

## Electronic Supplementary Information for

# Numerical evidence of the formation of a thin microscopic film of methane at the water surface: a free energy calculation

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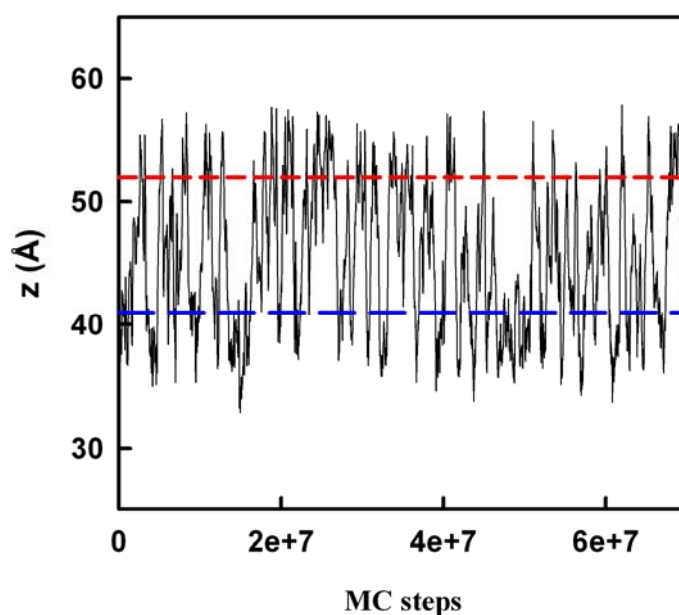
### Computational procedures

The simulation cell is a rectangular parallelepiped box of dimensions  $L_x L_y L_z$  ( $L_x = L_y$ ) with periodic boundary conditions in all the directions. The water phase has been surrounded by two methane phases in the  $z$  direction. The resulting simulation box presents two water-methane interfaces. The simulation box contains 2091 water molecules and 350 methane molecules. The Monte Carlo simulations were performed at  $T = 373$  K and at different pressures ranging from 1 to 50 MPa. The potential of mean force was calculated at 10 MPa. The surface tension of the water liquid-vapour interface calculated from the Kirkwood-Buff (KB) expression is  $56.1 \text{ mN m}^{-1}$  at 388 K where the water-methane interfacial tension is  $50.8 \text{ mN m}^{-1}$  at 373 K and 10 MPa (see the text of the paper for the corresponding references).

### Calculation of the statistical errors for the potential of mean force calculation.

The estimate of the statistical errors in the calculation of the potential of mean force has been carried out using the methodology described in the paper of Kästner and Thiel (J. Kästner, W. Thiel, J. Chem. Phys., 2006, **124**, 234106). We find that the statistical fluctuations of the free energy at each  $z$  value are smaller than  $0.1 \text{ kJ mol}^{-1}$ .

The statistical errors of the thickness are estimated from the standard deviations of the ensemble average of this property.



**Fig S1** : Average  $z$  position of the methane molecules located at the water side of the water-methane interface as a function of the number of MC moves. The upper dashed line (dashed line) represents the position of the Gibbs dividing surface whereas the lower dashed line represents the  $z$  position of a sphere of a radius  $5.2 \text{ \AA}$ .