Supporting information to the article: Thermodynamic Properties of Octamethylcyclotetrasiloxane

Monika Thol[1], Gabor Rutkai[2], Andreas Köster[2], Frithjof H. Dubberke[2], Thorsten Windmann[2], Roland Span[1], Jadran Vrabec[2*]

[1]Thermodynamics, Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum, Germany

[2]Thermodynamics and Energy Technology, Universität Paderborn, Warburger Straße 100, 33098 Paderborn, Germany

E-mail address corresponding author: jadran.vrabec@uni-paderborn.de

Ancillary equations

For computer calculations, it is helpful to use ancillary equations to generate starting values for density iterations. Therefore ancillary equations for vapor pressure, saturated liquid density, and saturated vapor density were developed. The equations and parameters are given below. These ancillary equations are no reference equations, so that the fundamental equation of state for octamethylcyclotetrasiloxane must be used to calculate accurate saturation properties.

Vapor pressure, Eq. (1):

$$\ln\left(\frac{p_\mathrm{v}}{p_\mathrm{c}}\right)=\left(\frac{T_\mathrm{c}}{T}\right)\sum_{i=1}^{5}n_i\left(1-\frac{T}{T_\mathrm{c}}\right)^{t_i} \tag{1}$$

Saturated liquid density, Eq. (2):

$$\frac{\rho'}{\rho_\mathrm{c}}=1+\sum_{i=1}^{5}n_i\left(1-\frac{T}{T_\mathrm{c}}\right)^{t_i} \tag{2}$$

Saturated vapor density, Eq. (3):

$$\ln\left(\frac{\rho''}{\rho_\mathrm{c}}\right)=\sum_{i=1}^{6}n_i\left(1-\frac{T}{T_\mathrm{c}}\right)^{t_i} \tag{3}$$

Table S6. Parameter values of the ancillary equations for vapor pressure, saturated liquid density, and saturated vapor density.

	p_v: Eq. (1)		ρ': Eq. (2)		ρ'': Eq. (3)	
i	n_i	t_i	n_i	t_i	n_i	t_i
1	$-0.928420\cdot10^{+1}$	1.00	$0.272160\cdot10^{+1}$	0.380	$-0.374500\cdot10^{+1}$	0.416
2	$0.381730\cdot10^{+1}$	1.50	$-0.157540\cdot10^{+1}$	0.890	$-0.920750\cdot10^{+1}$	1.350
3	$-0.444150\cdot10^{+1}$	2.10	$0.398870\cdot10^{+1}$	1.440	$-0.717860\cdot10^{+2}$	3.800
4	$-0.776280\cdot10^{+1}$	15.0	$-0.376830\cdot10^{+1}$	2.060	$0.108850\cdot10^{+3}$	4.800
5	$-0.692890\cdot10^{+1}$	3.90	$0.194450\cdot10^{+1}$	2.780	$-0.141610\cdot10^{+3}$	5.800
6					$-0.227190\cdot10^{+3}$	14.00

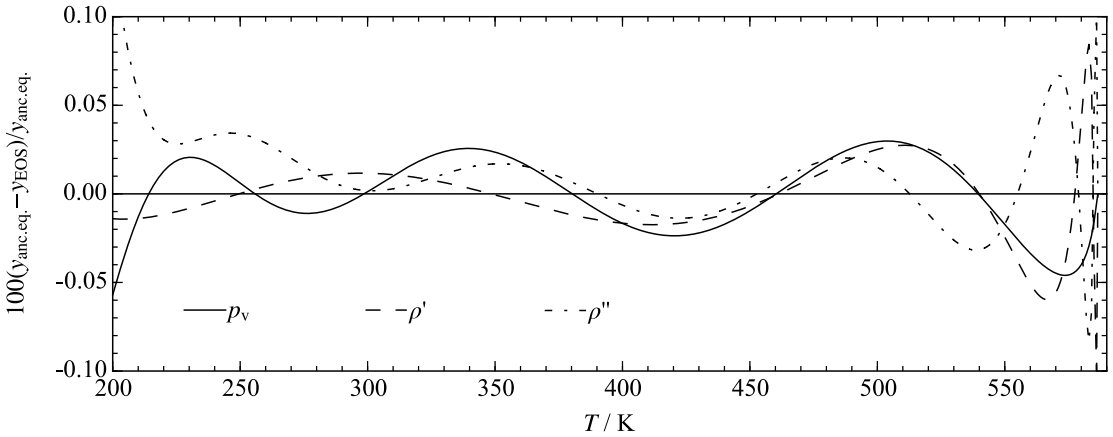

Figure S15. Relative deviations between the ancillary equations and the present fundamental equation of state for octamethylcyclotetrasiloxane.

Table S7. Test values for Computer implementation

T / K	ρ / mol·dm^3	p / MPa	c_p / J·mol^{-1}·K^{-1}	w / m·s^{-1}	h / J·mol^{-1}	s / J·mol^{-1}·K^{-1}	a / J·mol^{-1}
350	0.001	$2.8952836\cdot10^{-3}$	422.187662524	$9.9557286\cdot10^{+1}$	$-5.6066834\cdot10^{+3}$	$3.7361111\cdot10^{+0}$	$-9.8096059\cdot10^{+3}$
350	3.2	$3.8313384\cdot10^{+1}$	515.367386403	$1.0032303\cdot10^{+3}$	$-4.7367713\cdot10^{+4}$	$-1.5131880\cdot10^{+2}$	$-6.3790666\cdot10^{+3}$
500	0.08	$2.8137478\cdot10^{-1}$	549.715457833	$1.0054897\cdot10^{+2}$	$6.3803842\cdot10^{+4}$	$1.3162219\cdot10^{+2}$	$-5.5244399\cdot10^{+3}$
500	2.5	$8.0209605\cdot10^{+1}$	612.92148189	$4.7506521\cdot10^{+2}$	$3.1400054\cdot10^{+4}$	$5.9639266\cdot10^{+1}$	$-1.6279631\cdot10^{+3}$
600	3.0	$1.2685572\cdot10^{+2}$	650.740004998	$1.0716620\cdot10^{+3}$	$1.1870824\cdot10^{+5}$	$1.4134253\cdot10^{+2}$	$-8.3825142\cdot10^{+3}$

Table S8. Information for the sample used in the present speed of sound measurements.

Source	Analysis method	Fraction	Chemical name
Wacker	GC-PV20182	99.58%	Octamethylcyclotetrasiloxane (D4)
		0.21%	Hexamethylcyclotrisiloxane (D3)
		0.16%	Decamethylcyclopentasiloxane (D5)

Table S9. Experimental results for the speed of sound w at temperature T and pressure p of liquid Octamethylcyclotetrasiloxane. u denotes the standard uncertainty. The standard uncertainty for the pressure was 0.07 MPa throughout.

T / K	u_T / K	p / MPa	w / m·s^{-1}	u_w / m·s^{-1}	T / K	u_T / K	p / MPa	w / m·s^{-1}	u_w / m·s^{-1}
299.79	0.04	0.13	911.09	0.51	449.64	0.12	0.13	461.18	1.31
299.80	0.04	0.52	913.77	0.50	449.64	0.12	0.50	467.67	1.28
299.81	0.04	0.98	916.96	0.50	449.63	0.12	0.96	475.36	1.24
299.81	0.04	1.50	920.51	0.50	449.70	0.12	1.49	484.22	1.19
299.82	0.04	1.98	923.90	0.49	449.69	0.12	1.96	491.86	1.16
299.83	0.04	3.44	933.79	0.48	449.77	0.12	3.60	516.36	1.06
299.85	0.04	6.01	950.89	0.46	449.87	0.12	5.90	547.45	0.95
300.15	0.04	10.24	978.63	0.45	450.000	0.12	10.04	596.17	0.81
299.67	0.04	14.92	1006.82	0.45	450.19	0.12	15.08	646.97	0.70
					450.23	0.12	16.42	659.13	0.68
350.07	0.07	0.12	747.75	0.68					
350.06	0.07	0.53	751.64	0.68	499.92	0.14	0.33	321.35	2.08
350.05	0.07	0.96	755.62	0.67	499.94	0.14	0.52	329.04	2.02
350.05	0.07	1.48	760.43	0.66	499.92	0.14	1.49	354.75	1.76
350.04	0.07	1.96	764.80	0.65	499.91	0.14	2.03	367.40	1.65
350.04	0.07	3.53	778.49	0.63	499.88	0.14	3.48	398.42	1.43
350.03	0.07	6.21	800.86	0.59	499.88	0.14	6.03	444.06	1.18
350.00	0.07	10.20	832.31	0.55	500.000	0.14	10.65	509.56	0.93
349.98	0.07	14.97	866.97	0.51	499.93	0.14	11.15	515.95	0.91
350.35	0.07	22.66	915.86	0.46					
349.97	0.07	26.23	939.02	0.44	549.61	0.17	3.88	300.55	1.90
					549.56	0.17	4.55	317.10	1.74
399.71	0.09	0.12	600.99	0.92	549.55	0.17	5.07	329.01	1.64
399.71	0.09	0.51	605.91	0.91	549.54	0.17	5.51	338.90	1.56
399.70	0.09	1.03	612.25	0.89	549.97	0.17	6.64	364.29	1.41
399.70	0.09	1.46	617.43	0.88					
399.70	0.09	2.04	624.18	0.86					
399.68	0.09	3.61	641.86	0.81					
399.64	0.09	6.07	667.98	0.75					
399.64	0.09	10.12	706.83	0.67					
399.64	0.09	15.10	749.46	0.60					
399.69	0.09	19.29	782.02	0.56					
399.62	0.09	19.68	784.97	0.55					

Simulation details

Simulations were carried out with the molecular simulation tool *ms*2[1]. The statistical uncertainty of all simulation results was estimated with the method of Flyvbjerg and Petersen[2].

The Helmholtz energy derivatives A^{r}_{nm} and the speed of sound w (as combination of A^{r}_{nm}) were obtained directly from *NVT* ensemble MC simulations with 864 molecules using 300 000 production steps after sufficient equilibration using the formalism proposed by Lustig[3]. A^{r}_{00} was calculated by Widom's test particle method[4].

The Grand Equilibrium Monte Carlo (MC) method[5] was used for vapor-liquid equilibrium calculations, for which the liquid *NpT* ensemble runs had 400 000 production steps. The chemical potential was determined by inserting 3 456 virtual molecules into the simulation volume using Widom's test particle method[4]. The pseudo-μVT ensemble vapor simulations, that correspond to the liquid runs, continued with an average of 500 molecules using 200 000 production steps.

To calculate shear viscosity η and thermal conductivity λ data, first *NpT* molecular dynamics simulations were carried out at specified temperature and pressure to obtain the corresponding density (500 000 production time steps). In the second step, *NVT* MD simulations were carried out at the corresponding temperature and density to calculate the transport properties using 3 500 000 to 7 000 000 time steps for production runs. The simulation length was chosen to obtain at least 20 000 independent time origins of the autocorrelation functions. The sampling length of the autocorrelation functions was chosen to be between 6 und 24 ps, depending on the long-time behaviour of the shear viscosity autocorrelation function.

Table S10. Simulation results for A^{r}_{nm} at temperature T and density ρ of liquid and gaseous Octamethylcyclotetrasiloxane. Δ denotes the uncertainty calculated by the method of Flyvbjerg and Petersen[2]

The content is provided as a separate file due to its size.

[1] Glass, C. W.; Reiser, S.; Rutkai, G.; Deublein, S.; Koster, A.; Guevara-Carrion, G.;Wafai, A.; Horsch, M.; Bernreuther, M.; Windmann, T.; Hasse, H.; Vrabec, J. Comput. Phys. Commun. 2014, 185, 3302–3306.
[2] Flyvbjerg, H.; Petersen, H. G. J. Chem. Phys. 1989, 91, 461–466.
[3] Lustig, R. Mol. Phys. 2012, 110, 3041–3052.
[4] Widom, B. J. Chem. Phys. 1963, 39, 2808–2812.
[5] J. Vrabec and H. Hasse, Mol. Phys., vol. 100, pp. 3375–3383, 2002.

Table S11. Simulation results for the speed of sound w at temperature T and pressure p of liquid Octamethylcyclotetrasiloxane. Δ denotes the uncertainty calculated by the method of Flyvbjerg and Petersen[2].

T / K	p / MPa	Δ_p / MPa	w / m·s^{-1}	Δ_w / m·s^{-1}
350	0.73	0.10	775.04	22.63
350	3.80	0.10	780.24	23.03
350	6.70	0.11	825.35	25.04
350	9.98	0.11	861.58	22.14
350	11.07	0.11	867.02	22.42
350	13.01	0.12	873.11	24.63
350	16.30	0.11	897.34	25.53
350	19.29	0.13	913.55	24.11
350	22.22	0.14	919.68	26.92
400	2.87	0.06	649.81	17.79
400	5.94	0.06	668.13	18.70
400	9.04	0.07	713.99	17.12
400	10.13	0.07	719.86	18.08
400	12.11	0.08	734.59	19.94
400	15.31	0.08	764.92	18.11
400	18.12	0.08	801.58	18.65
400	21.11	0.09	800.31	20.08
450	2.68	0.04	508.19	17.75
450	5.64	0.05	569.83	15.26
450	8.76	0.05	596.67	15.51
450	9.82	0.05	601.03	16.78
450	11.80	0.05	624.23	16.27
450	14.70	0.05	643.03	16.80
450	17.89	0.06	670.02	15.73
450	20.94	0.06	715.90	15.61
500	2.56	0.03	396.37	18.20
500	5.69	0.04	456.74	17.73
500	8.76	0.04	484.86	17.11
500	9.81	0.04	503.03	16.31
500	11.86	0.03	533.17	15.51
500	14.81	0.04	575.51	14.76
500	17.96	0.05	600.95	13.15
500	20.94	0.04	622.26	14.89
550	2.64	0.02	282.36	16.99
550	5.78	0.03	360.55	14.39
550	8.89	0.03	412.29	14.41
550	9.95	0.03	421.27	15.01
550	11.96	0.03	456.09	14.30
550	14.98	0.03	509.50	13.80
550	18.05	0.04	535.71	13.56
550	21.04	0.04	574.21	12.78

Table S12. Simulation results for vapour pressure p_v, saturated liquid density ρ', saturated vapour density ρ'', and enthalpy of vaporization h_v for Octamethylcyclotetrasiloxane. Numbers in parentheses denote uncertainties in the last digit calculated by the method of Flyvbjerg and Petersen[2].

T / K	p_v / MPa	ρ' / mol·dm^{-3}	ρ'' / mol·dm^{-3}	h_v /kJ·mol^{-1}
320	0.0005 (1)	3.1276 (6)	0.00017 (3)	52.22 (2)
330	0.0008 (1)	3.082 (1)	0.0003 (4)	51.02 (2)
335	0.0017 (3)	3.058 (1)	0.0006 (1)	50.4 (3)
435	0.064 (2)	2.651 (1)	0.0187 (5)	40.77 (2)
450	0.098 (2)	2.584 (2)	0.0282 (6)	39.16 (2)
500	0.301 (8)	2.334 (3)	0.086 (2)	33.06 (3)
525	0.47 (1)	2.178 (7)	0.136 (3)	29.33 (7)
550	0.759 (9)	2.015 (8)	0.241 (3)	24.46 (8)

Table S13. Simulation results for the thermal conductivity λ and the shear viscosity η at temperature T and pressure p for liquid Octamethylcyclotetrasiloxane. Numbers in parentheses denote uncertainties in the last digit calculated by the method of Flyvbjerg and Petersen[2].

T / K	p / MPa	λ / W·m^{-1}·K^{-1}	T / K	p / MPa	η / mPa·s
290	0.1	0.091 (9)	300	0.1	3.0 (2)
340	0.1	0.09 (1)	310	0.1	2.0 (3)
390	0.1	0.071 (8)	330	0.1	1.4 (2)
440	0.1	0.07 (1)	340	0.1	1.3 (2)
			360	0.1	0.9 (1)
			370	0.1	0.8 (1)

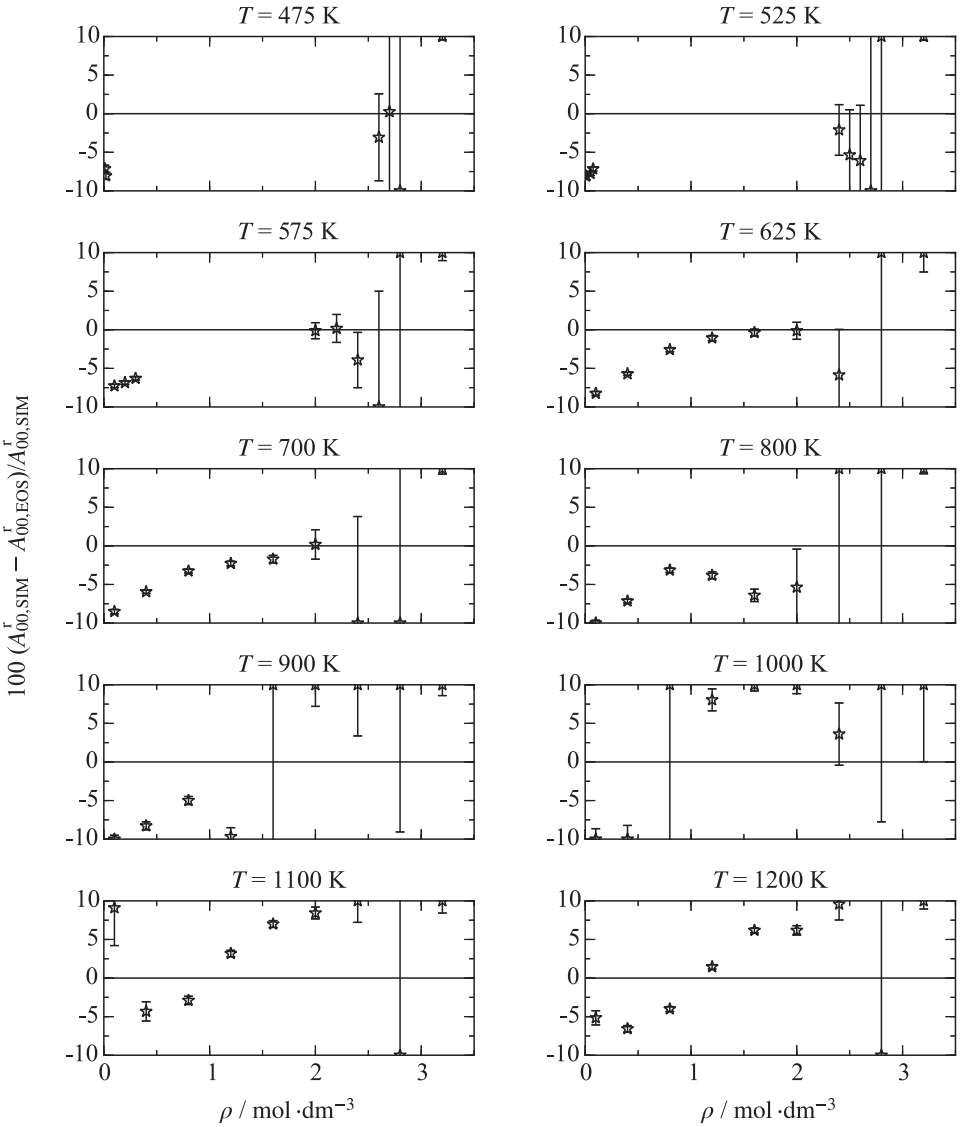

Figure S16. Relative deviation of simulated residual reduced Helmholtz energy data from the present equation of state.

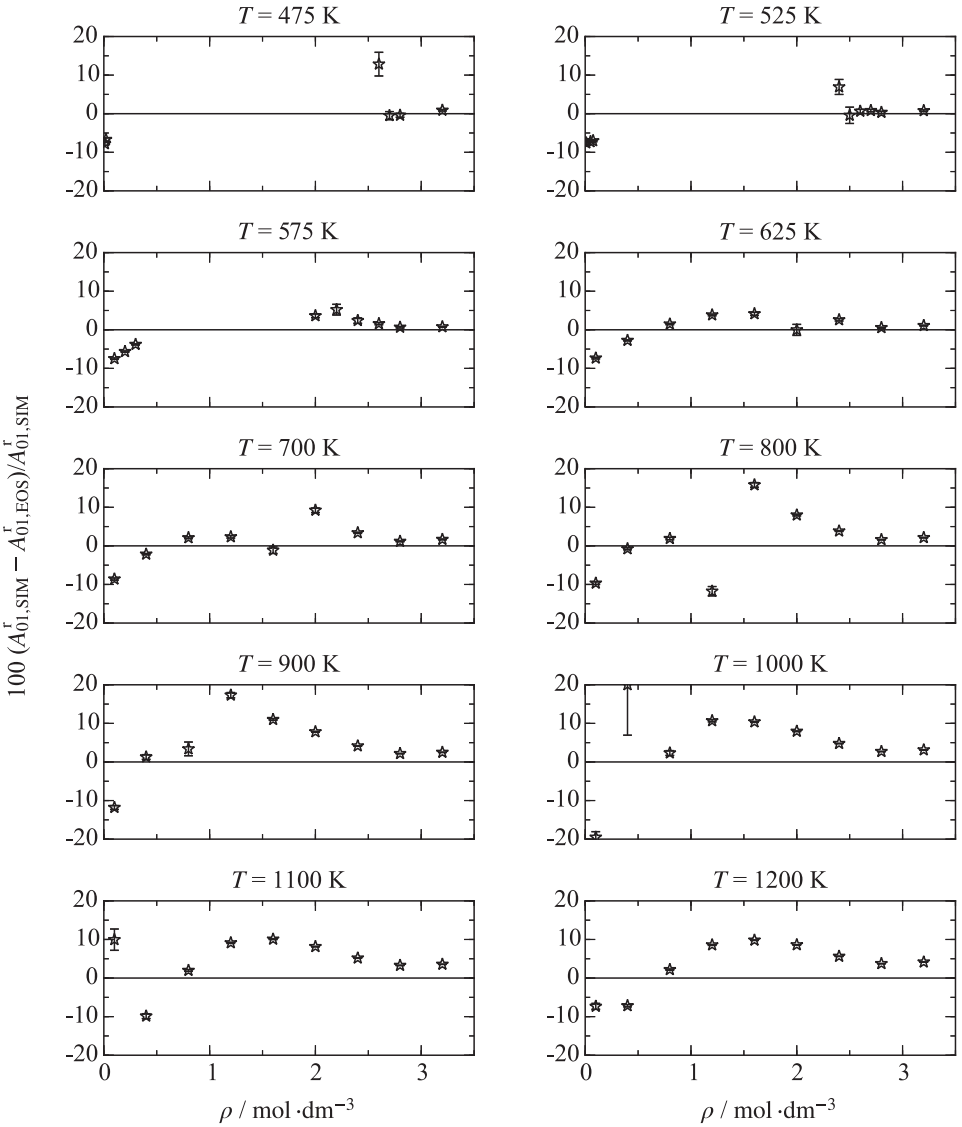

Figure S17. Relative deviation of simulated first derivative of the residual Helmholtz energy with respect to density data from the present equation of state.

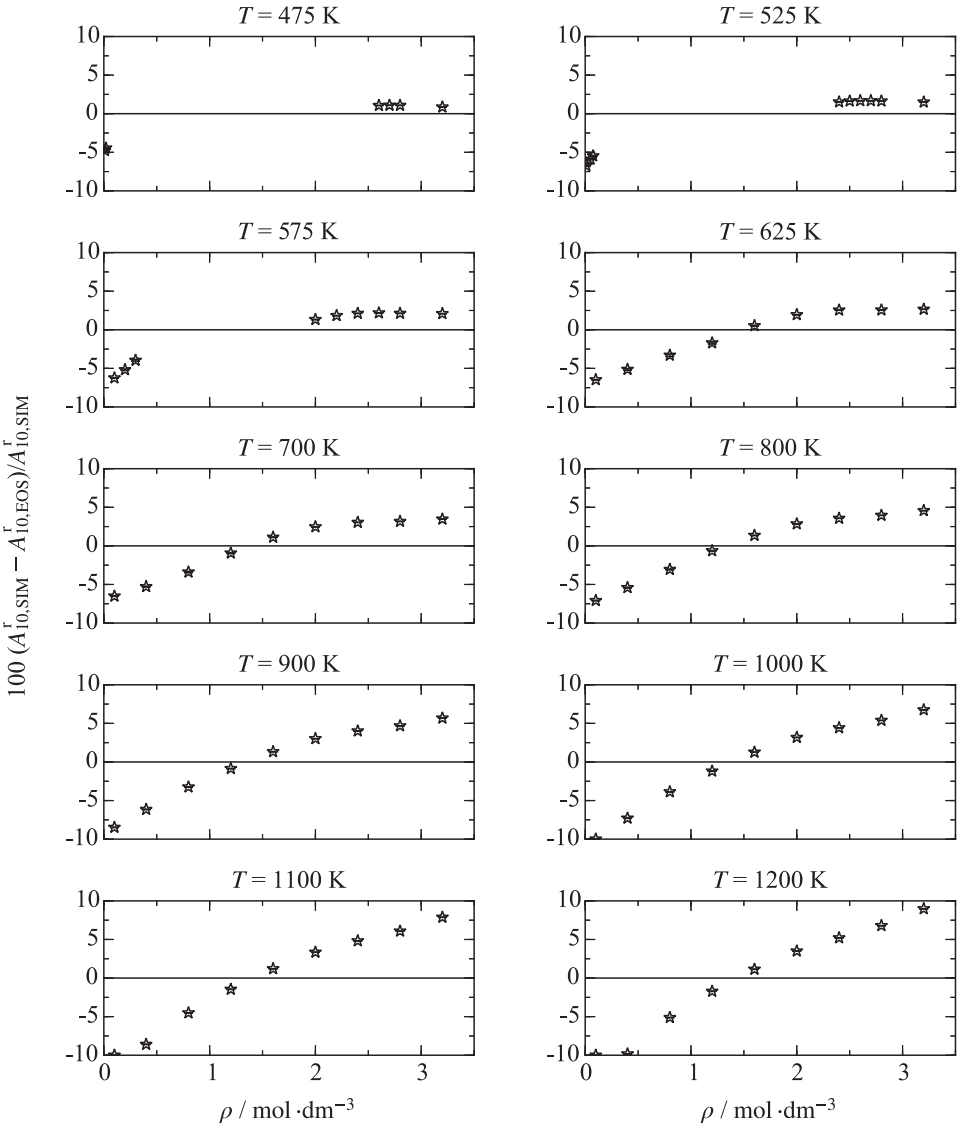

Figure S18. Relative deviation of simulated first derivative of the residual Helmholtz energy with respect to inverse temperature data from the present equation of state.

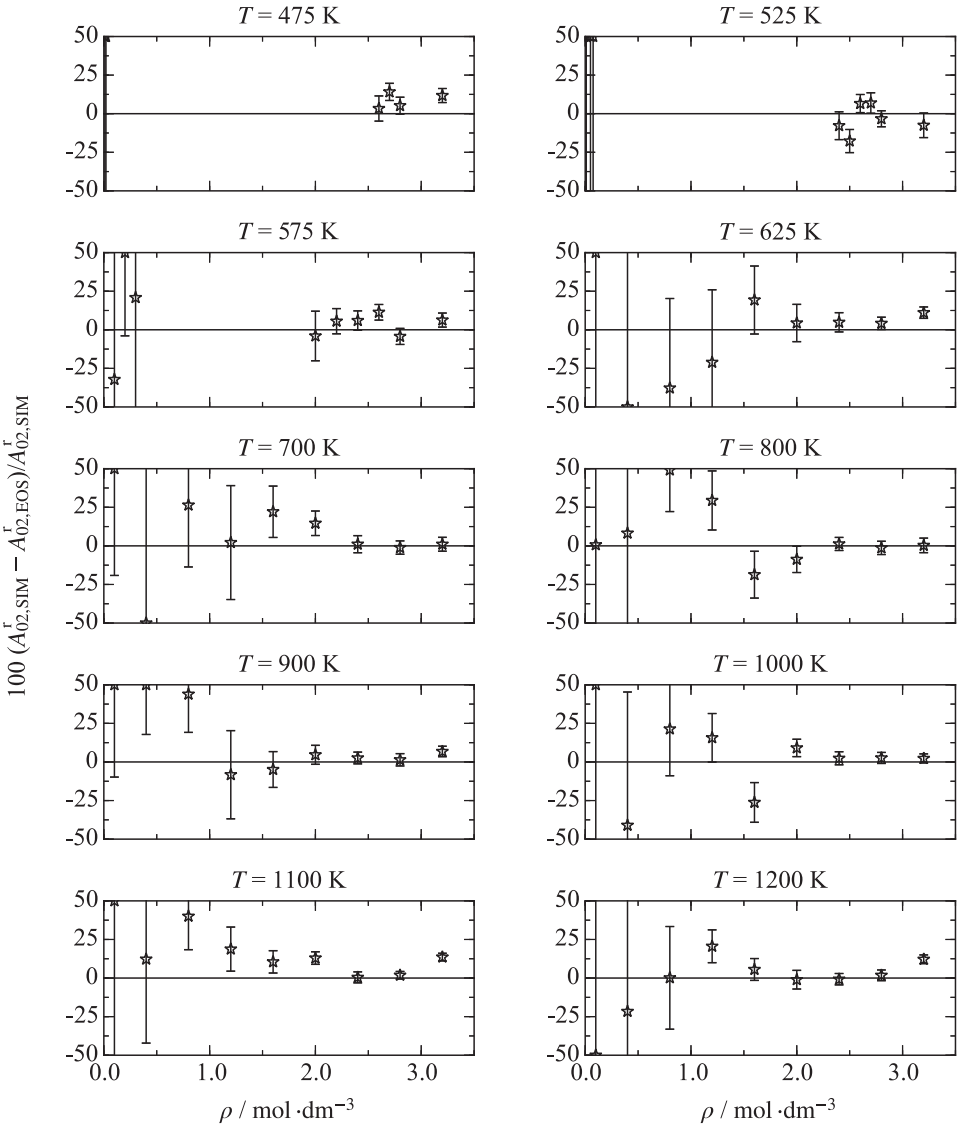

Figure S19. Relative deviation of simulated second derivative of the residual Helmholtz energy with respect to density data from the present equation of state.

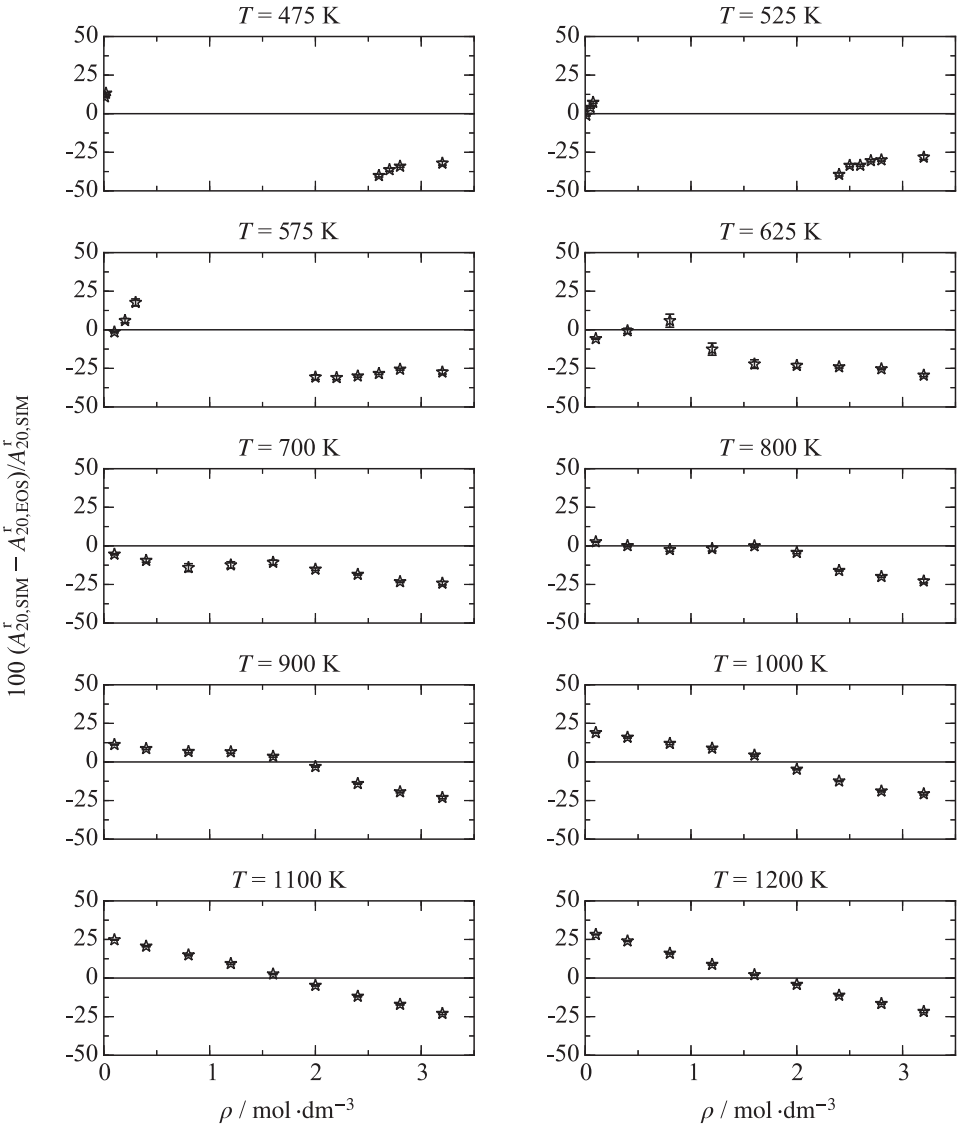

Figure S20. Relative deviation of simulated second derivative of the residual Helmholtz energy with respect to inverse temperature data from the present equation of state.

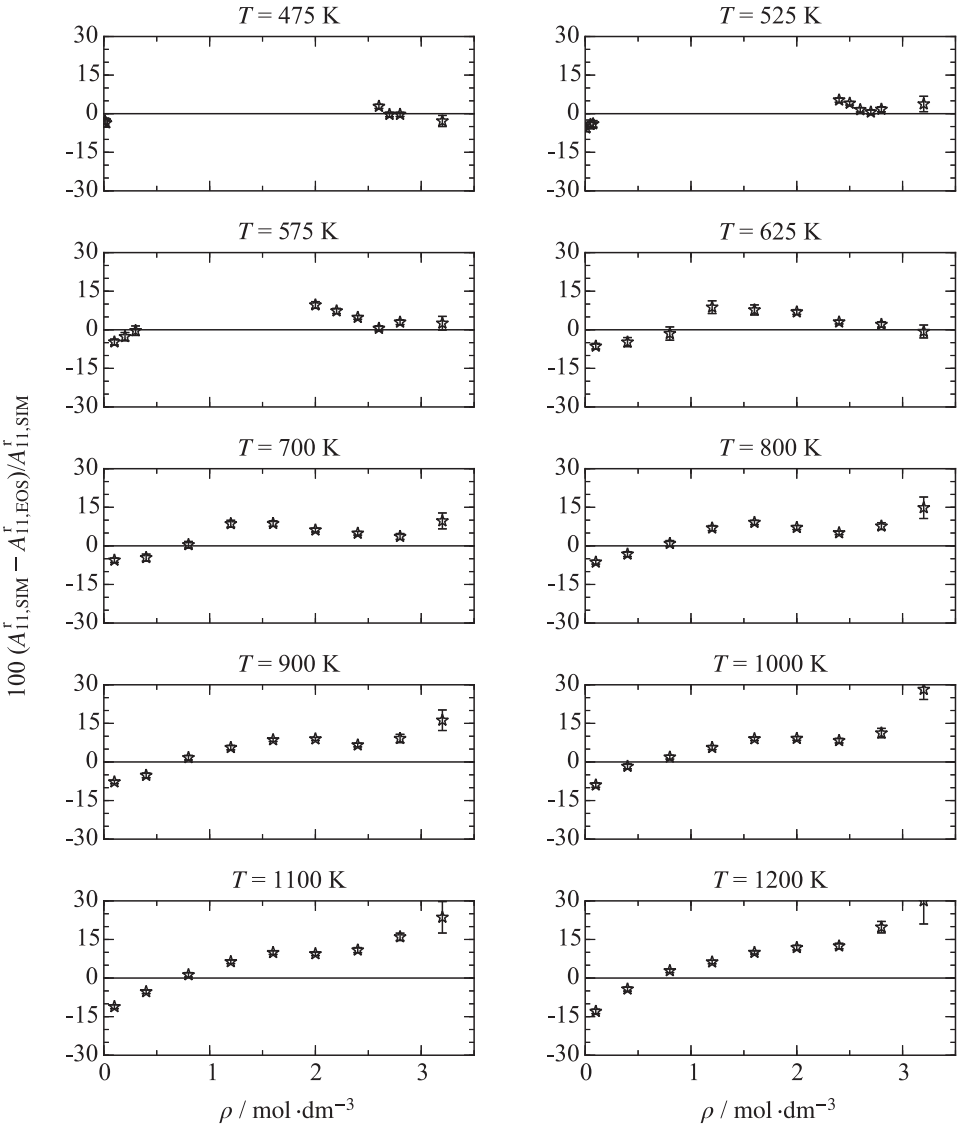

Figure S21. Relative deviation of simulated mixed derivative of the residual Helmholtz energy with respect to density and temperature data from the present equation of state.

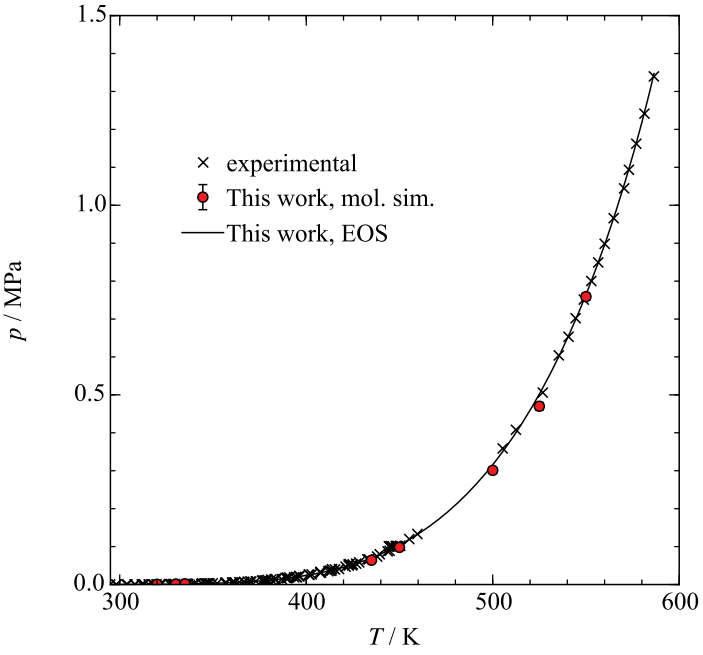

Figure S22. Representation of vapor pressure data.

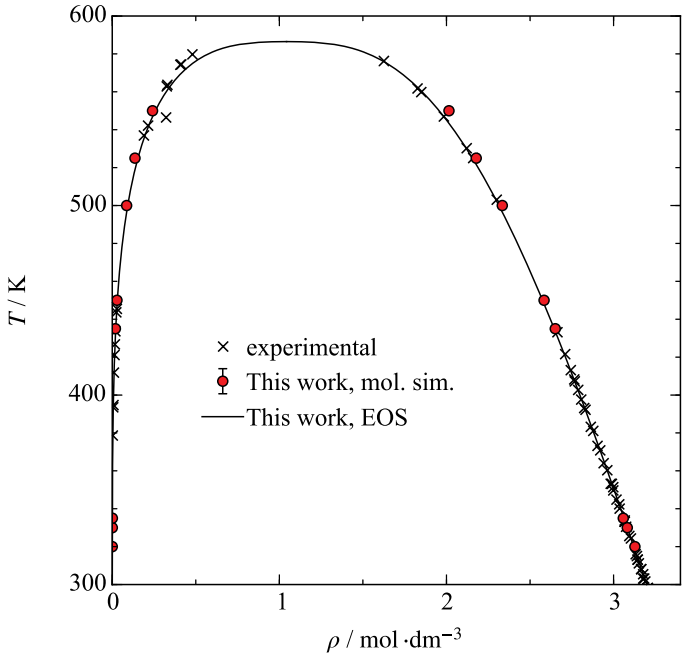

Figure S23. Representation of saturated liquid and vapor density data.

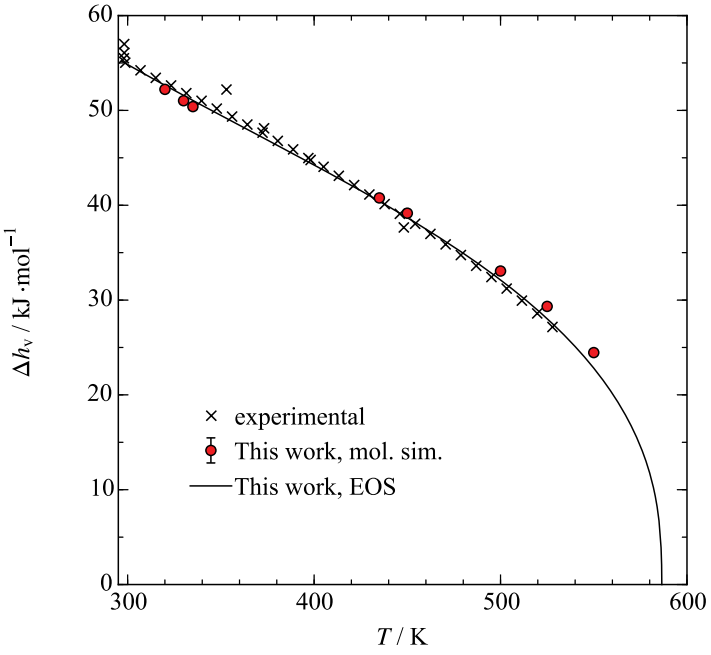

Figure S24. Representation of heat of vaporization data.