Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Fluctuation-dissipation analysis of nonequilibrium thermal transport at hydrate dissociation interface

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RDF of TIP4P, SPC/E and SPC/Fw under steady state

To ensure the methane hydrate is under steady state, the RDF of TIP4P, SPC/E and SPC/Fw are calculated at 300K under 42MPa[1]. It can be clearly seen that the peaks of these three water models correspond to each other.

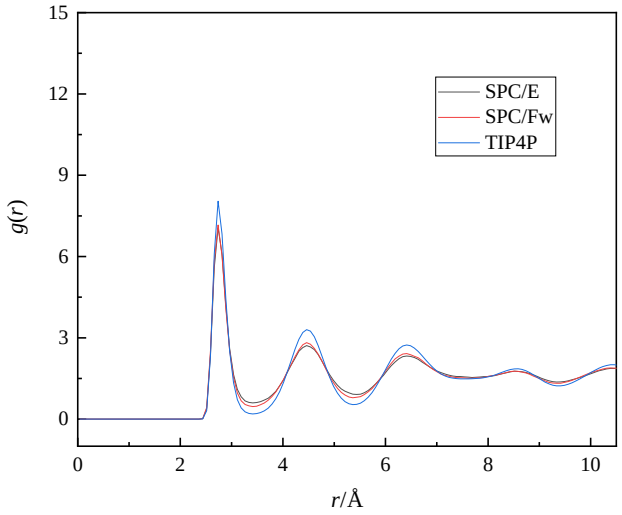
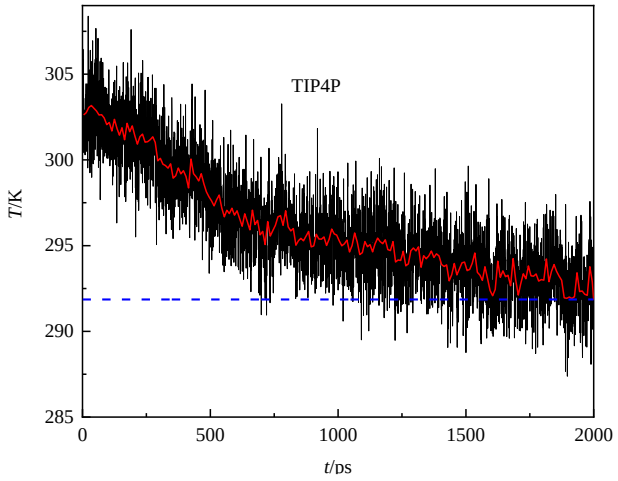


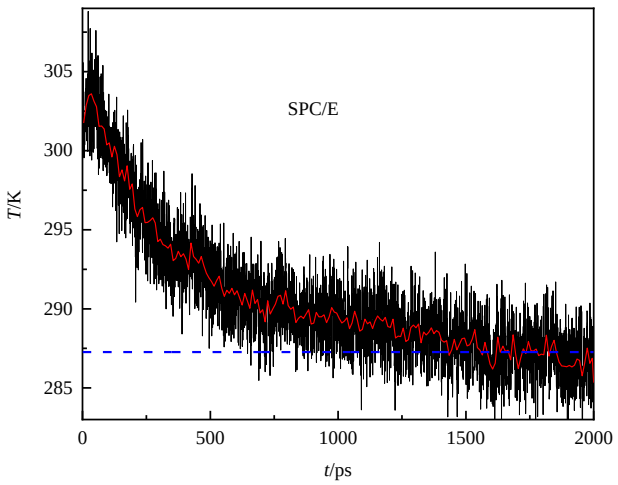
Fig. S1 RDF of oxygen atoms under different models.

Calculation of equilibrium temperature

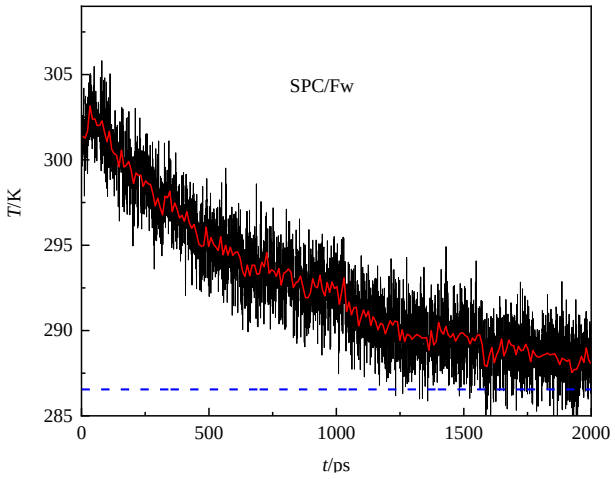
For TIP4P, SPC/E and SPC/Fw models, the decomposition of methane hydrate is simulated respectively under the same temperature and pressure conditions (10Mpa, 300K). The temperature distribution is shown in black lines in Fig. S2. Then the temperature variation along time is obtained by taking average of every 20 data points as shown in red lines. The equilibrium temperature is fitted according to the equation given by Baghel *et al*.[2] and marked with blue dotted lines. The predicted equilibrium temperatures of TIP4P, SPC/E and SPC/ Fw are 291.86 K, 287.27 K and 286.55 K respectively. Goel[3] obtained that the equilibrium temperature of methane hydrate under 10Mpa was 285K through experiments, which indicates that the predicted values of these three models are within a reasonable range.



(a)



(b)



(c)

Fig. S2 Equilibrium temperature under different models. (a) TIP4P model (b) SPC/E model (c) SPC/Fw model.

The time-variations of water, hydrate and overall temperature

It can be seen from Figure S3 that for the first stage, there exists an relative large temperature difference between water and hydrate, thus in this stage, heat diffusion (sensible heat) caused by heat conduction between water and hydrate dominates the decomposition process. However, when it enters the second stage, the temperature difference which becomes very small mainly presents fluctuation behavior. Sensible heat no longer occupies the dominant position. However, in this stage, the overall temperature drops, kinetic energy is converted into potential energy for the latent-heat thermal dissipation.

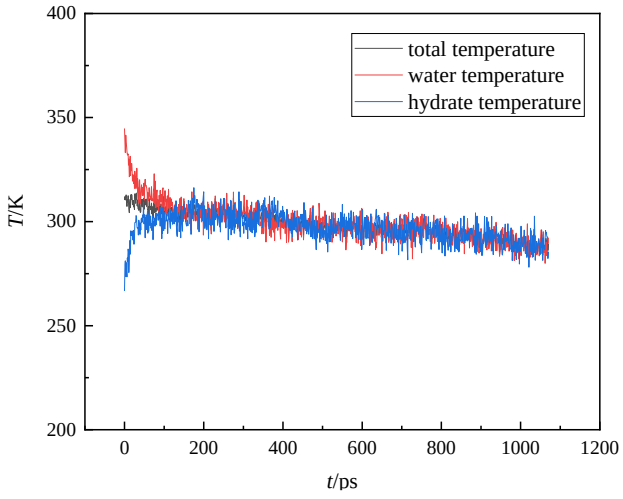


Fig. S3 The time-variations of water, hydrate and overall temperature.

References

[1] G. R. Dickens and M. S. Quinby-Hunt, Geophys. Res. Lett., 1994, 21(19),2115.

[2] V. S. Baghel, R. Kumar, and S. Roy, J. Phys. Chem. C, 2013, 117(23), 12172.

[3] N. Goel, J. Petrol. Sci. Eng., 2006, 51 (3−4), 169.