Supplementary information: details on the evaluation of the three phases coexistence temperature T_3 of the methane hydrate for SPC and SPC/E models.

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Most of the details of the simulations performed here are similar to those of our previous work [1]. For our study we used a methane hydrate configuration of 2×2×2 unit cells (a total of 368 water molecules and 64 methane molecules). The crystallographic parameters of the methane hydrate were taken from Yousuf *et al.* [2]. Hydrates present proton disorder [3–5]. We used the algorithm proposed by Buch *et al.*[6] to generate solid configurations satisfying the Bernal Fowler rules [7] and with zero (or almost zero) dipole moment the sI hydrate. We used the setup denoted as B in our previous work. In the initial configuration a slab of the methane hydrate (with 368 water and 64 methane molecules) was in contact with an slab of water (containing 368 molecules) and an slab of methane in the gas phase (containing 128 molecules). The global (including all phases within the simulation box) mole fraction of methane is $x_{\mathrm{CH_4}} \sim 0.21$. The typical size of the simulation box for the initial configuration was 67×24×24 Å^3 (system B). The interfaces between the three phases are perpendicular to the x axis. From the 67 Å in the direction perpendicular to the interface, about 24 Å were occupied by the methane hydrate, about 22 Å by water and about 21 Å by the methane gas. Periodic boundary conditions were employed in the three directions of space. The initial arrangements permits us to have each phase in contact with the other two. For a certain fixed pressure, the methane hydrate will melt at temperatures above T_3 yielding a liquid phase with water and a gas phase with methane. The potential energy of the system increases with time along the run and reach a plateau once all the methane hydrate melted. At temperatures below T_3 the methane hydrate will grow, and at the end of the simulation there will be only two phases the hydrate and the gas phase of methane. In this case the potential energy of the system will decrease with time along the run until a plateau is reached once all the water has been incorporated to the hydrate. By choosing several temperatures one can bracket the value of T_3 as the average between the highest temperature at which the methane hydrate grows and the lowest temperature at which the methane hydrate melts. The typical uncertainty in T_3 for a certain pressure is of about 4K. The value of T_3 was determined for the SPC and SPC/E models for two pressures p=100bar and p=400bar.

We performed NpT molecular dynamic simulations at different temperatures and pressures at 100 and 400 bar using the molecular dynamics package GROMACS [8]. The temperature was fixed using a Nosé-Hoover thermostat [9, 10] with a relaxation time of 2 ps. To keep the pressure constant, a Parrinello-Rahman barostat [11, 12] was used. The relaxation time of the barostat was 2 ps. The three different sides of the simulation box were allowed to fluctuate independently to allow changes in the shape of the solid region and to avoid the existence of stress in the solid. The time-step used in the simulations was 2 fs. The typical length of the simulations depended on the conditions of pressure and temperature but were typically of about 500 ns although in some cases they were or up to 1000 ns. The geometry of the water molecules was enforced using constraints [13]. The Lennard-Jones part of the potential was truncated at 9 Å. Ewald sums were used to deal with electrostatics. The real part of the Coulombic potential was truncated at 9 Å. The Fourier part of the Ewald sums was evaluated by using the particle mesh ewald (PME) method of Essmann *et al.* [14]. The width of the mesh was 1 Å and we used a fourth order polynomial.

Methane was described by a single LJ center with $\sigma = 3.75$Å and $\epsilon/k = 147.5$K. Water was described by the SPC and SPC/E models. Lorentz-Berthelot rules were used to get the cross water-methane interactions. They are simply obtained as:

$$\epsilon_{\mathrm{CH_4-H_2O}} = \chi\sqrt{\epsilon_{\mathrm{CH_4-CH_4}} \cdot \epsilon_{\mathrm{H_2O-H_2O}}} \qquad (1)$$

$$\sigma_{\mathrm{CH_4-H_2O}} = \frac{(\sigma_{\mathrm{CH_4-CH_4}} + \sigma_{\mathrm{H_2O-H_2O}})}{2} \qquad (2)$$

along with the value $\chi = 1$. In our previous work [1] when studying the TIP4P/2005 model, we considered two values of χ, $\chi = 1$ (i.e. the Lorentz-Berthelot combination rule) and the value $\chi = 1.07$ (i.e. a model where the strength of the water-methane interaction was increased by 7 %).

The results obtained for the SPC model of water at 100 bar are presented in Fig.1. In Fig.2 the results for the SPC/E are shown. From these two figures one can obtain $T_3 = 217(3)$K for the SPC and $T_3 = 232(7)$K for the SPC/E. Similar runs were performed at 400 bar. We obtained $T_3 = 220(4)$K for the SPC and $T_3 = 240(5)$K for the SPC/E models.

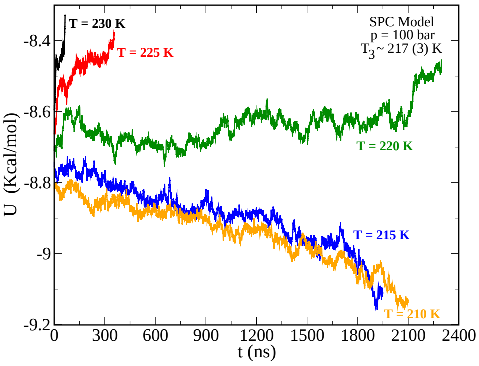

FIG. 1. Evolution of the potential energy as a function of time for SPC model at 100 bar for the three-phase system (water + hydrate + methane).

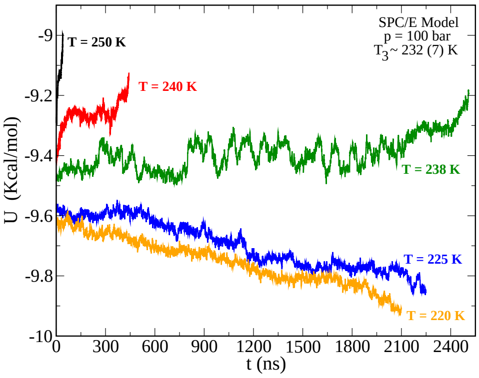

FIG. 2. Evolution of the potential energy as a function of time for SPC/E model at 100 bar for the three-phase system (water + hydrate + methane).

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