

## Electronic Supporting Information

### ReaxFF-Molecular Dynamics simulations of non-oxidative and non-catalyzed thermal decomposition of methane at high temperatures

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This supporting information provides details on the relation of the pressure to the temperature and density at the state points which were chosen for the simulations.

The combinations of initial system temperatures (2500 K to 3500 K in steps of 250 K) and system densities (0.05 g/cm<sup>3</sup>, 0.1 g/cm<sup>3</sup> and 0.2 g/cm<sup>3</sup>) for the simulations have corresponding initial pressures. The pressure is expected to show a development with time as the simulations start in non-equilibrium states and the composition of the systems will change due to reactions taking place. One possibility to determine the pressure at the beginning of the simulations is to estimate it by the van der Waals equation of state [1] from the chosen temperatures and densities, the molar weight of methane (16.04 g/mol) and the van der Waals constants for methane ( $a = 0.2283 \text{ Jm}^3/\text{mol}^2$ ,  $b = 4.278 \cdot 10^{-5} \text{ m}^3/\text{mol}$ ) [2]. The results are listed in Table 1.

During the simulations, the pressure is calculated from the virials [3]. We have averaged the values during the time interval from 0.5 ps to 5 ps (omitting the highly ordered initial configuration) in order to estimate the initial pressure at the beginning of the simulations. The obtained values are listed in Table 2. We limited the averaging to this short time interval because the pressure showed no drift to either lower or higher values in this time range. The data of both tables is displayed in Fig. 1a. The pressure as calculated by the virials

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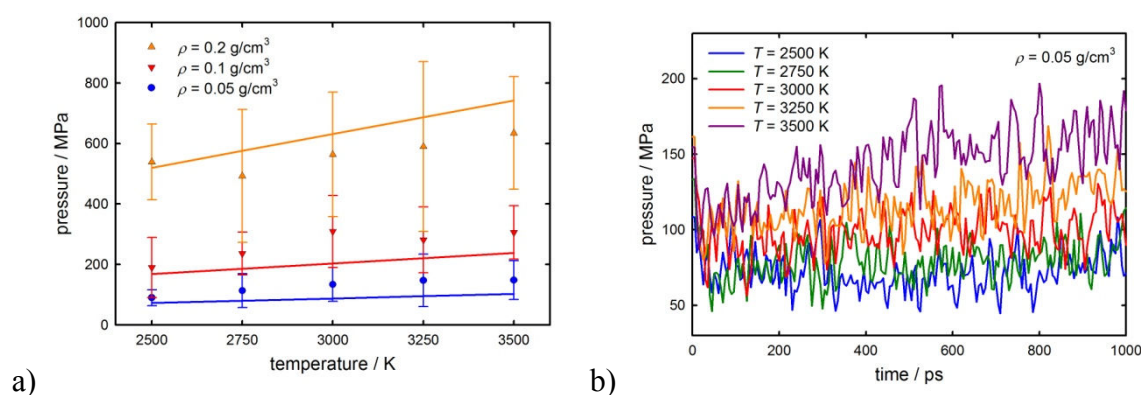
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fluctuates strongly which results in large error bars. However, the line indicating the  $p(T)$  development as calculated by the equation of state lies within most of the error bars. A drift could be observed on longer time scales which got stronger the more methane got decomposed and new molecules got formed. Fig. 1b shows this drift over the full simulation time by running averages of the pressure values calculated during the simulations.

## References

- [1] P. W. Atkins, *Physical Chemistry*, 5<sup>th</sup> edn., Oxford University Press, Oxford, 1994.
- [2] Handbook of Chemistry and Physics, 53<sup>rd</sup> edn., editor: R. C. Weast, Chemical Rubber Co., Cleveland, 1972.
- [3] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Oxford University Press, New York (1987).

## Figures



**Figure 1:** a) Pressure at the beginning of the simulation runs as calculated by the van der Waals equation of state (lines) and averaged from simulation data in the time interval 0.5 ps – 5 ps (symbols); b) Development of running averages of the pressure as calculated by virials during the simulation runs for the systems at  $0.05 \text{ g/cm}^3$  system density.

## Tables and Table captions

	2500 K	2750 K	3000 K	3250 K	3500 K
0.05 g cm <sup>-3</sup>	72.5	80.0	87.5	95.0	103
0.1 g cm <sup>-3</sup>	168	186	203	221	239
0.2 g cm <sup>-3</sup>	520	576	631	687	742

**Table 1:** Initial pressure values in MPa as calculated from the van-der-Waals equation of state, a molar weight of 16.04 g/mol (methane) and van-der-Waals constants of  $a = 0.2283 \text{ J}\cdot\text{m}^3\cdot\text{mol}^{-2}$  and  $b = 4.278\cdot 10^{-5} \text{ m}^3\cdot\text{mol}^{-1}$ . [2]

	2500 K	2750 K	3000 K	3250 K	3500 K
0.05 g cm <sup>-3</sup>	90 ± 26	113 ± 56	134 ± 56	147 ± 87	148 ± 64
0.1 g cm <sup>-3</sup>	190 ± 100	236 ± 71	309 ± 119	281 ± 109	306 ± 88
0.2 g cm <sup>-3</sup>	539 ± 125	493 ± 220	564 ± 206	590 ± 281	636 ± 186

**Table 2:** The table shows averages of the initial pressure values in MPa at the various state points which were calculated by virials during the simulations. The averages were taken in the time interval 0.5 ps – 5 ps.