Table S1 : Low pressures Monte Carlo simulation results on 400 molecules of methane after a run of 10^7 iterations. The subscripts give the statistical accuracies of the last decimal(s).

T/K	**P/Pa**	ρ**/kg.m**$^{-3}$	c_P^{res}**/Jmol**$^{-1}$**K**$^{-1}$	α_P**/K**$^{-1}$	β_T**/Pa**$^{-1}$	μ_{JT}**/KMPa**$^{-1}$
294.25	1	$6.56_1\ 10^{-6}$	$5.42\ 10^{-2}$	$3.41\ 10^{-3}$	1.004	$3.004\ 10^5$
	10^3	$6.56_1\ 10^{-3}$	$4.83\ 10^{-4}$	$3.39\ 10^{-3}$	$9.98\ 10^{-4}$	-140.51
	5.10^4	0.328_1	$2.97\ 10^{-2}$	$3.40\ 10^{-3}$	$1.99\ 10^{-5}$	-0.656
	10^5	0.657_1	$9.92\ 10^{-2}$	$3.42\ 10^{-3}$	$1.001\ 10^{-5}$	4.071
	5.10^5	3.309_1	0.453	$3.50\ 10^{-3}$	$2.02\ 10^{-6}$	4.149
	10^6	6.673_1	0.908	$3.61\ 10^{-3}$	$1.02\ 10^{-6}$	4.121

Table S2 : Monte Carlo simulation results on 400 molecules of methane after a run of 10^7 iterations except those signalled with a superscript. The subscripts give the statistical accuracies of the last decimal(s).

T/K	$\mathbf{c_P^{id}/Jmol^{-1}K^{-1}}$	**P/MPa**	ρ**/kg.m^{-3}**	$\mathbf{c_P^{res}/Jmol^{-1}K^{-1}}$	$\alpha_\mathbf{P}$**/K^{-1}**	$\beta_\mathbf{T}$**/Pa^{-1}**	$\mu_\mathbf{JT}$**/KMPa^{-1}**
294.25	35.53	1	6.673_5	0.91_{13}	$3.61_5\ 10^{-3}$	$1.016_{14}\ 10^{-6}$	4.12_{97}
		1.7	11.652_{11}	1.67_{13}	$3.797_{46}\ 10^{-3}$	$5.999_{68}\ 10^{-7}$	4.35_{49}
		3.4	24.05_4	3.51_{34}	$4.21_{13}\ 10^{-3}$	$3.073_{93}\ 10^{-7}$	4.1_6
		5.2	37.209_{12}	5.54_{36}	$4.66_{11}\ 10^{-3}$	$2.099_{44}\ 10^{-7}$	3.92_{32}
		6.9	51.14_5	8.13_{56}	$5.23_{18}\ 10^{-3}$	$1.629_{53}\ 10^{-7}$	3.89_{34}
		8.6	66.015_{158}	11.86_9	$6.06_{28}\ 10^{-3}$	$1.38_6\ 10^{-7}$	4.03_{34}
		10.3	81.56_{13}	14.18_{96}	$6.33_{25}\ 10^{-3}$	$1.104_{41}\ 10^{-7}$	3.43_{23}
		15	123.97_{17}	23.1_{24}	$7.74_{58}\ 10^{-3}$	$7.7_6\ 10^{-8}$	2.82_{25}
		20	164.07_{48}	22.8_{29}	$6.58_{63}\ 10^{-3}$	$4.3_4\ 10^{-8}$	1.57_{24}
		30	219.62_{49}	17.8_{17}	$4.35_{29}\ 10^{-3}$	$1.7_1\ 10^{-8}$	0.4_1
		40	253.1_6	17.8_{26}	$3.74_{36}\ 10^{-3}$	$1.111_{96}\ 10^{-8}$	0.2_1
		50	278.13_{48}	14.5_{16}	$2.86_{21}\ 10^{-3}$	$7.03_{48}\ 10^{-9}$	-0.18_9
		60	296.65_{46}	14.1_{17}	$2.57_{19}\ 10^{-3}$	$5.4_1\ 10^{-9}$	-0.27_{11}
		80	323.53_{44}	13_2	$2.07_{24}\ 10^{-3}$	$3.55_{19}\ 10^{-9}$	-0.401_{54}
		100	344.6_3	12_2	$1.78_{14}\ 10^{-3}$	$2.63_{16}\ 10^{-9}$	-0.47_5

Table S2 (continued)

T/K	$c_P^{id}/Jmol^{-1}K^{-1}$	P/MPa	$\rho/kg.m^{-3}$	$c_P^{res}/Jmol^{-1}K^{-1}$	α_P/K^{-1}	β_T/Pa^{-1}	$\mu_{JT}/KMPa^{-1}$
310.95	36.18	1.7	10.953_3	1.42_{17}	$3.53_6\ 10^{-3}$	$5.9_1\ 10^{-7}$	3.8_7
		3.4	22.48_2	2.84_{16}	$3.82_6\ 10^{-3}$	$3.02_4\ 10^{-7}$	3.5_3
		5.2	34.53_2	5.1_4	$4.3_1\ 10^{-3}$	$2.12_6\ 10^{-7}$	3.9_4
		6.9	47.09_3	6.59_{39}	$4.6_1\ 10^{-3}$	$1.57_4\ 10^{-7}$	3.4_3
		8.6	60.5_1	8.98_{71}	$5.1_2\ 10^{-3}$	$1.29_5\ 10^{-7}$	3.4_3
		10.3	73.97_{16}	10.9_6	$5.3_2\ 10^{-3}$	$1.07_3\ 10^{-7}$	3.07_{21}
327.55	36.89	1.7	10.36_2	1.37_{14}	$3.35_5\ 10^{-3}$	$6.002_{84}\ 10^{-7}$	3.99_{63}
		3.4	21.11_1	2.71_{22}	$3.61_7\ 10^{-3}$	$3.05_6\ 10^{-7}$	3.5_4
		5.2	32.32_2	3.96_{35}	$3.8_1\ 10^{-3}$	$2.03_5\ 10^{-7}$	3.1_7
		6.9	43.87_1	5.79_{36}	$4.2_1\ 10^{-3}$	$1.56_4\ 10^{-7}$	3.2_3
		8.6	55.82_1	7.61_{32}	$4.51_9\ 10^{-3}$	$1.27_2\ 10^{-7}$	3.1_2
		10.3	67.87_3	9.49_{73}	$4.8_2\ 10^{-3}$	$1.07_4\ 10^{-7}$	2.9_3
344.25	37.67	1.7	9.815_4	1.15_{12}	$3.13_4\ 10^{-3}$	$5.94_7\ 10^{-7}$	3.3_5
		3.4	19.946_8	2.18_{22}	$3.31_7\ 10^{-3}$	$2.98_6\ 10^{-7}$	2.8_5
		5.2	30.36_1	3.57_{19}	$3.57_5\ 10^{-3}$	$2.03_3\ 10^{-7}$	2.9_2
		6.9	41.05_5	4.78_{38}	$3.8_1\ 10^{-3}$	$1.52_4\ 10^{-7}$	2.7_3
		8.6	52.06_8	5.99_{48}	$3.95_{12}\ 10^{-3}$	$1.22_4\ 10^{-7}$	2.5_3
		10.3	63.04_{11}	7.96_{55}	$4.3_1\ 10^{-3}$	$1.05_3\ 10^{-7}$	2.7_2
360.95	38.51	1.7^a	9.332_1	0.87_9	$2.91_3\ 10^{-3}$	$5.81_6\ 10^{-7}$	2.15_{45}
		3.4	18.899_8	2.05_{22}	$3.14_6\ 10^{-3}$	$2.99_5\ 10^{-7}$	2.7_4
		5.2	28.66_1	3.07_{24}	$3.31_7\ 10^{-3}$	$2.01_4\ 10^{-7}$	2.6_3
		6.9	36.56_5	4.03_{27}	$3.44_7\ 10^{-3}$	$1.49_3\ 10^{-7}$	2.3_2
		8.6	48.82_5	5.4_4	$3.7_1\ 10^{-3}$	$1.22_3\ 10^{-7}$	2.4_2
		10.3	58.998_{71}	6.02_{32}	$3.69_8\ 10^{-3}$	$9.8_2\ 10^{-8}$	1.99_{16}

a - 9717300 iterations

Table S2 (continued)

$\mathbf{T/K}$	$\mathbf{c_P^{id}/Jmol^{-1}K^{-1}}$	$\mathbf{P/MPa}$	$\rho\mathbf{/kg.m^{-3}}$	$\mathbf{c_P^{res}/Jmol^{-1}K^{-1}}$	$\alpha_\mathbf{P}\mathbf{/K^{-1}}$	$\beta_\mathbf{T}\mathbf{/Pa^{-1}}$	$\mu_\mathbf{JT}\mathbf{/KMPa^{-1}}$
377.55	39.39	1.7	8.891_1	0.81_{13}	$2.77_4\ 10^{-3}$	$5.83_8\ 10^{-7}$	2.1_6
		3.4	17.97_1	1.76_{27}	$2.93_8\ 10^{-3}$	$2.95_7\ 10^{-7}$	2.4_6
		5.2	27.24_2	2.68_{28}	$3.08_8\ 10^{-3}$	$1.98_4\ 10^{-7}$	2.3_4
		6.9	36.56_5	3.9_2	$3.301_{48}\ 10^{-3}$	$1.53_2\ 10^{-7}$	2.5_2
		8.6	46.06_5	4.73_{43}	$3.4_1\ 10^{-3}$	$1.19_4\ 10^{-7}$	2.2_3
		10.3	55.54_3	5.4_4	$3.43_{11}\ 10^{-3}$	$9.8_3\ 10^{-8}$	1.9_2
		15	81.19_7	7.72_{58}	$3.65_{13}\ 10^{-3}$	$6.6_2\ 10^{-8}$	1.6_2
		20	107.5_3	10_2	$3.87_{24}\ 10^{-3}$	$4.8_3\ 10^{-8}$	1.4_2
		30^b	153.4_1	12_2	$3.66_{26}\ 10^{-3}$	$2.7_2\ 10^{-8}$	0.8_2
		40	189.35_{37}	12_1	$3.07_{14}\ 10^{-3}$	$1.6_6\ 10^{-8}$	0.26_8
		50	217.4_4	12_2	$2.79_{17}\ 10^{-3}$	$1.15_7\ 10^{-8}$	0.08_9
		60	239.5_5	11.4_7	$2.38_9\ 10^{-3}$	$8.2_3\ 10^{-9}$	-0.13_5
		80^c	273.1_8	9.9_8	$1.89_8\ 10^{-3}$	$5.1_2\ 10^{-9}$	-0.34_4
		100	298.6_4	9_2	$1.6_1\ 10^{-3}$	$3.6_2\ 10^{-9}$	-0.42_5

b - 9543600 iterations and c - 9845800 iterations

Table S3 : Monte Carlo simulation results on 200 molecules of ethane after a run of 10^7 iterations except those signalled with a superscript. The subscripts give the statistical accuracies of the last decimal(s).

T/K	$\mathbf{c_P^{id}/Jmol^{-1}K^{-1}}$	**P/MPa**	ρ**/kg.m^{-3}**	$\mathbf{c_P^{res}/Jmol^{-1}K^{-1}}$	$\alpha_\mathbf{P}$**/K^{-1}**	$\beta_\mathbf{T}$**/Pa^{-1}**	$\mu_\mathbf{JT}$**/KMPa^{-1}**
377.55	62.74	1.7	17.55_1	3.2_3	$3.24_7\ 10^{-3}$	$6.2_2\ 10^{-7}$	5.2_8
		3.4^d	37.59_5	7.4_3	$3.97_8\ 10^{-3}$	$3.301_{62}\ 10^{-7}$	5.8_3
		5.2	60.9_3	14.4_9	$5.2_2\ 10^{-3}$	$2.47_9\ 10^{-7}$	6.3_5
		6.9	88.99_8	24_2	$6.9_2\ 10^{-3}$	$2.05_6\ 10^{-7}$	6.3_3
		8.6^e	123_1	37_9	$8.9_5\ 10^{-3}$	$1.74_9\ 10^{-7}$	5.8_3
		10.3	162_3	50_6	$1.04_{11}\ 10^{-2}$	$1.4_2\ 10^{-7}$	4.8_4

d - 2.10^7 iterations and *e* - $2.6.10^7$ iterations

Table S4 : Monte Carlo simulation results on 400 molecules of 75% methane-25% ethane mixture after a run of 10^7 iterations except those signalled with a superscript. The subscripts give the statistical accuracies of the last decimal(s).

T/K	$\mathbf{c_P^{id}/Jmol^{-1}K^{-1}}$	**P/MPa**	$\boldsymbol{\rho}$**/kg.m^{-3}**	$\mathbf{c_P^{res}/Jmol^{-1}K^{-1}}$	$\boldsymbol{\alpha_P}$**/K^{-1}**	$\boldsymbol{\beta_T}$**/Pa^{-1}**	$\boldsymbol{\mu_{JT}}$**/KMPa^{-1}**
377.55	45.23	1.7^f	10.933_1	1.2_1	$2.85_3\ 10^{-3}$	$5.88_6\ 10^{-7}$	2.9_5
		3.4	22.301_{16}	2.7_2	$3.13_5\ 10^{-3}$	$3.04_4\ 10^{-7}$	3.3_3
		5.2	34.07_4	4.1_3	$3.34_6\ 10^{-3}$	$2.04_3\ 10^{-7}$	3.03_{26}
		6.9	46.21_3	5.5_4	$3.54_9\ 10^{-3}$	$1.53_4\ 10^{-7}$	2.8_3
		8.6	58.8_2	7.4_5	$3.8_1\ 10^{-3}$	$1.24_5\ 10^{-7}$	2.8_3
		10.3	71.46_7	8.9_7	$4.03_{16}\ 10^{-3}$	$1.04_4\ 10^{-7}$	2.7_3

f - 2.10^7 iterations

Table S5 : Monte Carlo simulation results on 400 molecules of *n*-butane after a run of 10^7 iterations except those signalled with a superscript. The subscripts give the statistical accuracies of the last decimal(s).

T/K	c_P^{id}/**Jmol^{-1}K^{-1}**	**P/MPa**	ρ/**kg.m^{-3}**	c_P^{res}/**Jmol^{-1}K^{-1}**	α_P/**K^{-1}**	β_T/**Pa^{-1}**	μ_{JT}/**KMPa^{-1}**
380	120.28	0.5^g	9.82_1	3.9_4	$3.2_1\ 10^{-3}$	$2.16_7\ 10^{-6}$	11_2
		0.8^h	16.416_8	7.1_5	$3.7_1\ 10^{-3}$	$1.41_5\ 10^{-6}$	12_2
		1	21.24_7	9.54_{98}	$4.2_2\ 10^{-3}$	$1.19_5\ 10^{-6}$	12_2
		1.4	32.41_1	19_2	$5.7_4\ 10^{-3}$	$9.9_6\ 10^{-7}$	15_2
		2	468_5	73_{13}	$4.95_{93}\ 10^{-3}$	$1.6_3\ 10^{-8}$	0.57_{21}
		2.6	469_3	60_8	$4.05_{56}\ 10^{-3}$	$1.3_2\ 10^{-8}$	0.37_{14}
		3.2^h	473_1	59_7	$3.9_4\ 10^{-3}$	$1.2_2\ 10^{-8}$	0.31_{10}
		4	476_2	59_{14}	$3.9_9\ 10^{-3}$	$1.15_{26}\ 10^{-8}$	0.3_2
		5^h	482.4_5	58_8	$3.68_{48}\ 10^{-3}$	$1.04_{14}\ 10^{-8}$	0.27_{11}

g - $2.6.10^7$ iterations and *h* - 2.10^7 iterations