Supporting Information for "Adsorption and diffusion of methane and carbon dioxide in amorphous regions of cross-linked polyethylene: a molecular simulation study"

Yafan Yang, Arun Kumar Narayanan Nair*, and Shuyu Sun†

Physical Science and Engineering Division (PSE),

Computational Transport Phenomena Laboratory,

King Abdullah University of Science and Technology (KAUST),

Thuwal, 23955-6900, Saudi Arabia.

March 20, 2019

*To whom correspondence should be addressed, email: arun.narayanannair@kaust.edu.sa

†To whom correspondence should be addressed, email: shuyu.sun@kaust.edu.sa

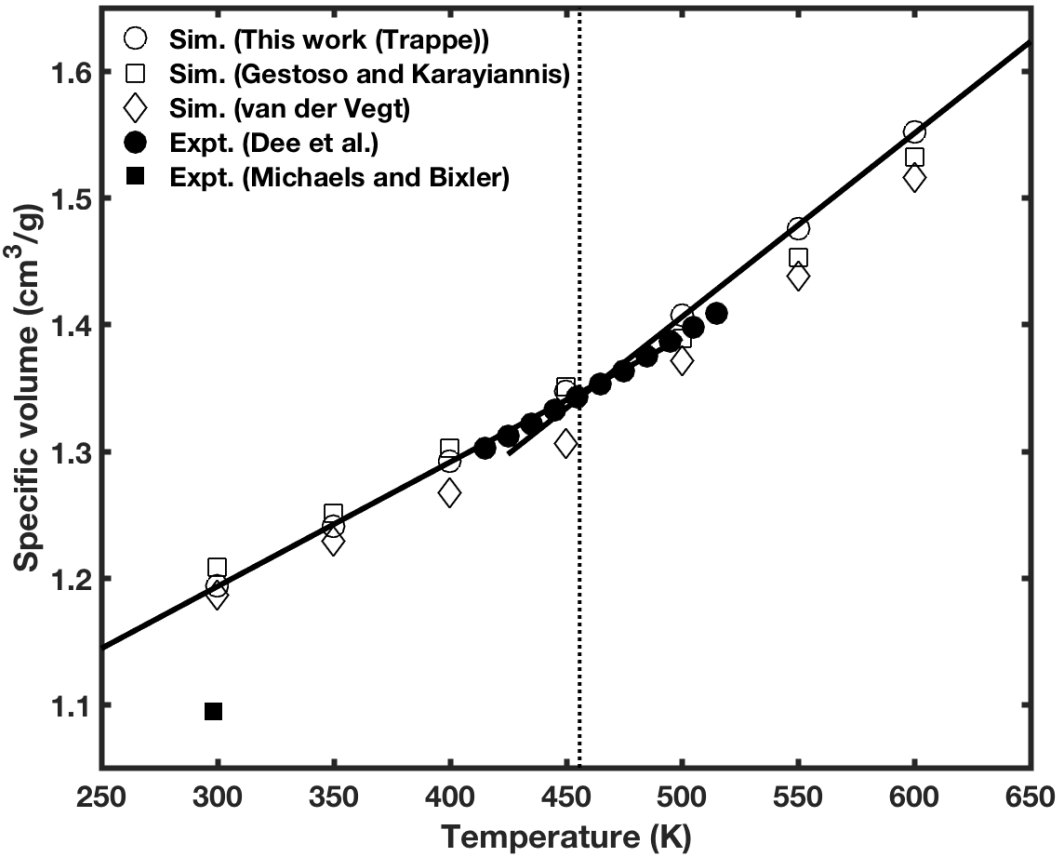

Figure S1: Temperature dependence of the specific volume of polyethylene at 1 atm. Error bars are smaller than the symbol size. Solid lines are a guide to the eye.

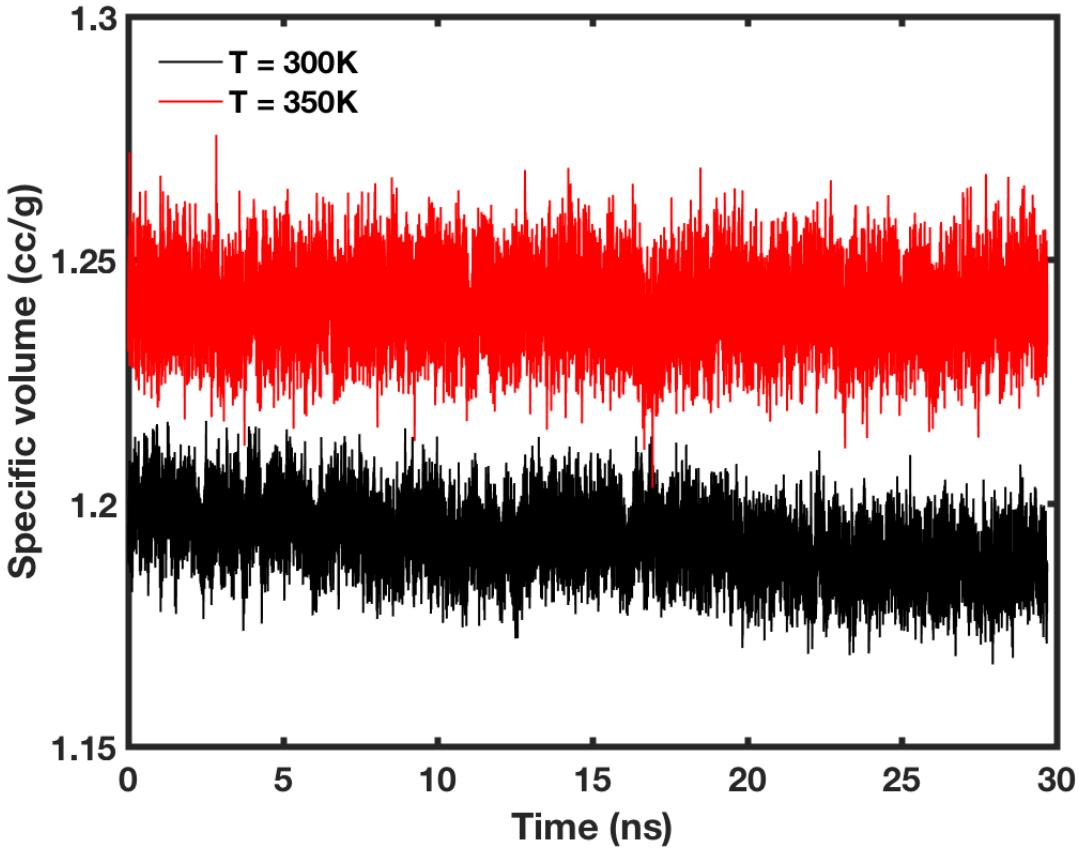

Figure S2: Time evolution of the specific volume of polyethylene at 1 atm. The system was rapidly (1 ns MD) brought to the required condition from a molten state at time 0. Some characteristic of polymer crystallization may be seen at low temperature, however, the homogeneous crystal nucleation may require several hundred ns (Yi et al., 2013).

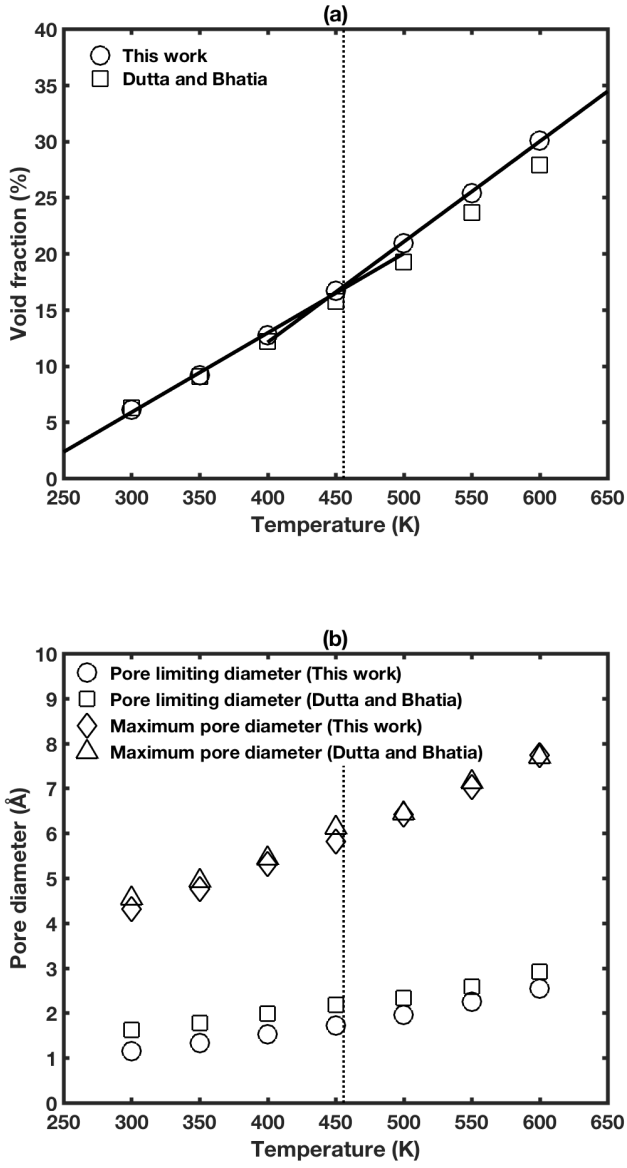

Figure S3: Temperature dependence of (a) void fraction and (b) pore diameters in the polyethylene system at 1 atm. Solid lines are a guide to the eye.

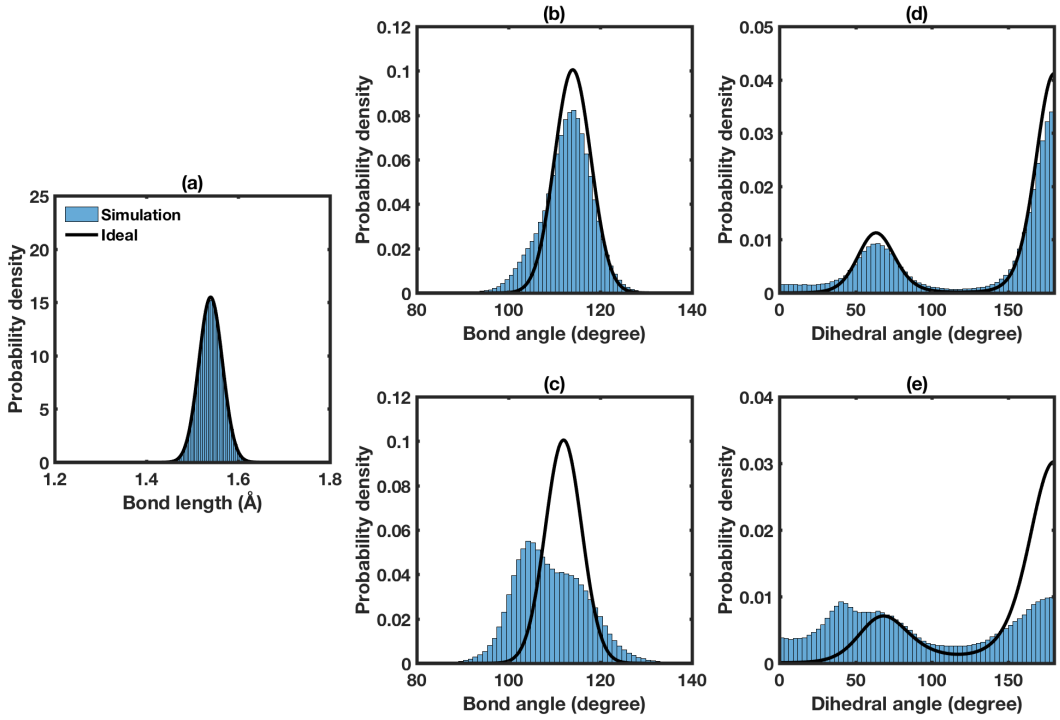

Figure S4: Probability distribution of (a) bond length, (b) CH_x-CH_2-CH_y bond angle, (c) CH_x-CH-CH_y bond angle, (d) CH_x-CH_2-CH_2-CH_y dihedral angle, and (e) CH_x-CH_2-CH-CH_y/CH_x-CH-CH-CH_y dihedral angle for cross-linked polyethylene (cross-linking degree of 20%) at 300 K and 1 atm.

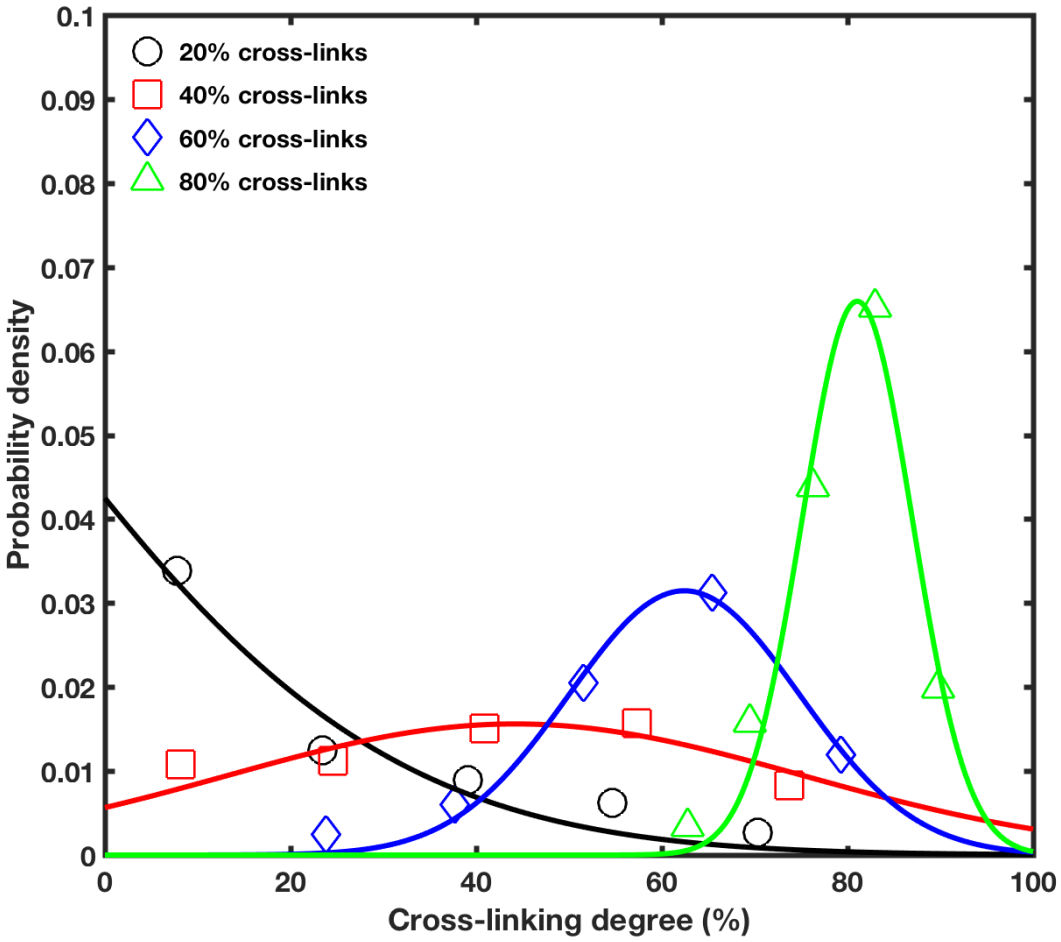

Figure S5: Probability distribution of the cross-linked units of polyethylene for different values of the cross-linking degree at 300 K and 1 atm. The lines are fitting results to the simulation data.

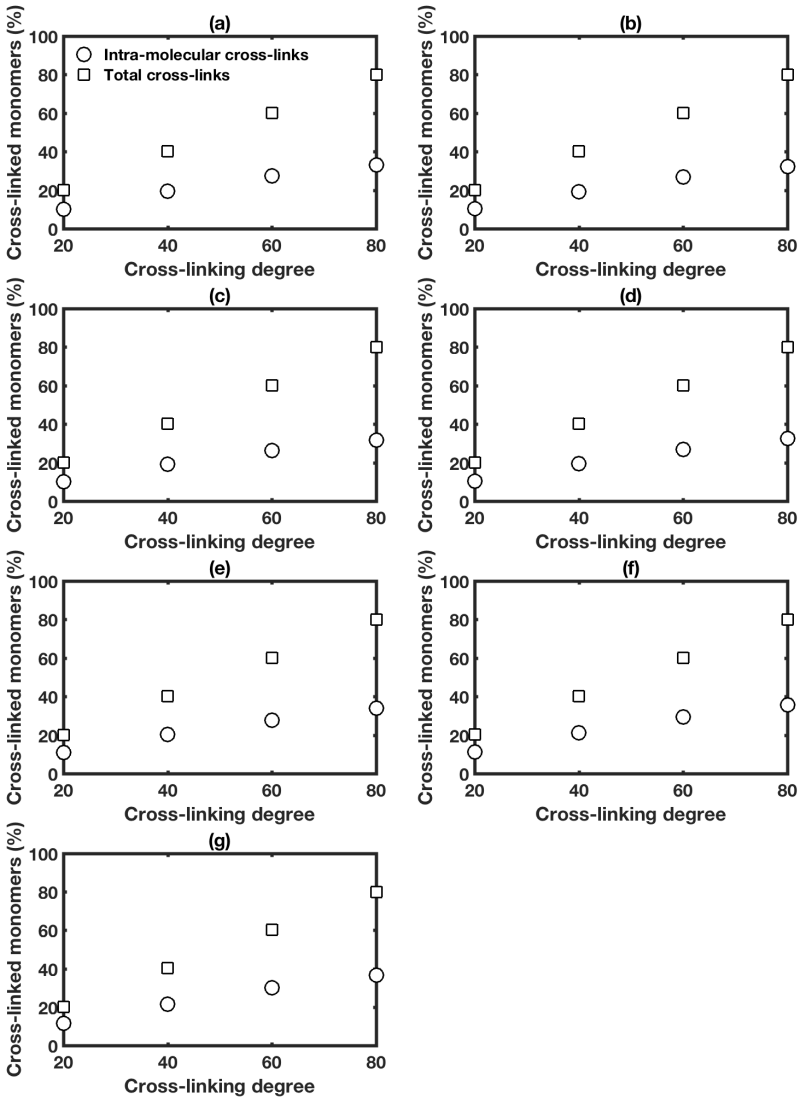

Figure S6: Number of intra-molecular cross-links as a function of cross-linking degree at (a) 300, (b) 350, (c) 400, (d) 450, (e) 500, (f) 550 and (g) 600 K, and 1 atm.

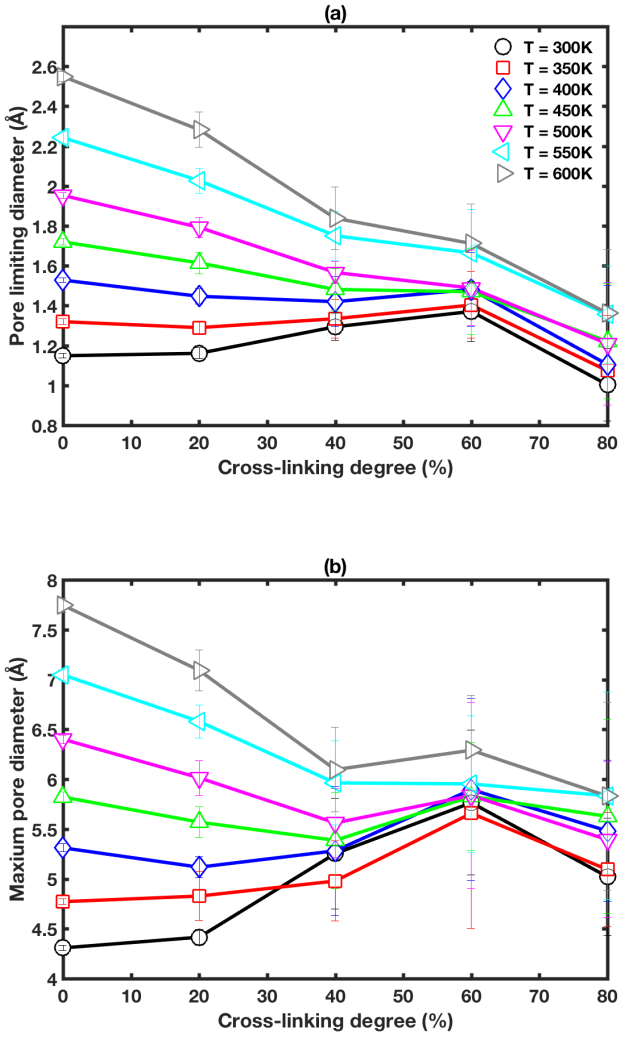

Figure S7: (a) Pore limiting diameter and (b) maximum pore diameter in the cross-linked polyethylene system as a function of cross-linking degree at 1 atm. The lines are a guide to the eye.

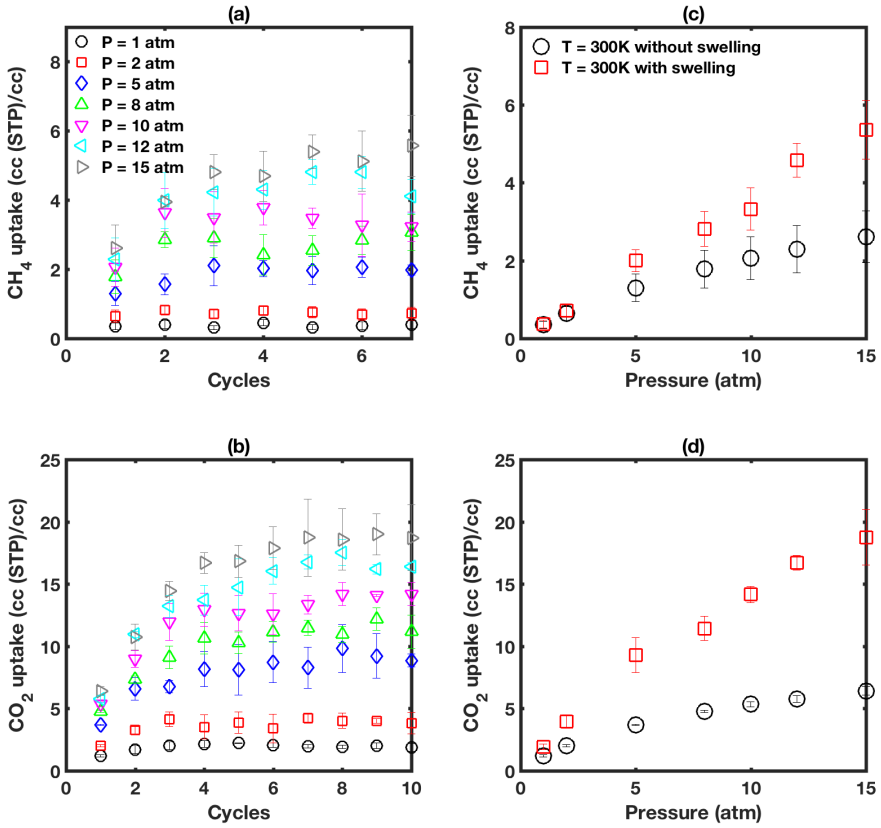

Figure S8: Variation of the adsorption amount for (a) methane and (b) CO_2 in polyethylene as a function of the number of hybrid MC/MD cycles at 300 K. Also shown is the effect of swelling on adsorption isotherms of (c) methane and (d) CO_2 in polyethylene at 300 K.

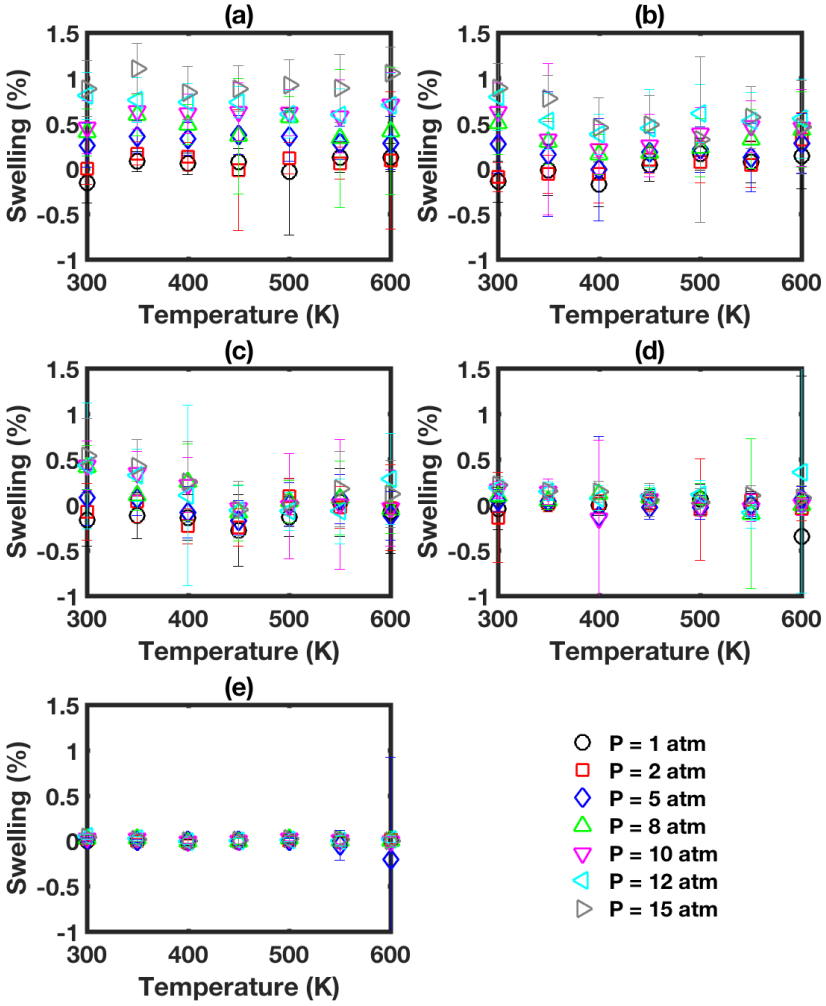

Figure S9: Temperature dependence of the swelling ($\Delta V/V$) of the cross-linked polyethylene in the presence of methane for cross-linking degree of (a) 0, (b) 20, (c) 40, (d) 60, and (e) 80%.

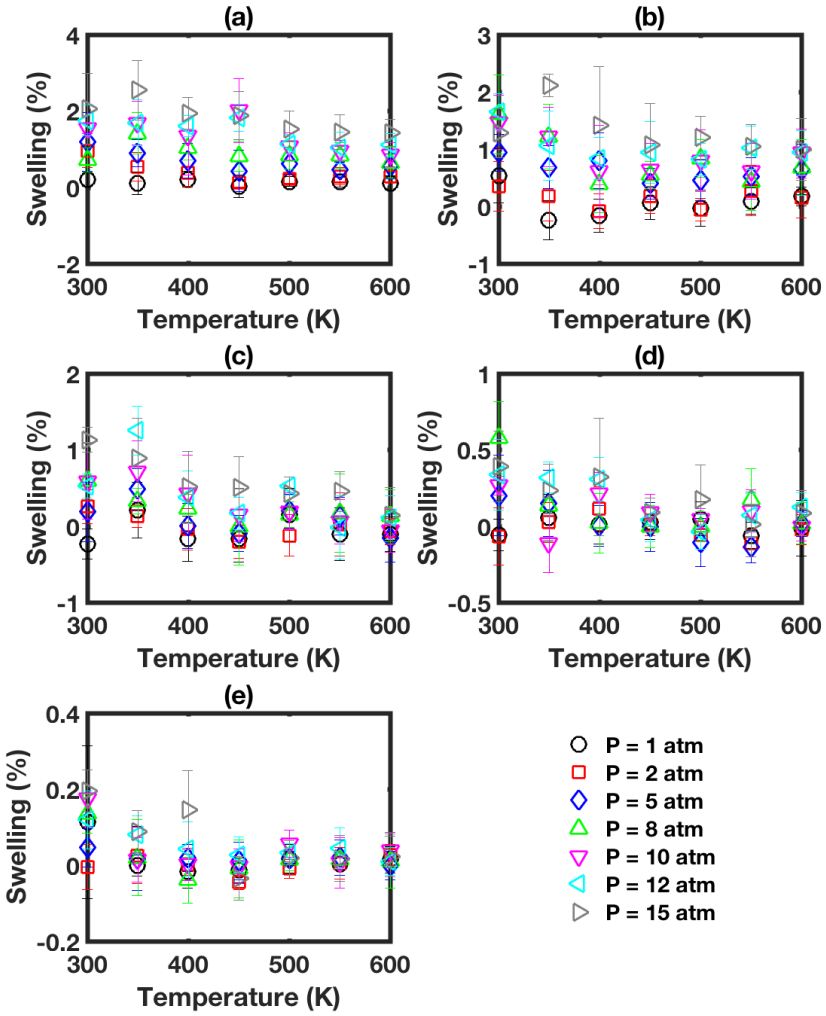

Figure S10: Same as in Fig. S9, but for the CO_2 case.

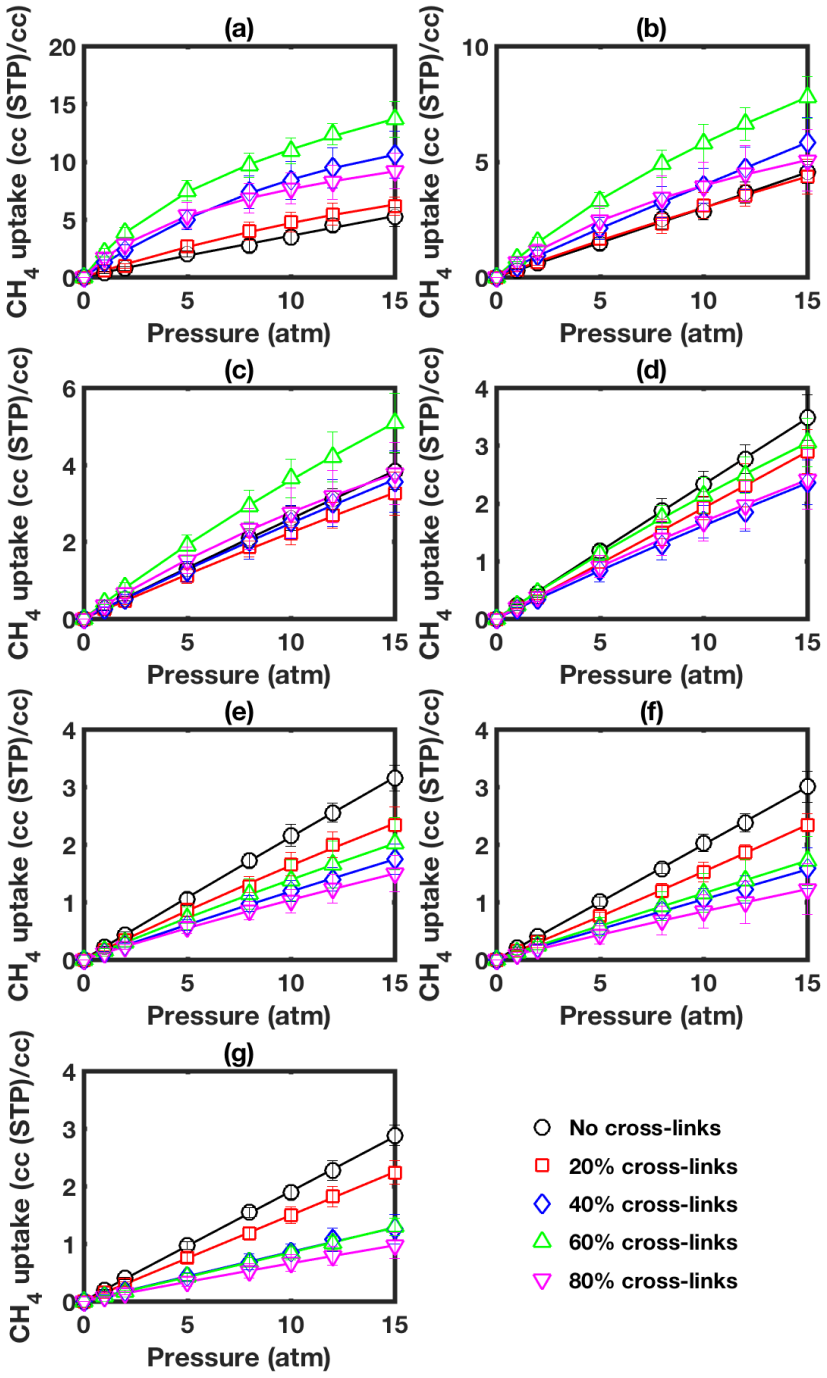

Figure S11: Adsorption isotherms as computed from simulations (symbols) of methane in the cross-linked polyethylene system at (a) 300, (b) 350, (c) 400, (d) 450, (e) 500, (f) 550, and (g) 600 K. The lines are fitting results to the simulation data.

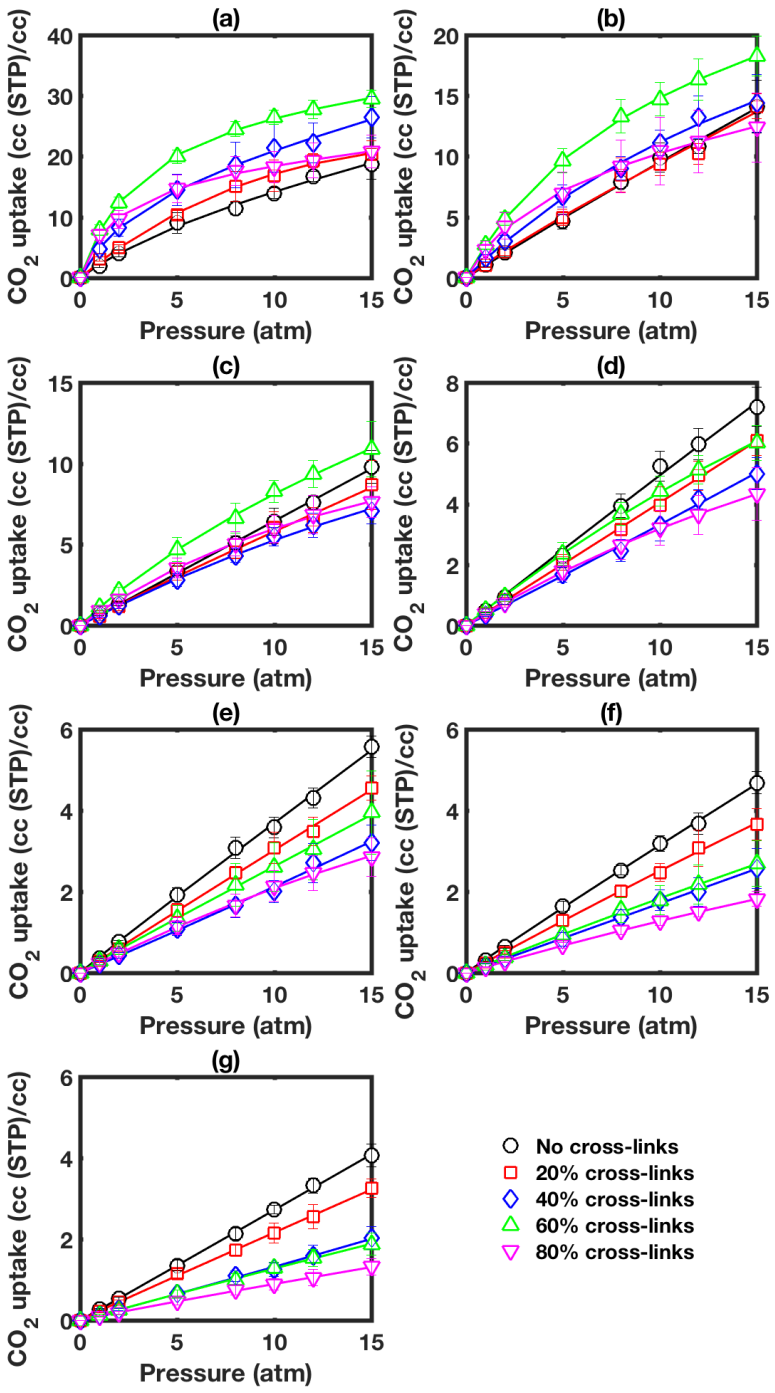

Figure S12: Same as in Fig. S11, but for the CO_2 case.

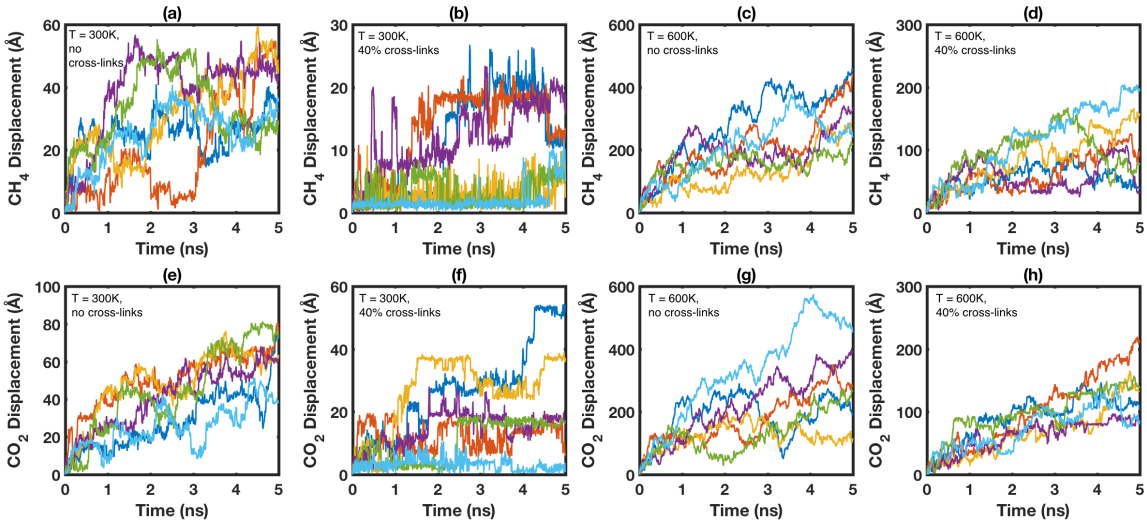

Figure S13: Six trajectories of methane (top panels) and CO_2 (bottom panels) molecules in the cross-linked polyethylene (cross-linking degree of 0 and 40%) at 300 and 600K. For clarity, only the first 5 ns of the production run is shown.

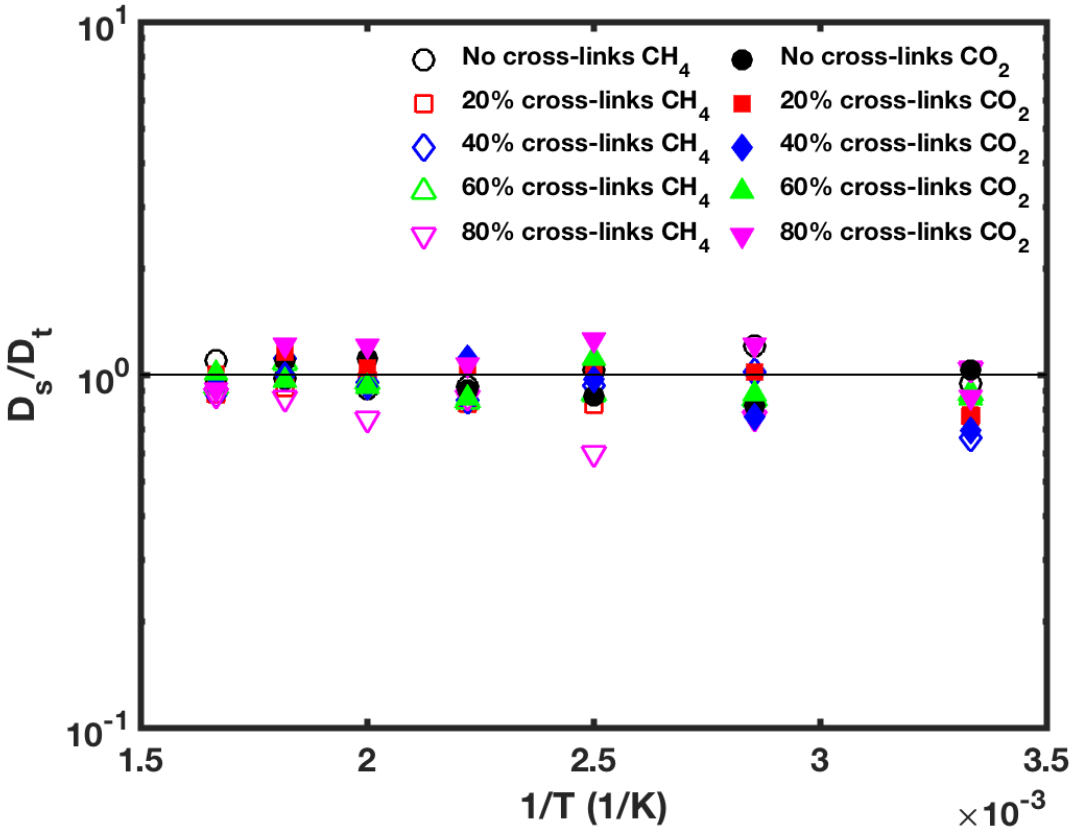

Figure S14: Comparison of the simulated self and transport diffusivities of methane and CO_2 in the cross-linked polyethylene at 1 atm.