

Supplementary Material for Proof of concept for fast equation of state development using an integrated experimental-computational approach

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1 Expenditure Calculations

To thoroughly compare data acquisition using simulation and experiment, and make a case for the use of either of them in favor of the other, it is necessary to not only compare them in terms of uncertainty, but to also examine their respective financial and temporal expenditures.

The following calculations rely on many assumptions, which resulted from discussions with experts from the respective field including the authors of Ref. [1], who conducted the measurements utilized for the present work.

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However, many of these assumptions cannot be generalized to other cases, substances, or thermodynamic regions.

Furthermore, we aim to only calculate the net time rather than the total time.

Some general assumptions regarding boundary conditions are summarized in the following.

- General
 - Located in Germany → 52 €/h personnel cost
 - 58 state points on 6 isotherms
 - Models are available (including molecular force fields, calibration models, etc.)
 - Respective equipment is available, set up, and/or calibrated
 - Personnel is trained has required experience
 - Required post-processing scripts are available
- Simulation
 - Running simulation requires less attention → factor of 0.1 is applied
 - All required state points can be simulated in parallel
- Experiment
 - Some tasks are partially automatable and require less supervision → a factor of 0.33 is applied
 - The substance and the apparatus is relatively well-known
 - Two additional isotherms need to be measured for testing and reproducibility purposes (with 5 state points each)
 - 10 % of the measurements need to be repeated
 - Depreciation cost of the apparatus is not included

Tables 1 and 2 provide an overview of the main time and cost components for the data acquisition using molecular simulation (MS) and experimentation. The estimated net sums are provided at the bottom of both tables.

Table 1: Time and cost assumptions for the simulation data acquisition (state point (SP)).

Item name	Approximated expenditure
Preparation	
Choosing state points	0.5 min/SP
Creating parameter files	1 ... 2 min/SP
Choosing models	1 ... 20 min/SP
Starting simulation at main frame	3 ... 5 sec
Execution	
Simulation	4 ... 8 h
Simulation cost	0.61 €/SP
Post processing	
Analysis of results	3 ... 5 sec
Quality assessment	0.5 min/SP
Sum	
Net time	9.2 h
Net cost	137 €

Table 2: Time and cost assumptions for the experimental data acquisition (state point (SP)).

Item name	Approximated expenditure
Preparation	
Preparation of apparatus and sample	1 ... 2 weeks
Cost for supplemental material	200 €/months
Execution	
Cost for nitrogen	40 €/isotherm
Cool-down time	2 ... 3 h/isotherm
Thermodynamic equilibrium	2 h/isotherm
Thermodynamic equilibrium	30 min/SP
Heating up after measurements	7 h/isotherm
Measurement time	5 ... 20 min/SP
Post processing	
Analysis of results	3 ... 5 sec/SP
Post processing and quality assessment	2 ... 10 min/SP
Post processing and quality assessment	20 ... 60 min/isotherm
Cleaning up	3 h
Sum	
Time	220 h
Cost	5500 €

As can be gathered from [Tables 1](#) and [2](#), experimentation involves significantly more time and effort. Besides the long preparation, the cooling down, heating up, and waiting to reach thermodynamic equilibrium, are some of the major time expenses.

While the calculated expenditures or the MS do approximately agree with the total ones, there is a large discrepancy for the experiments. In discussion with the authors of Ref. [\[1\]](#), the total time and cost for the experiments was approximately 10 ... 12 weeks and 20 000 ... 25 000 €. For one, the total cost reported by the authors contains all expenses, including the depreciation cost.

Furthermore, the total time is difficult to predict, as unexpected interruptions, delays, and problems are inevitable. Many of the tasks require intermittent supervision and take up many hours. These have to be conducted during working hours and cannot be interrupted at the end of the work day. These can thus not be started close the end of a work day, which is another large factor contributing to a more extended total time. Lastly, the attention factor for experimentation is very difficult to estimate, since it depends on a plethora of factors. Most certainly, the factor is not constant.

However, the expenditure calculations are nevertheless a useful itemization that may be used to as a basis to compare expenditures and/or plan hybrid data acquisition.

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Table 3: Parameters of Equation (2) developed using the simulation data and used as base for OED, Equation (8) developed using the weighted simulation data and the best four isotherms (Section 6) and Equation (9) developed using all weighted data.

Coefficient	Equation (2) based on sim. data	Equation (8) based on sim. data and 4 isotherms	Equation (9) based on all data
c_1	4.343	4.339	4.326
c_2	-0.505	2.067	0.470
c_3	5.233	2.403	7.464
c_4	0.444	0.375	-4.942
c_5	-2.392	6.710	-1.169
c_6	-2.323	-0.203	1.067
c_7	1.969	0.324	0.510

Table 4: Densities at temperatures T and pressures p from experiments ρ_{exp} [1] with their relative expanded combined uncertainty $U(\rho_{\text{exp}})$, from molecular dynamics simulations ρ_{sim} with the statistical uncertainty from block averaging $d(\rho_{\text{sim}})$ (without an offset for the model uncertainty), and calculated with REFPROP using the GERG-2008 generalized mixture model ρ_{GERG} [2, 3]. Values were rounded to three decimal places.

T / K	p / MPa	ρ_{exp} / kg/m ³	$U(\rho_{\text{exp}})$ / %	ρ_{sim} / kg/m ³	$d(\rho_{\text{sim}})$ / %	ρ_{GERG} / kg/m ³
100.000	7.950	794.290	0.087	794.861	0.016	796.440
100.000	6.038	787.036	0.087	787.849	0.013	789.200
100.000	4.423	780.425	0.088	781.454	0.013	782.630
100.000	3.007	774.201	0.089	774.794	0.018	776.440
100.000	1.976	769.367	0.089	770.533	0.015	771.640
100.000	0.976	764.402	0.090	765.571	0.016	766.720
100.000	0.777	763.372	0.090	764.616	0.016	765.700
100.000	0.667	762.802	0.090	764.061	0.016	765.130
100.000	0.570	22.736	1.179	22.441	0.017	22.732
100.000	0.500	19.553	0.069	19.344	0.015	19.550
100.000	0.300	11.118	0.084	11.056	0.010	11.117
100.000	0.200	7.235	0.109	7.208	0.009	7.233
115.000	7.984	716.907	0.084	716.553	0.021	718.490
115.000	6.054	704.052	0.086	703.849	0.027	705.720
115.000	4.631	693.095	0.088	693.451	0.024	694.860
115.000	3.033	678.578	0.092	680.047	0.033	680.530
115.000	2.477	672.741	0.094	674.622	0.031	674.790
115.000	1.872	665.781	0.097	667.999	0.032	667.960
115.000	1.669	663.259	0.102	665.784	0.034	601.050
115.000	1.526	62.627	1.525	60.673	0.033	62.549
115.000	1.501	61.071	0.067	59.242	0.032	60.998
115.000	1.000	35.688	0.057	35.183	0.016	35.671
115.000	0.801	27.432	0.057	27.156	0.016	27.424
115.000	0.500	16.261	0.063	16.172	0.011	16.260

T / K	p / MPa	$\rho_{\text{exp}} / \text{kg/m}^3$	$U(\rho_{\text{exp}}) / \%$	$\rho_{\text{sim}} / \text{kg/m}^3$	$d(\rho_{\text{sim}}) / \%$	$\rho_{\text{GERG}} / \text{kg/m}^3$
115.000	0.300	9.458	0.081	9.427	0.010	9.456
130.000	8.005	618.704	0.090	618.529	0.035	619.740
130.000	6.004	587.228	0.102	589.111	0.059	588.490
130.000	4.504	548.460	0.132	553.962	0.087	550.130
130.000	4.003	526.796	0.164	535.710	0.140	528.790
130.000	3.603	498.154	0.243	514.461	0.249	501.010
130.000	3.442	476.527	1.377	502.509	0.281	425.490
130.000	3.331	185.777	4.855	165.605	0.195	182.830
130.000	3.001	134.915	0.109	127.556	0.092	134.310
130.000	2.501	95.756	0.068	92.616	0.038	95.569
130.000	2.000	68.879	0.056	67.462	0.024	68.806
130.000	1.500	47.611	0.051	46.979	0.016	47.585
130.000	1.000	29.688	0.050	29.455	0.012	29.681
130.000	0.499	14.011	0.060	13.963	0.009	14.009
145.000	8.005	472.453	0.118	473.338	0.078	472.660
145.000	7.004	423.759	0.148	424.705	0.159	423.380
145.000	6.003	337.914	0.191	332.985	0.210	336.330
145.000	5.003	223.159	0.128	213.852	0.123	222.010
145.000	4.002	145.063	0.073	140.557	0.060	144.780
145.000	3.001	94.073	0.054	92.231	0.026	93.996
145.000	2.000	56.200	0.046	55.576	0.019	56.183
145.000	1.000	25.733	0.046	25.610	0.011	25.732
145.000	0.499	12.375	0.058	12.346	0.008	12.374
220.000	8.004	141.036	0.039	139.799	0.021	140.950
220.000	6.003	103.475	0.036	102.740	0.017	103.430
220.000	4.001	67.148	0.034	66.821	0.014	67.136
220.000	2.000	32.570	0.033	32.486	0.010	32.570
220.000	1.000	16.031	0.039	16.011	0.010	16.031
220.000	0.500	7.945	0.059	7.941	0.008	7.946
298.150	8.004	94.072	0.030	93.643	0.012	94.049
298.150	6.004	70.578	0.029	70.363	0.012	70.569
298.150	4.002	46.977	0.029	46.871	0.008	46.976
298.150	2.001	23.408	0.030	23.381	0.008	23.408
298.150	1.001	11.675	0.040	11.670	0.008	11.675

Table 5: Density for a grid of state points at 11 temperatures ((100, 120, 140, 160, 180, 200, 210, 220, 240, 260, 280, and 300) K) and 7 pressures ((0.1, 0.5, 1, 2, 4, 6, and 8) MPa), based on MS ρ_{sim} and their uncertainty $d(\rho_{\text{sim}})$. Values were rounded to three decimal places.

T/K	p/MPa	$\rho_{\text{sim}} / \text{kg/m}^3$	$d(\rho_{\text{sim}}) / \%$	T/K	p/MPa	$\rho_{\text{sim}} / \text{kg/m}^3$	$d(\rho_{\text{sim}}) / \%$
100	0.1	3.538	0.007	200	4.0	75.773	0.013
100	0.5	19.341	0.012	200	6.0	118.455	0.019
100	1.0	765.819	0.015	200	8.0	163.924	0.022
100	2.0	770.714	0.014	220	0.1	1.580	0.007

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T/K	p/MPa	$\rho_{\text{sim}} / \text{kg/m}^3$	$d(\rho_{\text{sim}}) / \%$	T/K	p/MPa	$\rho_{\text{sim}} / \text{kg/m}^3$	$d(\rho_{\text{sim}}) / \%$
100	4.0	779.475	0.013	220	0.5	7.946	0.007
100	6.0	787.781	0.011	220	1.0	16.008	0.009
100	8.0	795.219	0.012	220	2.0	32.486	0.009
120	0.1	2.925	0.007	220	4.0	66.787	0.012
120	0.5	15.347	0.007	220	6.0	102.673	0.015
120	1.0	32.972	0.014	220	8.0	139.780	0.016
120	2.0	82.008	0.041	240	0.1	1.448	0.007
120	4.0	650.297	0.036	240	0.5	7.267	0.007
120	6.0	670.470	0.031	240	1.0	14.602	0.007
120	8.0	686.912	0.023	240	2.0	29.486	0.008
140	0.1	2.497	0.007	240	4.0	60.001	0.010
140	0.5	12.857	0.007	240	6.0	91.308	0.014
140	1.0	26.762	0.011	240	8.0	123.143	0.017
140	2.0	58.845	0.017	260	0.1	1.336	0.006
140	4.0	161.071	0.059	260	0.5	6.696	0.007
140	6.0	449.568	0.169	260	1.0	13.435	0.006
140	8.0	530.450	0.051	260	2.0	27.031	0.008
160	0.1	2.179	0.006	260	4.0	54.613	0.011
160	0.5	11.106	0.008	260	6.0	82.587	0.011
160	1.0	22.772	0.010	260	8.0	110.716	0.013
160	2.0	48.066	0.012	280	0.1	1.240	0.007
160	4.0	109.288	0.022	280	0.5	6.211	0.007
160	6.0	192.141	0.043	280	1.0	12.442	0.007
160	8.0	298.246	0.067	280	2.0	24.969	0.007
180	0.1	1.934	0.007	280	4.0	50.219	0.009
180	0.5	9.794	0.009	280	6.0	75.588	0.009
180	1.0	19.913	0.009	280	8.0	100.902	0.011
180	2.0	41.195	0.012	300	0.1	1.157	0.006
180	4.0	88.480	0.015	300	0.5	5.790	0.006
180	6.0	142.995	0.022	300	1.0	11.591	0.008
180	8.0	204.065	0.031	300	2.0	23.218	0.007
200	0.1	1.739	0.007	300	4.0	46.522	0.008
200	0.5	8.771	0.007	300	6.0	69.805	0.010
200	1.0	17.736	0.008	300	8.0	92.933	0.010
200	2.0	36.254	0.010				

References

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