

# Supporting Information

## Thermal Conductivity of Methane Hydrate from Experiment and Molecular Simulation

*Eilis J. Rosenbaum<sup>†,+</sup>, Niall J. English<sup>\*,†,‡,1</sup>, J. Karl Johnson<sup>†,‡</sup>, David W. Shaw<sup>#</sup>,*

*and Robert P. Warzinski<sup>\*,†</sup>*

National Energy Technology Laboratory, United States Department of Energy, P.O. Box 10940, Pittsburgh, Pennsylvania 15236; NETL Support Contractor, Parsons, P.O. Box 618, South Park, PA 15129; Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261; and Geneva College, Department of Engineering, 3200 College Avenue, Beaver Falls, Pennsylvania 15010

\*Address correspondence to these authors. Emails: modeling - [niall.english@ucd.ie](mailto:niall.english@ucd.ie), experimental - [robert.warzinski@netl.doe.gov](mailto:robert.warzinski@netl.doe.gov)

<sup>†</sup>National Energy Technology Laboratory

<sup>+</sup>Parsons

<sup>‡</sup>University of Pittsburgh

<sup>#</sup>Geneva College

---

<sup>1</sup> Current address: School of Chemical and Bioprocess Engineering, The Centre for Synthesis and Chemical Biology, Conway Institute of Biomolecular and Biomedical Research, University College Dublin, Belfield, Dublin 4, Ireland.

Compaction Pressure (MPa)	Thermal Conductivity (W/m·K)	Thermal Diffusivity (m <sup>2</sup> /s)	Data points
Data at 261.5 K, 4.68 MPa methane pressure			
37.59 ± 0.14	0.665 ± 0.013	2.00E-07 ± 5.69E-09	17
31.76 ± 0.15	0.679 ± 0.012	1.96E-07 ± 2.91E-09	5
25.03 ± 0.38	0.684 ± 0.012	1.91E-07 ± 6.41E-09	16
19.62 ± 0.04	0.669 ± 0.024	2.03E-07 ± 8.90E-09	3
13.24 ± 0.24	0.680 ± 0.020	1.94E-07 ± 5.66E-09	4
7.45 ± 0.02	0.676 ± 0.011	1.93E-07 ± 4.18E-09	21
43.74 ± 0.40	0.684 ± 0.006	1.94E-07 ± 4.97E-09	4
41.95 ± 0.31	0.695 ± 0.004	1.96E-07 ± 3.54E-09	3
2.50 ± 0.16	0.689 ± 0.008	2.03E-07 ± 1.53E-09	3
Data at 275.4 K, 4.62 MPa methane pressure			
26.88 ± 0.21	0.677 ± 0.011	2.07E-07 ± 6.05E-09	3

**Table S1.** Thermal conductivity and thermal diffusivity results for compacted methane hydrate as a function of compaction pressure and temperature. Thermal conductivity results are shown in Figure 5 and represent data taken during three out of four cycles of releasing and applying compaction pressure.

Temperature (K)	Methane Pressure (MPa)	Thermal Conductivity (W/m·K)	Thermal Diffusivity (m <sup>2</sup> /s)	Data points
261.55 ± 0.01	(*See caption)	0.685 ± 0.011	2.01E-07 ± 5.76E-09	91
275.40 ± 0.03	(*See caption)	0.679 ± 0.013	2.08E-07 ± 1.09E-08	16
277.38 ± 0.01	6.30 ± 0.02	0.684 ± 0.002	2.14E-07 ± 1.36E-10	2

**Table S2.** Thermal conductivity and thermal diffusivity results for compacted methane hydrate as a function of temperature. Thermal conductivity and thermal diffusivity results are shown in Figures 6 and 7, respectively. Data were taken over a range of compaction pressures from 2.5 to 43.7 MPa and include the data in Table S1 and the data in Table S6 that were collected at similar methane pressures (marked with #).

Pressure (MPa)	Potential	100 % Occupation	90 % Occupation	80 % Occupation
0.1	TIP4P-FQ	972.9 $\pm$ 4.2		948.8 $\pm$ 3.5
	SPC/E	944.2 $\pm$ 3.9		921.9 $\pm$ 4.5
9.5	TIP4P-FQ	974.7 $\pm$ 3.1	963.7 $\pm$ 6.3	950.5 $\pm$ 3.2
	SPC/E	945.1 $\pm$ 3.4	935.7 $\pm$ 6.2	922.9 $\pm$ 3.6
	TIP4P-Ew	939.9 $\pm$ 3.9	927.9 $\pm$ 5.7	917.1 $\pm$ 4.1
15	TIP4P-FQ	976.3 $\pm$ 3.5		951.8 $\pm$ 3.6
	SPC/E	945.7 $\pm$ 3.2		923.7 $\pm$ 3.8
30	TIP4P-FQ	978.7 $\pm$ 3.3		954.5 $\pm$ 3.8
	SPC/E	947.8 $\pm$ 4.1		925.0 $\pm$ 4.4
50	TIP4P-FQ	981.4 $\pm$ 3.8		956.7 $\pm$ 3.0
	SPC/E	950.2 $\pm$ 3.3		928.2 $\pm$ 3.3
100	TIP4P-FQ	984.0 $\pm$ 3.9		956.7 $\pm$ 4.2
	SPC/E	954.9 $\pm$ 3.8		932.8 $\pm$ 3.7

**Table S3.** Density results (kg/m<sup>3</sup>) for 8-unit cell systems at 276 K for 80 to 100% methane occupations.

Pressure (MPa)	Potential	100% Occupation	90% Occupation	80% Occupation
0.1	TIP4P-FQ	23.55 $\pm$ 0.034		23.55 $\pm$ 0.029
	SPC/E	23.79 $\pm$ 0.033		23.78 $\pm$ 0.039
9.5	TIP4P-FQ	23.54 $\pm$ 0.025	23.53 $\pm$ 0.051	23.54 $\pm$ 0.026
	SPC/E	23.78 $\pm$ 0.028	23.76 $\pm$ 0.052	23.77 $\pm$ 0.031
	TIP4P-Ew	23.83 $\pm$ 0.033	23.83 $\pm$ 0.049	23.82 $\pm$ 0.035
15	TIP4P-FQ	23.53 $\pm$ 0.028		23.53 $\pm$ 0.030
	SPC/E	23.78 $\pm$ 0.027		23.76 $\pm$ 0.032
30	TIP4P-FQ	23.51 $\pm$ 0.026		23.50 $\pm$ 0.031
	SPC/E	23.76 $\pm$ 0.034		23.75 $\pm$ 0.038
50	TIP4P-FQ	23.49 $\pm$ 0.030		23.49 $\pm$ 0.024
	SPC/E	23.74 $\pm$ 0.027		23.72 $\pm$ 0.028
100	TIP4P-FQ	23.46 $\pm$ 0.031		23.49 $\pm$ 0.034
	SPC/E	23.70 $\pm$ 0.031		23.68 $\pm$ 0.031

**Table S4.** Lattice parameters (Å) for 8-unit cell systems at 276 K for 80 to 100% methane occupations.

Pressure (MPa)	Potential	100 % Occupation	90 % Occupation	80 % Occupation
0.1	TIP4P-FQ	0.725±0.016		0.754±0.014
	SPC/E	0.526±0.010		0.551±0.011
9.5	TIP4P-FQ	0.711±0.015	0.722±0.020	0.742±0.017
	SPC/E	0.517±0.015	0.547±0.013	0.561±0.016
	TIP4P-Ew	0.562±0.012	0.565±0.011	0.588±0.015
15	TIP4P-FQ	0.721±0.013		0.743±0.012
	SPC/E	0.528±0.014		0.563±0.015
30	TIP4P-FQ	0.733±0.012		0.754±0.011
	SPC/E	0.538±0.010		0.557±0.011
50	TIP4P-FQ	0.722±0.018		0.767±0.019
	SPC/E	0.537±0.015		0.578±0.017
100	TIP4P-FQ	0.741±0.012		0.764±0.015
	SPC/E	0.546±0.011		0.573±0.013

**Table S5.** Thermal conductivity results (W/m·K) for 8-unit cell systems at 276 K for 80 to 100% methane occupation.

Methane Pressure (MPa)	Thermal Conductivity (W/m·K)	Thermal Diffusivity (m <sup>2</sup> /s)	Data points
<b>Data at 261.54 ± 0.01 K</b>			
10.06 ± 0.02	0.713 ± 0.004	2.09E-07 ± 4.68E-09	2
7.59 ± 0.00	0.669 ± 0.043	2.25E-07 ± 1.35E-08	2
5.64 ± 0.00 #	0.709 ± 0.008	2.10E-07 ± 6.63E-09	7
4.50 ± 0.01 #	0.703 ± 0.006	2.12E-07 ± 8.72E-09	4
3.78 ± 0.00 #	0.686 ± 0.009	2.17E-07 ± 9.97E-09	4
<b>Data at 275.41 ± 0.02 K</b>			
3.78	0.694	2.20E-07	1
5.59 ± 0.01 #	0.684 ± 0.016	2.20E-07 ± 7.28E-09	5
7.47 ± 0.01	0.674 ± 0.010	2.13E-07 ± 5.31E-09	3
8.75 ± 0.00	0.666 ± 0.004	2.16E-07 ± 1.97E-09	3
12.43 ± 0.03	0.676 ± 0.004	2.12E-07 ± 2.33E-09	4
14.01 ± 0.04	0.678 ± 0.015	2.12E-07 ± 6.03E-09	4
<b>Data at 277.40 ± 0.01 K</b>			
14.15 ± 0.04	0.664 ± 0.008	2.15E-07 ± 2.74E-09	5
12.58 ± 0.02	0.656 ± 0.001	2.16E-07 ± 1.21E-09	3
8.85 ± 0.01	0.662 ± 0.012	2.16E-07 ± 6.16E-09	2
7.54 ± 0.01	0.663 ± 0.011	2.17E-07 ± 5.14E-09	3
6.30 ± 0.02 #	0.684 ± 0.002	2.14E-07 ± 1.36E-10	2

**Table S6.** Thermal conductivity and thermal diffusivity results for compacted methane hydrate as a function of methane gas pressure and temperature. Thermal conductivity results are shown in Figure 11. Data were taken at a minimal compaction pressure of approximately 3 MPa. (Figure 11 also includes data from Table S1; the thermal conductivity results at 261.5 K averaged to give  $0.680 \pm 0.01$  W/m·K. The data marked with a # were also used with the data in Table S2 in preparing Figures 6 and 7.)