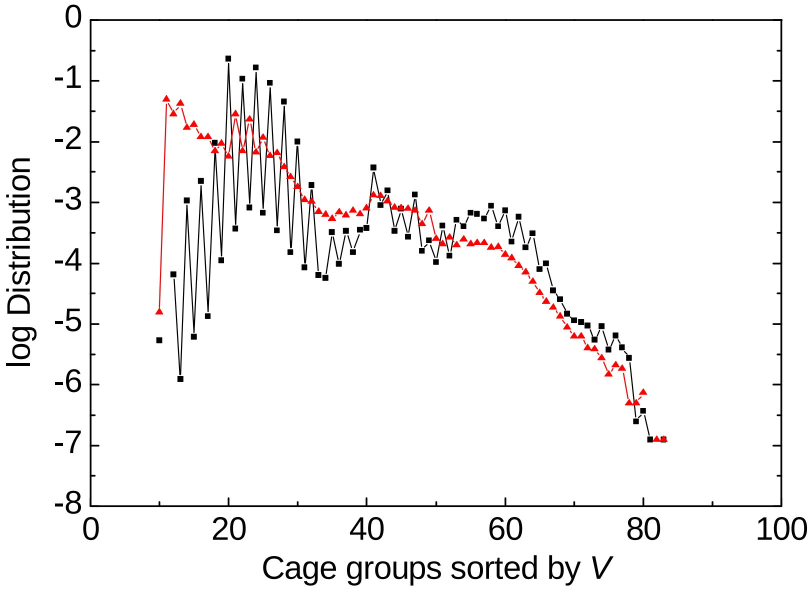

Fig. S4 Distribution of CC- (black squares) and FSIC-groups (red triangles) sorted by the number of cage vertices (V) for T5μs.

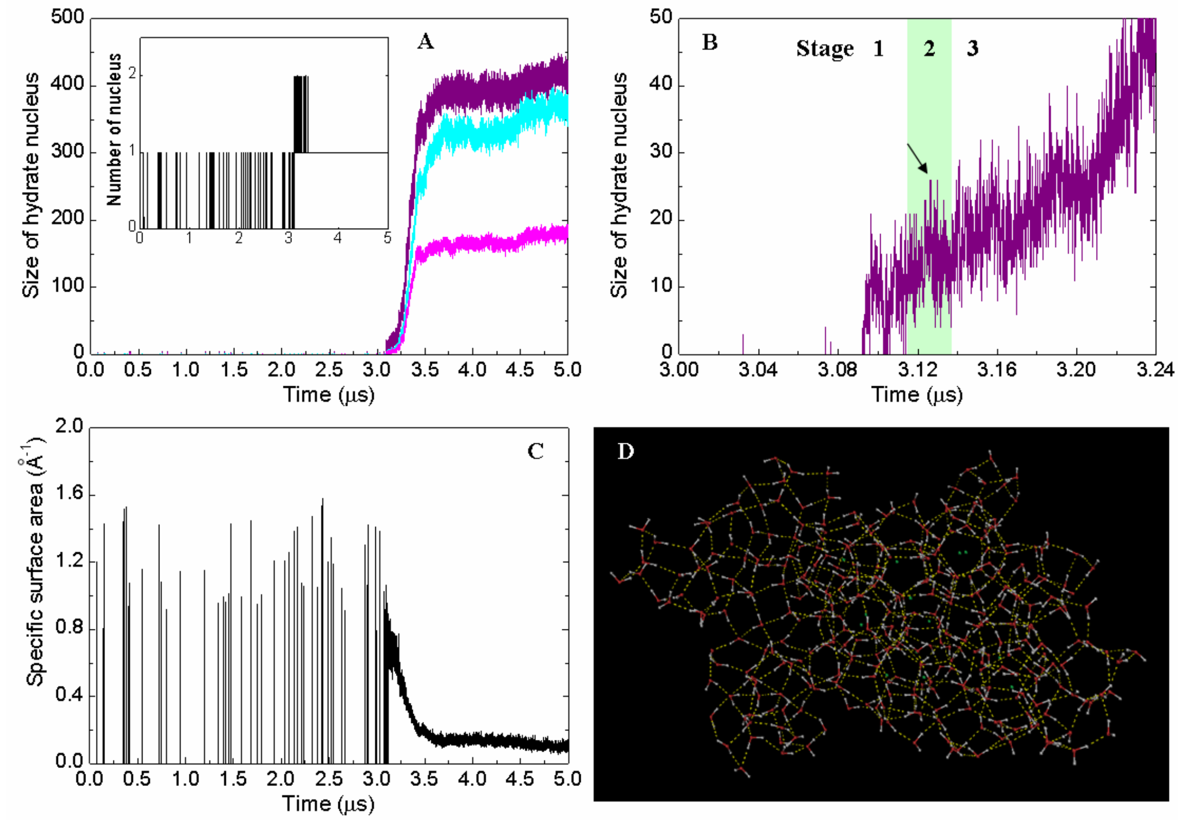

Fig. S5 (**A**) Evolution of the size of the hydrate nucleus. The coloured lines correspond to total cages (purple), CCs (cyan), and standard hydrate cages (magenta). The inset shows the number of nuclei, in which the value of 2 actually reflects the intermittent breakdown of bridging cages in the large nucleus and does not represent another independent nucleus. In the case of two nuclei occurring, only the larger one was considered. (**B**) The magnification of the purple line in (A). Stages 1-3 correspond to the induction, the effective nucleation, and the growth of a hydrate nucleus. Stage 2 (green region) begins from the last time the nucleus reached zero size, and extends to the last time the nucleus reached the minimum value after the start of the stage. (**C**) The change of the specific surface area of nucleus with time. (**D**) A snapshot of the upper-limit that the critical nucleus takes at the time indicated by the arrow in (B).

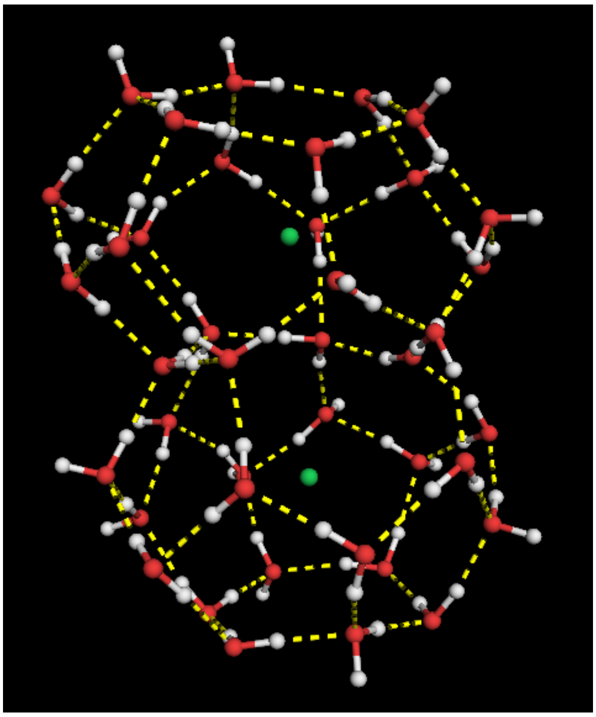

Fig. S6 A complex CC of $4^2 5^{20} 6^3$ taken from the last 200 ns in T2μs. It is a combination of two ICs, *i.e.*, $4^2 5^9 6^1 7^1$(top) and $[5^{11} 6^2 7^1]_1$ (bottom) which share a 7-membered ring.

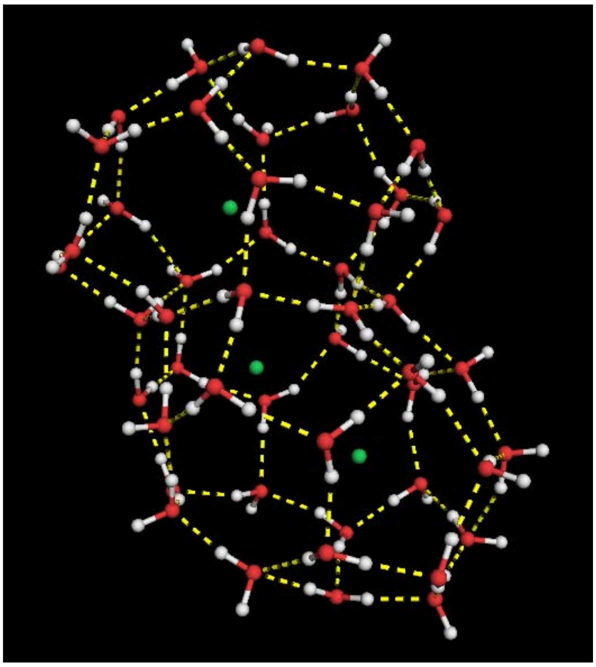

Fig. S7 A complex CC of $4^6 5^{14} 6^9$ taken from the last 200 ns in T2μs. It is a combination of two ICs, *i.e.*, $4^4 5^6 6^3 8^1$ (top) and $[4^2 5^8 6^6 8^1]_1$ (bottom) which share an 8-membered ring.

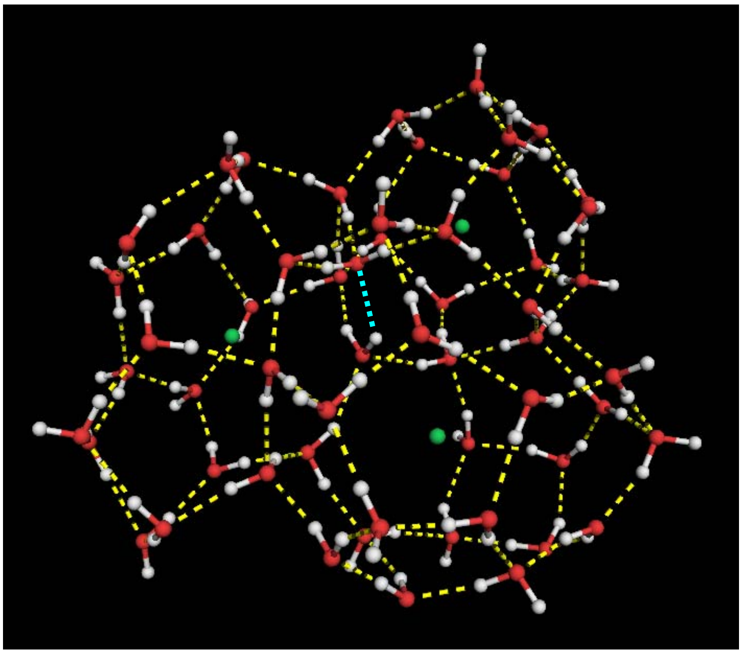

Fig. S8 A complex CC of $4^4 5^{24} 6^7$ taken from the last 200 ns in T2μs. Initially, it is a combination of three CCs, *i.e.*, $4^2 5^8 6^3$(left, named X), $4^2 5^8 6^2$(top right, named Y), and $4^2 5^8 6^6$ (bottom right, named Z). They form three cage links of X-4-Y, X-6-Z, and Y-6-Z. At this stage, the edge shared by X, Y, and Z (indicated by the cyan dashed line) is broken. As a result, X changes to $[4^1 5^8 6^2 8^1]_2$, Y to $[4^1 5^8 6^1 8^1]_2$, and Z to $[4^2 5^8 6^4 10^1]_2$. Correspondingly, they form three complex cage links of X-8-[YZ], Y-8-[XZ], and Z-10-[XY].

Table S1 The top 10 CCs in T5μs[a]

Type	Distribution	R_{vertex} / Å	R_{face} / Å	Area / Å^2	Volume /Å^3
5^{12}	0.209	3.901	3.097	160.4	163.6
$5^{12}6^{2}$	0.108	4.316	3.568	201.0	231.2
$4^{1}5^{10}6^{2}$	0.093	4.136	3.363	182.0	196.7
$5^{12}6^{3}$	0.052	4.501	3.772	221.4	269.7
$5^{12}6^{4}$	0.036	4.676	3.964	241.7	310.6
$4^{1}5^{10}6^{3}$	0.036	4.337	3.599	202.1	229.7
$4^{1}5^{10}6^{4}$	0.030	4.518	3.797	222.5	268.5
$4^{2}5^{8}6^{4}$	0.018	4.353	3.612	203.6	231.5
$4^{2}5^{8}6^{2}$	0.015	3.967	3.170	163.9	164.5
$4^{2}5^{8}6^{1}$	0.009	3.737	2.917	142.7	131.7

[a] In Tables S1 and S2, the cage distribution is calculated as the fraction of cage number to total cage number (including both FSICs and CCs). R_{vertex} and R_{face} mean the vertex- and face-radii of cage, respectively.

Table S2 The top 10 FSICs in T5μs

Type	Distribution	R_{vertex} / Å	R_{face} / Å	Area / Å^2	Volume / Å^3
$[5^{2}6^{3}]_{5}$	0.043	3.054	1.688	79.8	37.6
$[5^{2}6^{4}]_{5}$	0.034	3.289	2.048	98.2	54.4
$[5^{10}6^{2}]_{1}$	0.019	4.035	3.198	172.4	176.6
$[4^{1}5^{2}6^{3}]_{4}$	0.019	3.156	1.930	88.6	47.7
$[5^{2}6^{5}]_{5}$	0.010	3.509	2.360	116.8	73.6
$[5^{10}6^{3}]_{1}$	0.009	4.241	3.440	191.8	206.1
$[4^{1}5^{8}6^{4}]_{1}$	0.008	4.252	3.452	193.4	209.2
$[5^{4}6^{3}]_{4}$	0.007	3.362	2.228	106.1	66.5
$[5^{10}6^{4}]_{1}$	0.006	4.427	3.653	212.2	242.8
$[4^{1}5^{2}6^{4}]_{4}$	0.005	3.393	2.260	107.2	65.8

Table S3 Average values of some parameters showing the structural difference between the solution phase and amorphous phase in T5μs[a]

Parameters	Solution Phase		Amorphous Phase	
Number of FSIC	45.2(5)		47(2)	
Number of CC	0.006(3)		372(2)	
Number of hydrate cage	0.001(1)		181.6(1)	
Occupancy for all cages	0.010(1)		0.909(1)	
Fraction of cage water	0.194(2)		0.987(0)	
Fraction of guest methane	0.001(0)		0.800(1)	
Fraction of adsorbed methane	0.110(3)		0.160(1)	
Top 10 cage types	$[5^2 6^3]_5$	/0.220	5^{12}	/0.259
	$[5^2 6^4]_5$	/0.172	$5^{12}6^2$	/0.137
	$[4^1 5^2 6^3]_4$	/0.092	$4^1 5^{10} 6^2$	/0.127
	$[5^2 6^5]_5$	/0.051	$5^{12}6^3$	/0.073
	$[5^4 6^3]_4$	/0.031	$4^1 5^{10} 6^3$	/0.053
	$[4^1 5^2 6^4]_4$	/0.029	$5^{12}6^4$	/0.047
	$[6^5]_6$	/0.027	$4^1 5^{10} 6^4$	/0.035
	$[4^2 5^2 6^2]_3$	/0.024	$4^2 5^8 6^2$	/0.022
	$[5^4 6^4]_4$	/0.021	$4^2 5^8 6^4$	/0.019
	$[5^2 6^6]_5$	/0.015	$[5^{10} 6^2]_1$	/0.017
Fraction of planar ring	0.159(1)		0.932(1)	
Links per cage	0.150(1)		5.97(1)	
Total crystallinity	0		0.2123(7)	
sI crystallinity	0		0.1128(4)	
sII crystallinity	0		0.0991(7)	
sH crystallinity	0		0.0004(1)	
Sampling region	0.4-0.6 μs		4.8-5.0 μs	
Total CC amount	12		743585	
Total FSIC amount	90451		94070	
Total CC types	10		629	
Total FSIC types	1153		1648	

[a] The numbers after the slashes are the fractions of the cage number for each type to the total number of all cages. The numbers in parentheses are the standard errors of mean estimated from 4 blocks with each covering 500 frames.