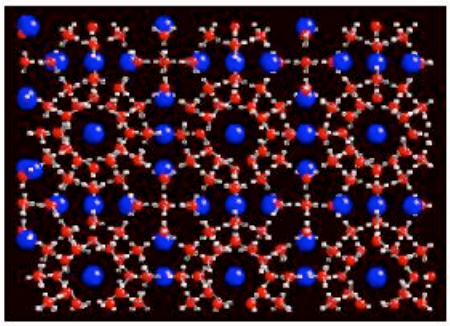
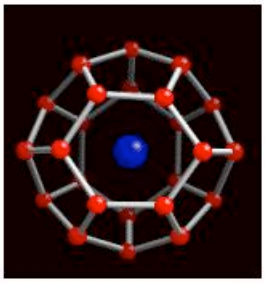
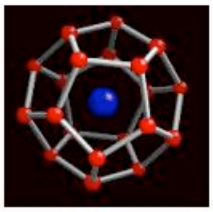
Supporting Information

Methane hydrate structure sI:



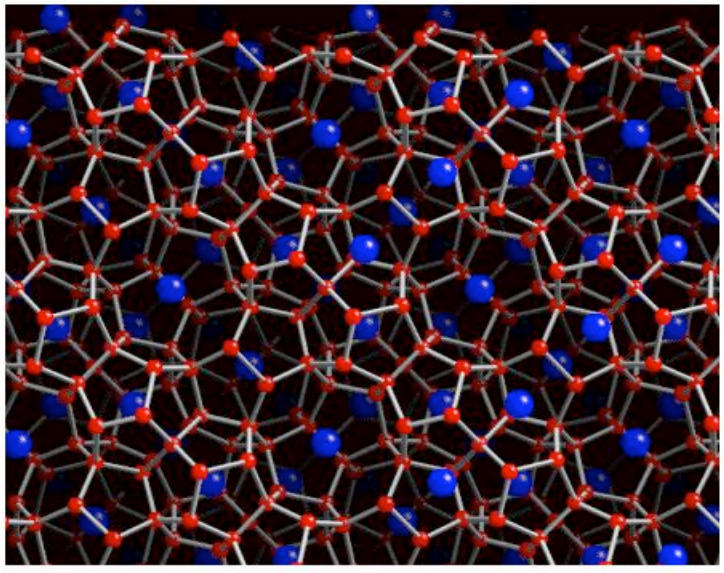


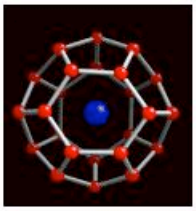
large ($5^{12}6^2$) cages



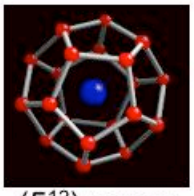
small (5^{12}) cages

Methane hydrate structure sII:

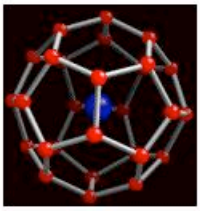




($5^{12}6^2$) cages

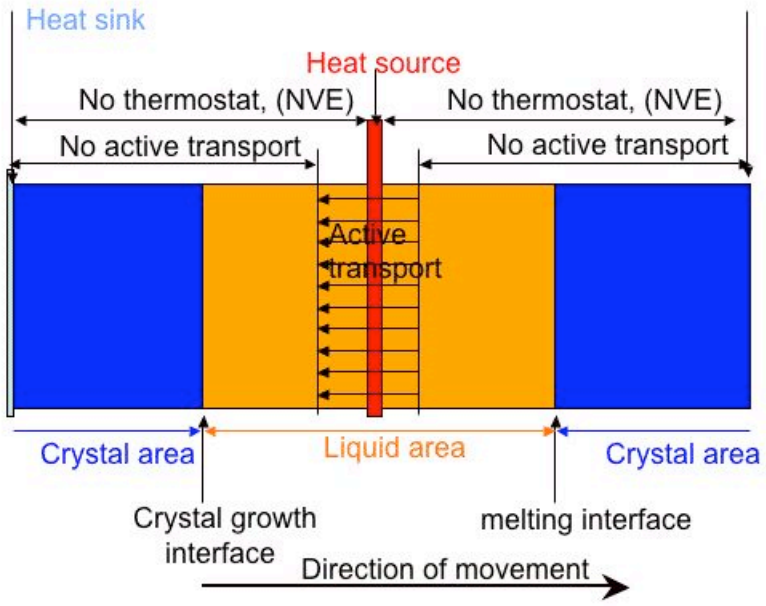


(5^{12}) cages

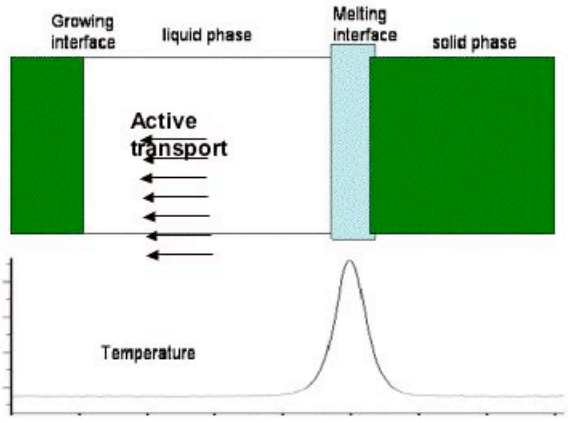


($5^{12}6^4$) cages

MD setup 1: with local thermostats and temperature gradient. For details see Gulam Razul et al., *Mol. Phys,* **2005,** 103, 1929.

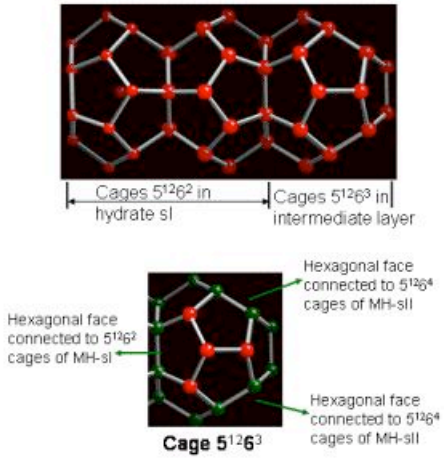


MD setup 2: without temperature gradients. For details see Vatamanu J., Kusalik P. G., *submitted*, *J. Chem. Phys.*

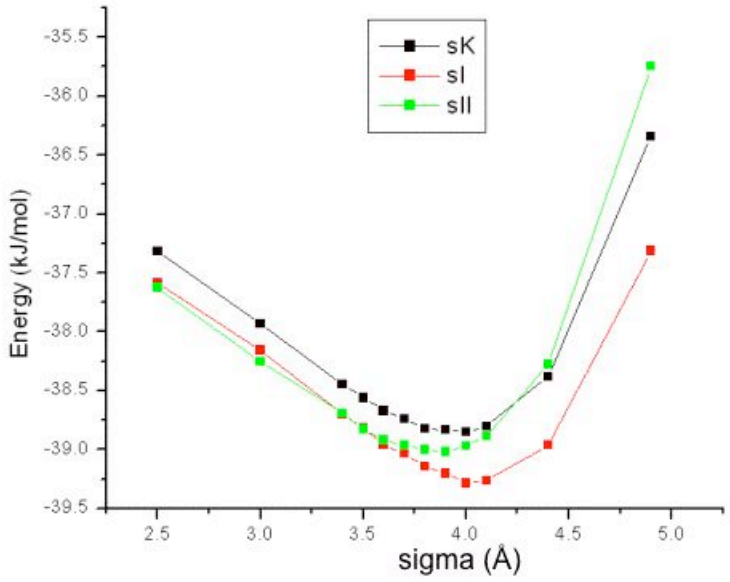


It is sufficient here to note that the measured interfacial properties, as well as the observed growth rates are independent of the choice of setup 1 or 2 (within our uncertainties). Here we have chosen to use setup 2 as it affords a superior environment from with to observed growth of hydrate crystals.

A configuration showing the $5^{12}6^2$ cages of MH-sI connecting to an intermediate layer consisting of 5^26^3 cages. The $5^{12}6^3$ cages provide the right geometry to connect MH sI and sII.
This image clarifies how it is possible to form a polycrystal consisting of MH-sI and MH-sII *[as reported in Vatamanu J., and Kusalik P. G., J. Phys. Chem. B., **110**, 15896 (2006)].*



The total potential energies for different model hydrate crystal structures versus the LJ sigma of the guest molecule at 100 atm and 245 K. MH-sI (red line), MH-sII (green line) and MH-sK (black line). We point out that for molecular sizes bigger than 4.1 Å, the newly identified MH-sK appears energetically preferred to MH-sII.

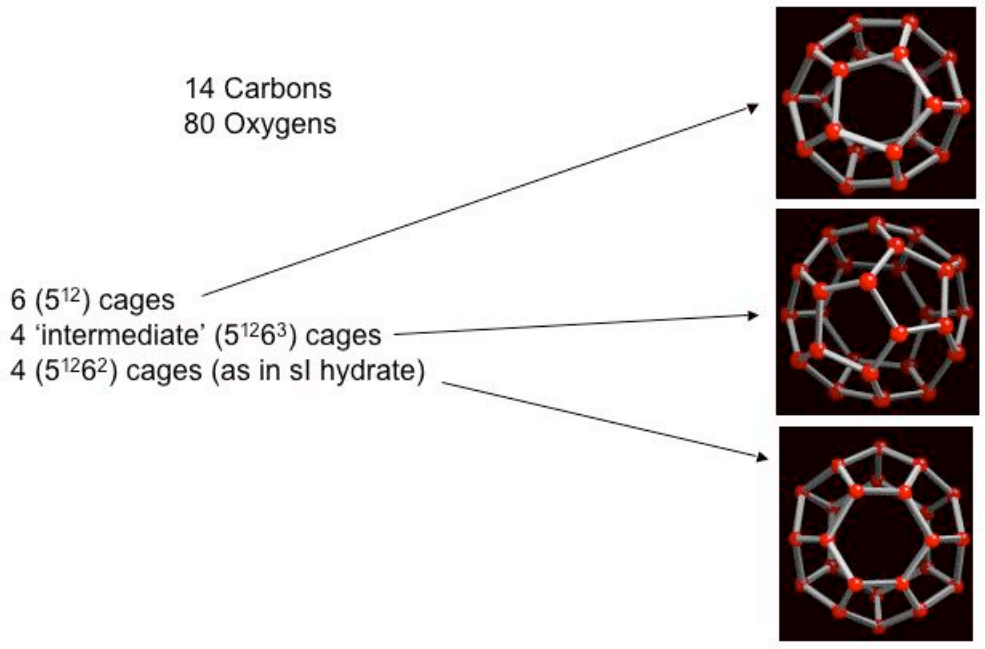


Coordinates of the 94 molecules (80 water and 14 methane) making up a repeating unit.

The dimensions of the orthorhombic box are (12.116, 12.116, 20.824). All units in Å.

O	0.7558	-4.0752	-7.3860
O	-0.6294	1.8843	-9.1690
O	0.6861	4.2881	-0.9607
O	-5.2974	-2.6406	-9.2702
O	-0.7387	-4.1916	-3.1946
O	5.2354	1.1253	9.4328
O	-5.3023	3.3530	-3.2032
O	-5.4002	-4.1957	-3.1064
O	0.7565	-2.6053	-4.9159
O	-2.9863	3.1664	-9.9875
O	-1.7191	5.6527	-4.4633
O	2.9163	-3.2474	-1.0249
O	0.8536	3.3879	-7.3905
O	5.0708	-5.0523	-1.0179
O	5.2964	3.3721	-7.3758
O	-2.9868	-0.4121	-3.7693
O	-5.2555	5.6526	-7.0828
O	5.2316	4.1622	-1.0362
O	-3.0776	1.9392	-2.3261
O	2.9287	-3.4434	9.4615
O	-1.6170	-0.3622	-7.8980
O	5.3310	-4.1307	-7.4535
O	-4.4075	-0.3822	-7.9179
O	2.9694	2.8719	9.3849
O	3.0337	1.1457	-3.4558
O	3.0379	-1.7667	-3.5056
O	3.0508	4.2530	-8.8741
O	-5.3173	-0.4735	-5.3353
O	-5.3208	1.8650	-9.1797
O	-0.7459	-2.6259	-9.2055
O	2.9701	-4.9722	-8.7993
O	-0.6755	5.6703	-7.0424
O	2.8947	2.6207	-0.9866
O	5.2763	1.8252	-4.9815
O	0.7861	1.1235	9.3082
O	0.7436	-1.7036	9.4106
O	-3.0076	-4.0594	-9.9690
O	-0.6934	-0.2909	-5.3110
O	-3.0622	-2.8302	-2.4230
O	0.7156	-4.9541	-0.9667
O	5.2012	-2.7164	-4.9696
O	-0.8226	3.4228	-3.1238
O	-2.9550	5.5787	-8.6357
O	0.7863	2.0240	-4.8844
O	5.1597	-1.7402	9.4459
O	-4.4768	5.6696	-4.4560
O	0.6628	1.8503	2.9147
O	-5.4100	-2.5787	7.2495
O	-0.8783	-0.4288	3.2804
O	-5.4651	3.4225	1.2333
O	-0.7571	1.9542	7.1597
O	-5.4053	1.9401	7.1991
O	0.5475	-4.0418	5.5161
O	-5.4470	-4.1865	1.1199
O	0.7153	3.4602	5.3360
O	-0.8453	-2.4855	7.3013
O	-5.4800	-0.3657	3.3403
O	-3.1250	5.7063	6.7105
O	5.2004	-4.0786	5.4150
O	-3.1248	-3.9589	8.0765
O	-1.7649	-0.2941	5.9026
O	-0.8761	-4.0634	1.1697
O	-1.7540	5.7488	2.4921
O	5.0789	1.9549	3.0035
O	-4.5424	5.6881	2.5396
O	2.8988	-4.7569	6.8604
O	2.9565	4.3826	6.8457
O	-5.4286	5.6631	5.1313
O	-0.8247	3.4836	1.2168
O	2.9037	-1.8399	1.4455
O	0.7181	-2.6842	2.9490
O	5.1141	-2.6598	2.8988
O	2.9247	1.0040	1.4930
O	-3.1520	2.1229	0.4170
O	-0.8723	5.7131	5.1012
O	-3.2061	-0.3071	1.7277
O	-3.0774	3.2576	8.0455
O	-3.1827	-2.7274	0.3442
C	-3.0153	2.6317	-6.1764
C	2.9708	-0.3499	-7.9132
C	-3.0623	-0.3489	9.4070
C	-3.0239	-3.4080	-6.2063
C	5.9418	5.7024	9.4379
C	5.9040	-0.3648	-1.0160
C	-0.0256	-0.3562	-0.9877
C	2.9903	5.6890	-4.4324
C	-3.1082	5.6712	-0.9739
C	-3.1518	-3.3558	4.2208
C	2.9401	5.6721	2.4583
C	-3.1311	2.6835	4.2013
C	2.9488	-0.3635	5.9360
C	0.0300	5.7054	9.3863

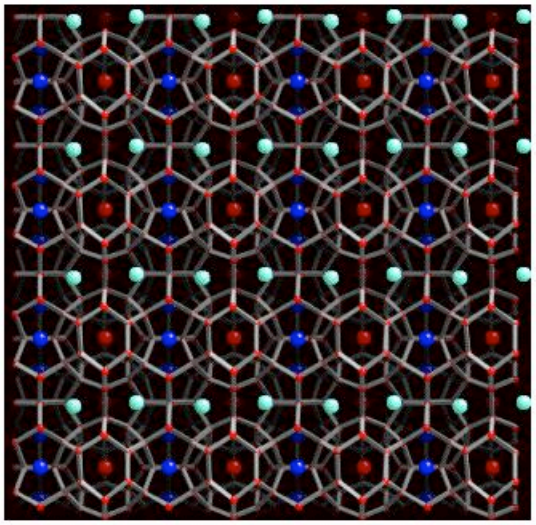
The new hydrate structure (sK) identified in this study.



[001] face of sK hydrate

Oxygen atoms are shown as small connected red spheres.

The centers of each cage are labeled as follows:
blue: small 5^{12} cage
aqua: $5^{12}6^2$ cages
red: intermediate $5^{12}6^3$ cages



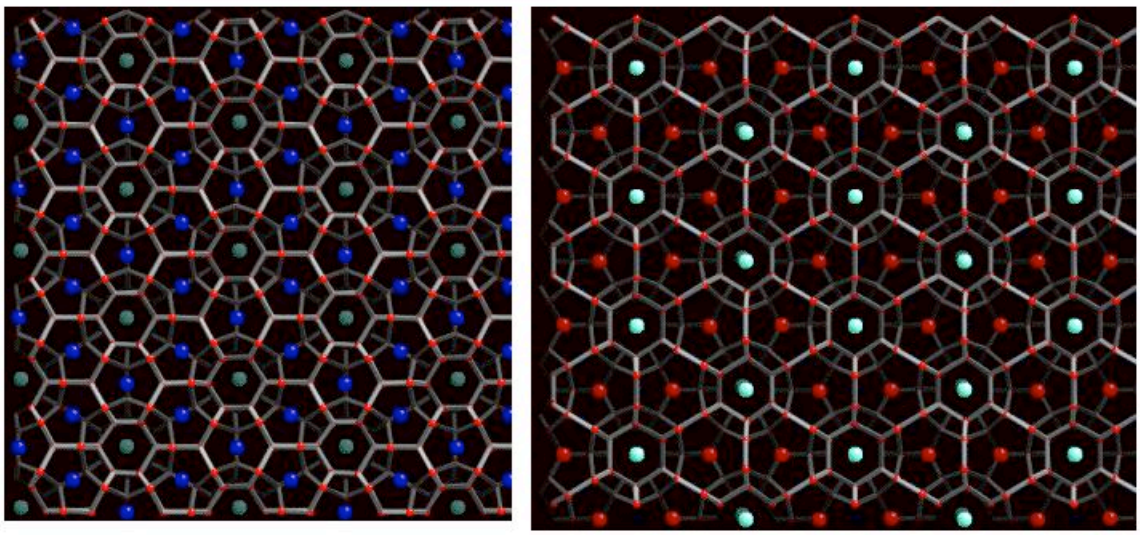
Note: depth shading has been applied

[010] face of sK hydrate

Oxygen atoms are shown as small connected red spheres.

Note: depth shading has been applied

The centers of each cage are labeled as follows:
blue: small 5^{12} cage
aqua: $5^{12}6^2$ cages
red: intermediate $5^{12}6^3$ cages



The hexagonal symmetry of the crystal is apparent from these images.