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Unleashing Empirical Equations with "Nonlinear Fitting" and "GUM Tree Calculator"

J. W. Lovell-Smith[1] · **P. Saunders**[1] · **R. Feistel**[2]

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Abstract Empirical equations having large numbers of fitted parameters, such as the international standard reference equations published by the International Association for the Properties of Water and Steam (IAPWS), which form the basis of the "Thermodynamic Equation of Seawater—2010" (TEOS-10), provide the means to calculate many quantities very accurately. The parameters of these equations are found by least-squares fitting to large bodies of measurement data. However, the usefulness of these equations is limited since uncertainties are not readily available for most of the quantities able to be calculated, the covariance of the measurement data is not considered, and further propagation of the uncertainty in the calculated result is restricted since the covariance of calculated quantities is unknown. In this paper, we present two tools developed at MSL that are particularly useful in unleashing the full power of such empirical equations. "Nonlinear Fitting" enables propagation of the covariance of the measurement data into the parameters using generalized least-squares methods. The parameter covariance then may be published along with the equations. Then, when using these large, complex equations, "GUM Tree Calculator" enables the simultaneous calculation of any derived quantity and its uncertainty, by automatic propagation of the parameter covariance into the calculated quantity. We demonstrate these tools in exploratory work to determine and propagate uncertainties associated with the IAPWS-95 parameters.

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✉ J. W. Lovell-Smith
jeremy.lovell-smith@measurement.govt.nz

[1] Measurement Standards Laboratory (MSL), PO Box 31-310, Lower Hutt, New Zealand

[2] Leibniz Institute for Baltic Sea Research (IOW), 18119 Warnemünde, Germany

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1 Introduction

Empirical equations having large numbers of fitted parameters, such as the extremely valuable international standard reference equations published by the International Association for the Properties of Water and Steam (IAPWS) that form the basis of the Thermodynamic Equation of Seawater (TEOS-10) [1], provide the means to calculate many quantities very accurately (see Fig. 1). The equation parameters are found by least-squares fitting to large bodies of measurement data. However, the full usefulness of these equations is limited because:

- Uncertainties are not readily available for most of the quantities able to be calculated;
- The covariance of the measurement data is not considered; and
- The covariance of calculated quantities is unknown, thus restricting further propagation.

One such equation is IAPWS-95, which is the IAPWS equation for the thermodynamic properties of fluid water [2,3]. In a recent paper [4], we reported on our investigation

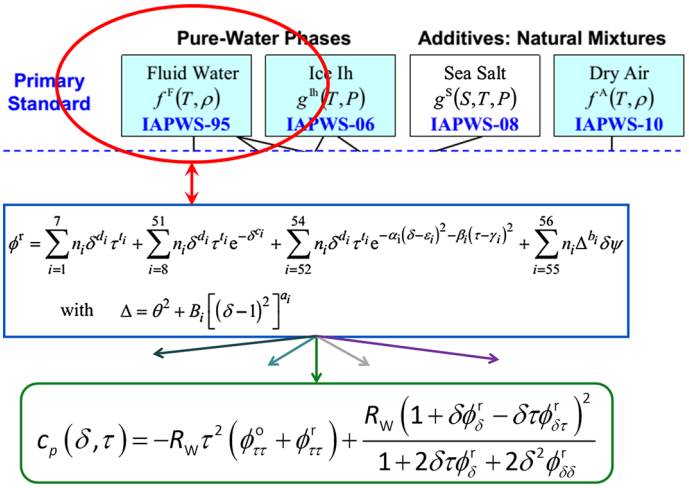

Fig. 1 Schematic outlining the calculation of the isobaric heat capacity of fluid water using IAPWS-95, here represented at *top* as one of the four primary thermodynamic potentials within TEOS-10 [1]. The IAPWS-95 equation for the reduced specific Helmholtz energy, ϕ, is expressed as the sum of ideal gas, ϕ^{o}, and residual, ϕ^{r}, parts that are functions of the reduced density $\delta = \rho/\rho_c$ and reduced inverse temperature $\tau = T_c/T$, where $\rho_c = 322\,\mathrm{kg\cdot m^{-3}}$ is the critical density and $T_c = 647.096\,\mathrm{K}$ is the critical temperature. The residual part (middle box) contains one fitted parameter (labeled n_i) for each of 56 regressors, which include polynomials, exponentials, modified Gaussians and "nonanalytical terms." Many physical quantities that are functions of derivatives of $\phi^{o}+\phi^{r}$ can be calculated, such as pressure p, speed of sound w, virial coefficients B^{ww} and C^{www} and the isobaric heat capacity c_p (see lower box, where the subscripts represent first and second partial derivatives with respect to δ and τ)

to refit IAPWS-95 to the original data and thereby: (a) propagate the covariance of the input data into the covariance of the IAPWS-95 equation parameters; and (b) propagate the parameter covariance further into the calculated quantities. Here we report on two tools developed at the Measurement Standards Laboratory of New Zealand (MSL) that have been critical in this work to help unleash the full power of such empirical equations. "Nonlinear Fitting" (NLF) [5] enables propagation of measurement data covariance into the parameters using generalized least-squares methods, allowing parameter covariance to be published with the fitted equations. When using these equations, "GUM Tree Calculator" (GTC) [6,7] enables simultaneous calculation of any derived quantity and its uncertainty, by automatic propagation of the parameter covariance into the calculated quantity.

In Sect. 2 we discuss methods to generate the covariance matrix for the input data derived from an uncertainty budget, where it is important that the budget clearly identifies the random components and the systematic components common to all measurements. A brief description of the structure of the IAPWS-95 equations is given in Sect. 3. The NLF and GTC software tools used to determine and propagate uncertainties associated with the IAPWS-95 parameters are discussed in Sects. 4 and 5, and some preliminary results are demonstrated, and finally, a discussion and some conclusions are given in Sect. 6.

2 Input Data Covariance

2.1 Variance–Covariance Matrix

An empirical equation is a summary of potentially vast sets of data resulting from experimental measurements. The input data, like all measurements, are subject to unknown errors. These will propagate into the parameters and into any value calculated using the equation. Each measurement of an input data quantity Y (the measurand) can be modeled as a reading, y, minus a sum of the unknown errors, E:

$$\begin{aligned} Y_1 &= y_1 - E_{1,1} - E_{1,2} - E_{1,3} - \ldots \\ Y_2 &= y_2 - E_{2,1} - E_{2,2} - E_{2,3} - \ldots \\ &\vdots \end{aligned} \tag{1}$$

Here, the lower-case symbols y_1, y_2, etc., represent known measured values and the upper-case symbols $E_{1,1}$, $E_{1,2}$, etc., represent unknown measurement errors. The errors can arise from various sources, and assuming all biases (known errors) have been removed (corrected), they are estimated to have expectation values $e_{1,1} = 0$, $e_{1,2} = 0$, etc., and are characterized by corresponding standard uncertainties $u(e_{1,1})$, $u(e_{1,2})$, etc. In this case, y_1 is considered to be the best estimate of Y_1, etc.

Each of the error terms in Eq. 1 will either be independent (zero correlation) or have some degree of correlation with other error terms, leading to correlation between the uncertainties in the measured y values as estimates of the Y measurands. For example,

it will be common to have zero correlation for different error terms within a single measurement, but often there will be a significant correlation for the same error term when multiple measurements are taken within a set of experiments.

The off-diagonal elements of the symmetric covariance matrix **V** (sometimes known as the variance–covariance matrix) describing correlation between two measured values y_k and y_l are

$$u\left(y_k, y_l\right)_{k\neq l} = \sum_{i=1}^{m}\sum_{j=1}^{n} \frac{\partial y_k}{\partial e_{k,i}} \frac{\partial y_l}{\partial e_{l,j}} r(e_{k,i}, e_{l,j}) u(e_{k,i}) u(e_{l,j}) \tag{2}$$

(see [8] Eqs. F1, F2, and H9) where there are m error terms associated with the measurement of Y_k and n error terms associated with Y_l (if Y_k and Y_l are the same quantity, e.g., pressure, then often $m = n$), and $r(e_{k,i}, e_{l,j})$ is the correlation coefficient between the estimated errors $e_{k,i}$ and $e_{l,j}$. Elements along the diagonal of the matrix **V** describe the variance of a measurement; i.e.,

$$u^2\left(y_k\right) = \sum_{i=1}^{m} \left(\frac{\partial y_k}{\partial e_{k,i}}\right)^2 u^2(e_{k,i}). \tag{3}$$

For the model under discussion, Eq. 1, the sensitivity coefficients, $\partial y_k/\partial e_{k,i}$, etc., in Eqs. 2 and 3 are all equal to 1.

From Eqs. 2 and 3, we can define a (symmetric) correlation-coefficient matrix, **R**, such that

$$\mathbf{V} = \begin{bmatrix} u(y_1) & 0 & 0 & \cdots \\ 0 & u(y_2) & 0 & \cdots \\ 0 & 0 & u(y_3) & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \times \mathbf{R} \times \begin{bmatrix} u(y_1) & 0 & 0 & \cdots \\ 0 & u(y_2) & 0 & \cdots \\ 0 & 0 & u(y_3) & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}, \tag{4}$$

where

$$\mathbf{R} = \begin{bmatrix} 1 & r_{1,2} & r_{1,3} & \cdots \\ r_{2,1} & 1 & r_{2,3} & \cdots \\ r_{3,1} & r_{3,2} & 1 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \tag{5}$$

and the off-diagonal elements are the correlation coefficients

$$r_{k,l} = r\left(y_k, y_l\right) = \frac{u\left(y_k, y_l\right)}{u\left(y_k\right) u\left(y_l\right)} = r_{l,k}. \tag{6}$$

Consider just two measurements, y_1 and y_2 in this model; if we suppose that each of the measurands Y_1 and Y_2 has only three error terms and that just the first errors are

correlated, i.e., only $r(e_{1,1}, e_{2,1})$ is nonzero, then the covariance between y_1 and y_2, according to Eq. 2, is

$$u(y_1, y_2) = r\left(e_{1,1}, e_{2,1}\right) u(e_{1,1})u(e_{2,1}), \tag{7}$$

the covariance matrix, $\mathbf{V}$, is

$$\mathbf{V} = \begin{bmatrix} u^2(e_{1,1}) + u^2(e_{1,2}) + u^2(e_{1,3}) & r(e_{1,1}, e_{2,1})u(e_{1,1})u(e_{2,1}) \\ r(e_{1,1}, e_{2,1})u(e_{1,1})u(e_{2,1}) & u^2(e_{2,1}) + u^2(e_{2,2}) + u^2(e_{2,3}) \end{bmatrix}. \tag{8}$$

and the off-diagonal correlation coefficients are

$$r_{1,2} = r_{2,1} = \frac{r(e_{1,1}, e_{2,1})u(e_{1,1})u(e_{2,1})}{\sqrt{u^2(e_{1,1}) + u^2(e_{1,2}) + u^2(e_{1,3})}\sqrt{u^2(e_{2,1}) + u^2(e_{2,2}) + u^2(e_{2,3})}}. \tag{9}$$

2.2 Origin of Correlation

Correlation between measurements arises when they are subject to the same uncontrolled influence variable or error source (representing a systematic error). Given that each error term in Eq. 1 is associated with a single source, any two error terms that share the same source are fully correlated; otherwise, they are uncorrelated (independent). In the simplest situation, assume the first error terms for the Y_1 and Y_2 measurands in Eq. 1 share the same source, so that $r(e_{1,1}, e_{2,1}) = 1$, the second error terms come from different sources, so that $r(e_{1,2}, e_{2,2}) = 0$, and the remaining error terms are zero (i.e., $u(e_{1,3}) = u(e_{2,3}) = 0$). In this case, the first error term represents the systematic part and the second the random part of the total error, and the covariance matrix reduces to

$$\mathbf{V} = \begin{bmatrix} u^2(e_{1,1}) + u^2(e_{1,2}) & u(e_{1,1})u(e_{2,1}) \\ u(e_{1,1})u(e_{2,1}) & u^2(e_{2,1}) + u^2(e_{2,2}) \end{bmatrix}. \tag{10}$$

The effect of the error has many different forms. Commonly, the error may be either constant across the measurement range,

$$E_{1,1} = E_{2,1} = \ldots = E_{\text{syst}}, \tag{11}$$

where E_{syst} is a constant absolute error, or the error may scale with the measurement,

$$E_{k,1} = y_k E_{\text{rel,syst}}, \tag{12}$$

where $E_{\text{rel,syst}}$ is a constant relative error.

We now consider cases represented by Eqs. 11 and 12.

Case 1 The systematic uncertainties are identical, such that $u(e_{1,1}) = u(e_{2,1}) = u(e_{\text{syst}})$, and the random uncertainties are also identical, such that $u(e_{1,2}) = u(e_{2,2}) = u(e_{\text{rand}})$. Equation 10 then becomes

$$\mathbf{V} = \begin{bmatrix} u^2(e_{\text{syst}}) + u^2(e_{\text{rand}}) & u^2(e_{\text{syst}}) \\ u^2(e_{\text{syst}}) & u^2(e_{\text{syst}}) + u^2(e_{\text{rand}}) \end{bmatrix} \tag{13}$$

and the off-diagonal elements of the correlation-coefficient matrix are

$$r_{1,2} = r_{2,1} = \frac{u^2(e_{\text{syst}})}{u^2(e_{\text{syst}}) + u^2(e_{\text{rand}})} = \frac{1}{1+k^2}, \tag{14}$$

where k is the ratio of the random uncertainty to the systematic uncertainty:

$$k = \frac{u(e_{\text{rand}})}{u(e_{\text{syst}})}. \tag{15}$$

In the limits as k tends to 0 (purely systematic) or ∞ (purely random), the cross-correlation terms (off-diagonals) of the correlation-coefficient matrix approach 1 or 0, respectively.

Case 2 The systematic errors are proportional to the reading, so that $u(e_{1,1}) = y_1 u(e_{\text{rel,syst}})$ and $u(e_{2,1}) = y_2 u(u_{\text{rel,syst}})$. We assume, firstly, that the random errors are also proportional to the reading, $u(e_{1,2}) = y_1 u(e_{\text{rel,rand}})$ and $u(e_{2,2}) = y_2 u(e_{\text{rel,rand}})$. Then we have for the covariance matrix

$$\mathbf{V} = \begin{bmatrix} y_1^2 u^2(e_{\text{rel,syst}}) + y_1^2 u^2(e_{\text{rel,rand}}) & y_1 y_2 u^2(e_{\text{rel,syst}}) \\ y_1 y_2 u^2(e_{\text{rel,syst}}) & y_2^2 u^2(e_{\text{rel,syst}}) + y_2^2 u^2(e_{\text{rel,rand}}) \end{bmatrix}, \tag{16}$$

and the off-diagonal elements of the correlation-coefficient matrix are

$$\begin{aligned} r_{1,2} = r_{2,1} &= \frac{y_1 y_2 u^2(e_{\text{rel,syst}})}{\sqrt{y_1^2 u^2(e_{\text{rel,syst}}) + y_1^2 u^2(e_{\text{rel,rand}})}\sqrt{y_2^2 u^2(e_{\text{rel,syst}}) + y_2^2 u^2(e_{\text{rel,rand}})}} \\ &= \frac{1}{1+k^2}, \end{aligned} \tag{17}$$

where k is the ratio of the random relative uncertainty to the systematic relative uncertainty:

$$k = \frac{u(e_{\text{rel,rand}})}{u(e_{\text{rel,syst}})}. \tag{18}$$

Case 3 The systematic errors are again proportional to the reading, so that $u(e_{1,1}) = y_1 u(e_{\text{rel,syst}})$ and $u(e_{2,1}) = y_2 u(u_{\text{rel,syst}})$, but the random errors are now constant, $u(e_{1,2}) = u(e_{2,2}) = u(e_{\text{rand}})$. In this case, the covariance matrix is

$$\mathbf{V} = \begin{bmatrix} y_1^2 u^2(e_{\text{rel,syst}}) + u^2(e_{\text{rand}}) & y_1 y_2 u^2(e_{\text{rel,syst}}) \\ y_1 y_2 u^2(e_{\text{rel,syst}}) & y_2^2 u^2(e_{\text{rel,syst}}) + u^2(e_{\text{rand}}) \end{bmatrix} \tag{19}$$

and the off-diagonal elements of the correlation-coefficient matrix are

$$r_{1,2} = r_{2,1} = \frac{y_1 y_2 u^2(e_{\text{rel,syst}})}{\sqrt{y_1^2 u^2(e_{\text{rel,syst}}) + u^2(e_{\text{rand}})}\sqrt{y_2^2 u^2(e_{\text{rel,syst}}) + u^2(e_{\text{rand}})}} = \frac{1}{\sqrt{1+k_1^2}\sqrt{1+k_2^2}}, \tag{20}$$

where

$$k_1 = \frac{u(e_{\text{rand}})}{y_1 u(e_{\text{rel,syst}})} \text{ and } k_2 = \frac{u(e_{\text{rand}})}{y_2 u(e_{\text{rel,syst}})}. \tag{21}$$

The covariance and correlation coefficients for larger sets of measurements can be calculated similarly for each measurement paired with every other. The off-diagonal elements will all be the same for cases 1 and 2 but not for case 3.

2.3 Uncertainty Budgets

The correlation-coefficient or covariance matrices for a set of measurement data may be constructed readily if sufficient information is given in the uncertainty budget. Ideally, each line in the budget refers to a component of uncertainty accounting for a single error source, and it should be clear which measurements each error source affects and whether the error affects each measurement randomly or in the same way, though possibly subject to scaling. Note that uncertainty components of the same type (systematic or random) that are constant over the range can be combined in quadrature and treated as a single component for the purposes of determining the correlation-coefficient matrix.

An example of a modified uncertainty budget to include information necessary to calculate **V** and **R** is presented in Table 1. The off-diagonal terms of **R** are all the same and, from Eq. 14, are equal to $r_{i,j} = u^2(P_{\text{syst}})/u^2(P_{\text{total}}) = 0.85$.

Alternatively, for large data sets where the different error sources apply over different parts of the range, the uncertainty budget can be included line by line, as in the simple example of Table 2. In this case, all systematic and random components of uncertainty are represented as appropriately labeled columns, although not all rows will necessarily have a corresponding entry for each column. The variance for each measurement is found by adding the squares of all the components in that row. The covariance between measurements represented by two rows is found by adding in quadrature those systematic components in each row that have a corresponding component in the other row and then multiplying the two quadrature sums together. The resulting correlation-coefficient matrix is shown in Fig. 2.

3 IAPWS-95

The IAPWS-95 equation for the specific Helmholtz free energy, f, of fluid water is expressed in terms of a dimensionless quantity $\phi(\rho, T) = f(\rho, T)/(R_{\text{W}}T)$, where ρ

Table 1 An example of modification of a measurement data uncertainty budget to enable calculation of a correlation-coefficient matrix. Here the components are all constant

Source of uncertainty in pressure	Symbol	Uncertainty (Pa)	Type	
Calibration uncertainty (sensor and indicator unit)	P_{calib}	50	Syst	Constant
Long-term stability (sensor and indicator)	P_{drift}	50	Syst	Constant
Temperature coefficient	P_{tempco}	10	Syst	Constant
Resolution and accuracy or linearity (indicator unit)	P_{res}	1	Rand	Constant
Stability of the pressure (standard deviation of readings)	P_{stab}	30	Rand	Constant
Combined systematic uncertainty	$u(P_{\text{syst}})$	71.4		
Combined random uncertainty	$u(P_{\text{rand}})$	30.0		
Total combined standard uncertainty	$u(P_{\text{total}})$	77.5		

	Symbol	Coefficient
Off-diagonal correlation coefficients	$r_{i,j}$	0.85

and T are the density and temperature of the fluid, respectively, and R_{W} is the specific gas constant of water. This equation can be expressed as the sum of an ideal-gas part and a residual part, $\phi(\rho, T) = \phi^{\text{o}}(\delta, \tau) + \phi^{\text{r}}(\delta, \tau)$, where the reduced density $\delta = \rho/\rho_{\text{c}}$ and reduced inverse temperature $\tau = T_{\text{c}}/T$, and ρ_{c} and T_{c} are the critical density and critical temperature, respectively. The ideal-gas part of the equation, ϕ^{o}, and its parameters were derived from the well-established equation of Cooper [9] for the isobaric heat capacity in the ideal-gas state, $c_p(T)$. The residual part of the equation, ϕ^{r}, contains 56 fitted parameters—one for each of 56 regressors—and a set of unfitted coefficients and exponents for each of the regressors.

Following a structural optimization that determined the functional form of the IAPWS-95 equation, the IAPWS-95 authors used a nonlinear weighted least-squares method to fit the 56 parameters to ~6000 data points corresponding to 16 data types, each drawn from many different data sets. Each data type corresponds to a different quantity, such as pressure, speed of sound and heat capacity, modeled as a function of partial derivatives of $\phi(\rho, T)$, such as for c_p in Fig. 1. The data were treated as uncorrelated, no uncertainties were derived for the fitted parameters, and uncertainties were given for just 6 of the 16 calculable quantities (e.g., c_p in Fig. 3).

4 Nonlinear Fitting (NLF)

NLF [5] is a general purpose curve-fitting program that will fit any curve or hypersurface of the form $y = f(x_1, x_2, \ldots, x_n; a_1, a_2, \ldots, a_N)$ to a set of M data points ($M \leq 100,000$) in $(n + 1)$-dimensional space, $(x_{1,i}, x_{2,i}, \ldots, x_{n,i}, y_i)$ for $i = 1$ to M. The function can have up to 30 real variables, $x_k (k = 1 \text{ to } n)$, and up to 99 real

Table 2 Modified table of measurement data to include an uncertainty budget to enable calculation of a correlation-coefficient. The rows numbered L1, L2, … and H1, H2, … correspond to measurements using the same transducer, in low and high dew-point humidity generators, respectively. Some components are specific to the generator, and others are associated with the transducer. The corresponding correlation-coefficient matrix is given in Fig. 2

	Components of uncertainty in measurement of saturation pressure (Pa)									
	Saturation pressure (Pa)	Calibn.	Drift	Temp. co.	Resoln.	Stab.	Grad. sat.	Grad. sat.	Grad. tubing	Grad. tubing
	Ps	Syst	Syst	Syst	Rand	Rand	Syst	Syst	Syst	Syst
L1	427479	45	50	10	1	200	10		30	
L2	374769	42	50	10	1	200	10		30	
L3	334368	39	50	10	1	180	10		30	
L4	302652	36	50	10	1	160	10		30	
L5	277250	35	50	10	1	140	10		30	
L6	256556	34	50	10	1	120	10		30	
L7	239403	33	50	10	1	100	10		30	
H1	204264	33	50	10	1	61		15		40
H2	193544	33	50	10	1	58		15		40
H3	184430	33	50	10	1	55		15		40
H4	176617	33	50	10	1	52		15		40
H5	169867	32	50	10	1	49		15		40
H6	163994	32	50	10	1	46		15		40
H7	158846	32	50	10	1	43		15		40
H8	115280	32	50	10	1	40		15		40

parameters, a_j ($j = 1$ to N). The software allows each parameter to be treated as a constant or as a fitted value. Uncertainties for all the input data values can be included and used to define weights for weighted nonlinear least-squares fitting, and correlations for any pair of input values may be specified, allowing generalized nonlinear least-squares fitting to be performed.

A range of fitting algorithms are available, including the Levenberg–Marquardt method [10] and the downhill simplex method (Amoeba) [11]. Algebraic functions can be entered into the software directly, but more complicated functions, such as numerical integrals and iterative equations, can be coded as user-defined functions within dynamic link libraries (DLLs). The user interface is shown in Fig. 4.

Outputs include:

- Fitted parameters, parameter uncertainties and parameter correlation matrix;
- Fitted curve, residuals plot and propagated uncertainty curve;
- Sensitivity coefficients $\partial y/\partial x_{k,i}$, $\partial y/\partial y_i$, $\partial a_j/\partial x_{k,i}$ and $\partial a_j/\partial y_i$ for each data point ($i = 1$ to M), for each independent variable, x_k ($k = 1$ to n), and for each parameter, a_j ($j = 1$ to N).

Re-fitting the residual part of IAPWS-95 (ϕ^{r}) to the original data with uncertainty required the generation in the NLF software of a user-defined function containing all 16 of the IAPWS-95 models representing the different physical quantities (all functions

	L1	L2	L3	L4	L5	L6	L7	H1	H2	H3	H4	H5	H6	H7	H8
L1	1.00	0.12	0.13	0.14	0.16	0.17	0.20	0.20	0.21	0.21	0.21	0.22	0.22	0.22	0.23
L2	0.12	1.00	0.13	0.14	0.15	0.17	0.19	0.20	0.20	0.20	0.21	0.21	0.21	0.22	0.22
L3	0.13	0.13	1.00	0.15	0.16	0.18	0.21	0.21	0.21	0.22	0.22	0.23	0.23	0.23	0.24
L4	0.14	0.14	0.15	1.00	0.18	0.20	0.23	0.23	0.23	0.23	0.24	0.24	0.25	0.25	0.26
L5	0.16	0.15	0.16	0.18	1.00	0.22	0.25	0.25	0.26	0.26	0.27	0.27	0.27	0.28	0.28
L6	0.17	0.17	0.18	0.20	0.22	1.00	0.28	0.28	0.29	0.29	0.30	0.30	0.31	0.31	0.32
L7	0.20	0.19	0.21	0.23	0.25	0.28	1.00	0.32	0.32	0.33	0.34	0.34	0.35	0.35	0.36
H1	0.20	0.20	0.21	0.23	0.25	0.28	0.32	1.00	0.61	0.62	0.63	0.64	0.66	0.67	0.68
H2	0.21	0.20	0.21	0.23	0.26	0.29	0.32	0.61	1.00	0.63	0.65	0.66	0.67	0.68	0.69
H3	0.21	0.20	0.22	0.23	0.26	0.29	0.33	0.62	0.63	1.00	0.66	0.67	0.68	0.69	0.71
H4	0.21	0.21	0.22	0.24	0.27	0.30	0.34	0.63	0.65	0.66	1.00	0.68	0.70	0.71	0.72
H5	0.22	0.21	0.23	0.24	0.27	0.30	0.34	0.64	0.66	0.67	0.68	1.00	0.71	0.72	0.73
H6	0.22	0.21	0.23	0.25	0.27	0.31	0.35	0.66	0.67	0.68	0.70	0.71	1.00	0.73	0.75
H7	0.22	0.22	0.23	0.25	0.28	0.31	0.35	0.67	0.68	0.69	0.71	0.72	0.73	1.00	0.76
H8	0.23	0.22	0.24	0.26	0.28	0.32	0.36	0.68	0.69	0.71	0.72	0.73	0.75	0.76	1.00

Fig. 2 Correlation-coefficient matrix calculated using the information in Table 2. Cells are shaded *red* to *blue* for smallest to largest correlations (Color figure online)

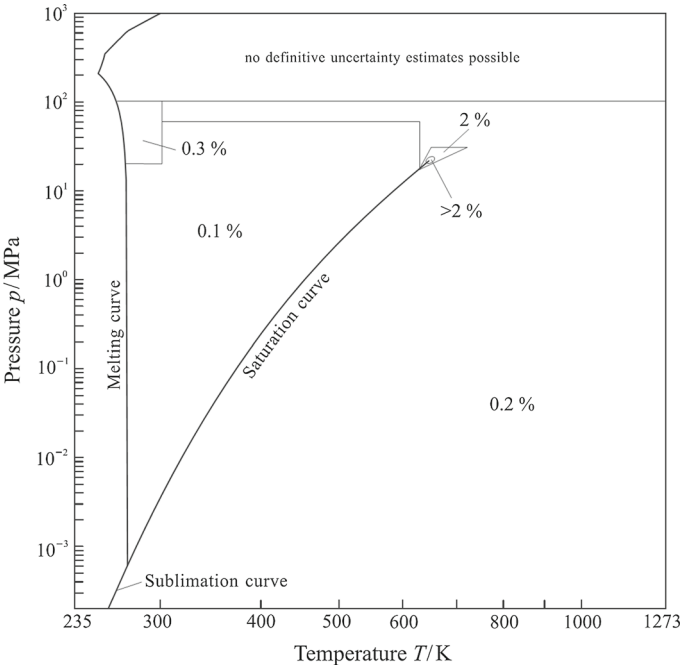

Fig. 3 Uncertainty in c_p as presented in IAPWS-95

of the same 56 parameters, labeled n_j in Figs. 1 and 6). The parameters were fitted simultaneously to the entire data set. Because of the complexity of IAPWS-95, it is not possible to write the equations in algebraic form, so the IAPWS-95 equations were

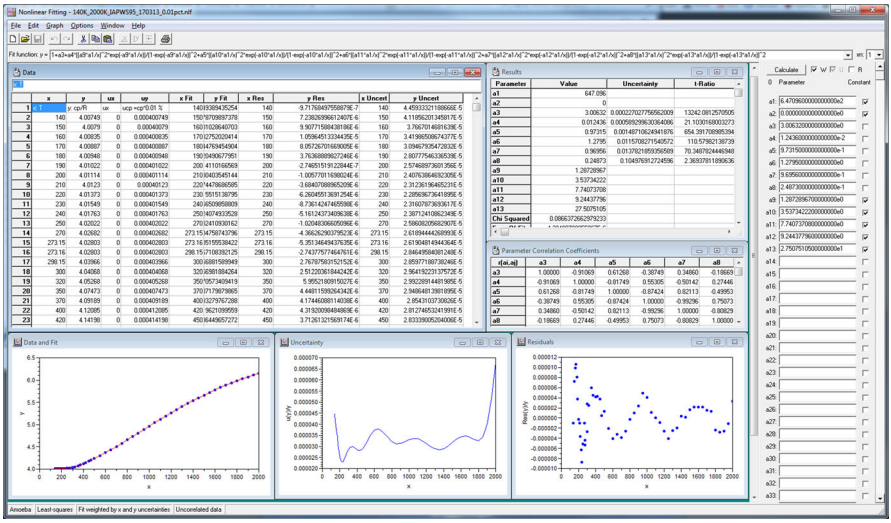

Fig. 4 A screenshot of the NLF interface as used to re-fit Cooper's equation for the isobaric heat capacity for water [9] to the data calculated by Woolley [12] over the range from 140 K to 2000 K. The parameters shown are used for ϕ^{o}. Fitting using NLF provides uncertainty for the fitted parameters (here a_3 to a_8 representing n_{03} to n_{08} in IAPWS-95) and the parameter correlation coefficients. Note, the other parameters were determined by the IAPWS-95 authors in the phase of structural optimization and are treated as constant here (see Sect. 3)

written into a DLL. While each of the 16 different physical quantities is a function of τ and δ (or of τ alone), the experimental data are in terms of T and ρ (or p) which are represented in NLF by the independent variables x_1 and x_2. An additional variable, x_3, was required to select the specific IAPWS-95 function (from the 16 functions) appropriate to each data point. A further variable, x_4, was required to specify the phase—liquid or vapor—for those quantities, such as isobaric heat capacity and speed of sound, where ρ needed to be calculated from the measured p at each iteration.

While no information regarding the measurement data covariance was available, it is likely that within data sets, the data are highly correlated. For the purposes of initial investigation, it was assumed that systematic and random errors were proportional to the measured value, as in Case 2 in Sect. 2.2, which yields for each data set a submatrix **R** with the same constant off-diagonal correlation coefficients. Consequently, several model sparse matrices with up to 36×10^6 elements were constructed with each block of off-diagonal elements, corresponding to each individual data set, successively set to 0.1, 0.3, 0.5, 0.7 and 0.9. A small portion of one such correlation-coefficient matrix is shown in Fig. 5, and the effect of different degrees of correlation on c_p is shown in Fig. 9.

A preliminary version of the matrix of the correlation coefficients for the 56 fitted parameters, obtained by applying the NLF software to the data, is shown in Fig. 6.

5 GUM Tree Calculator (GTC)

GTC [6,7] is a software tool designed to simplify the application of the GUM [8]. It also extends the approach recommended for real-valued quantities so that

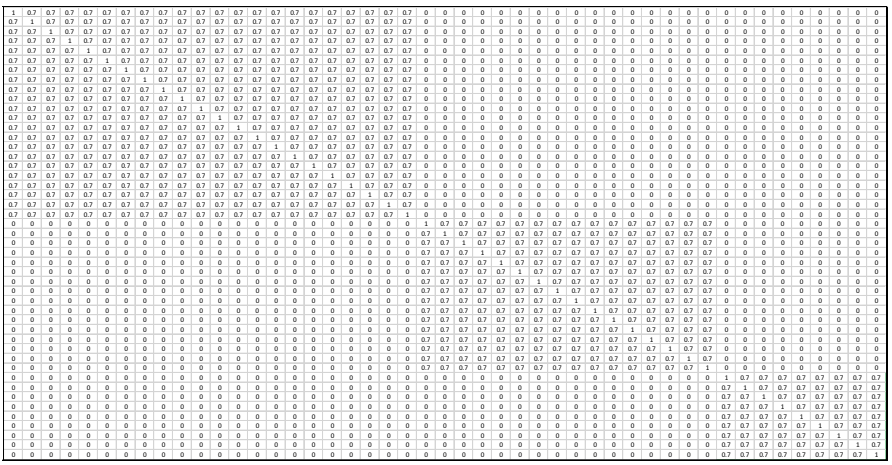

Fig. 5 A small portion of a model correlation-coefficient matrix with $r = 0.7$ for the approximately 6000 measurement data

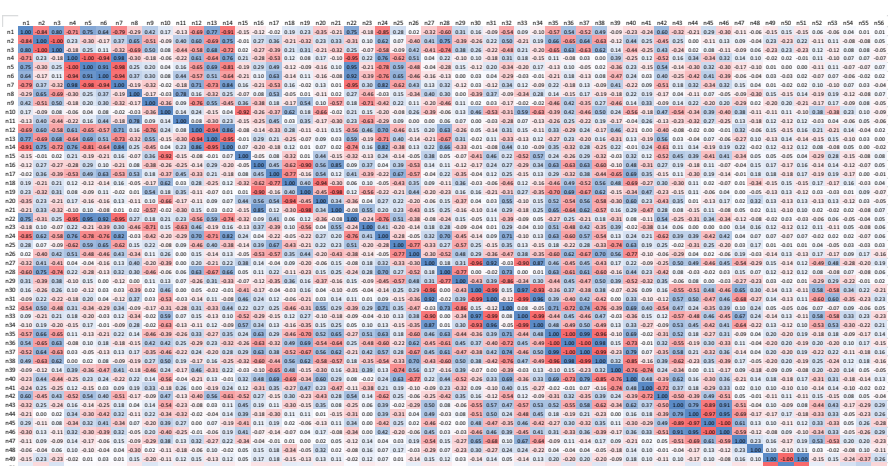

Fig. 6 Preliminary matrix of parameter correlation coefficients for the residual part parameters of IAPWS-95. Cells are shaded *blue* and *red* for $r(n_i, n_j) >$ and < 0, respectively, and more darkly as $|r(n_i, n_j)|$ increases (Color figure online)

problems involving the uncertainty of complex-valued quantities can be handled. GTC can be used as an interactive calculator or as a batch processing tool. It is self-contained (requiring no supporting software), programmable (using the Python language) and can be configured for specific applications. GTC provides full support for uncertainty in data processing calculations by using a special data type, called an uncertain number, to represent quantities that have been measured, or estimated in some way. They are the key feature of GTC that distinguishes it from other data processing tools. An uncertain number in GTC is a variable data struc-

```
Representing the parameters as uncertain numbers
ureal(value, uncertainty, dof, label)
ni = la.array([
ureal(0.0125, 0.0028, inf, "n1"),
ureal(7.896, 0.047, inf, "n2"),
…
ureal(0.318, 0.037,  inf, "n56"),
])
Setting the correlations
corr_ninj = la.array([
[1, -0.824, 0.7857, …]
…
[…, 0.1870, -0.9903, 1]
])
for i in range(1,56):
     for j in range(i+1,57):
          set_correlation(corr_ninj[i-1,j-1], ni[i-1], ni[j-1])
```

Fig. 7 Sample GTC code setting the IAPWS-95 parameter covariance in uncertain number representation

ture containing a value, a standard uncertainty, a number of degrees of freedom and, optionally, a label. Correlation coefficients for any two uncertain numbers can also be assigned.

When using Python, for example, coding is carried out with uncertain number variables in the same way that normal single-value variables would be used, in whatever algorithm is required to calculate a quantity of interest. GTC automatically propagates the uncertainties through these calculations, using the method of automatic differentiation, which implements the chain rule of calculus, to implement the GUM propagation law [8]. GTC delivers a value, standard uncertainty and number of degrees of freedom for the quantity of interest.

The propagation of uncertainty through large equations such as IAPWS-95 is immensely simplified using GTC. In this case, the first step was to rewrite the IAPWS-95 equations in Python. Secondly, the parameters, their uncertainties and the correlations between them, as derived from NLF, were represented by uncertain numbers—sample code is given in Fig. 7. Thirdly, executing the equations in GTC gave the usual value calculation, as well as the standard uncertainty and degrees of freedom. Furthermore, uncertainty budgets for the calculated quantities are available and the correlation coefficients between calculated quantities can be obtained directly. Note that other variables, such as temperature and density, were also represented as uncertain numbers and their uncertainties propagated accordingly.

Figure 8 shows uncertainties in c_p calculated using GTC for a series of isobars in the range given in Fig. 3 from IAPWS-95. Here, in addition to the uncertainties in the ϕ^{r} parameters reported in [4], uncertainties in the ϕ^0 parameters were included by fitting Cooper's equation [9] to Woolley's data [12] assuming relative uncertainty in each data point of 0.01 %. The uncertainties in c_p are considerably less than those estimated in IAPWS-95, but increase when possible correlations within each data set are included using NLF, as demonstrated in Fig. 9 for the 22.064 MPa (critical pressure) isobar.

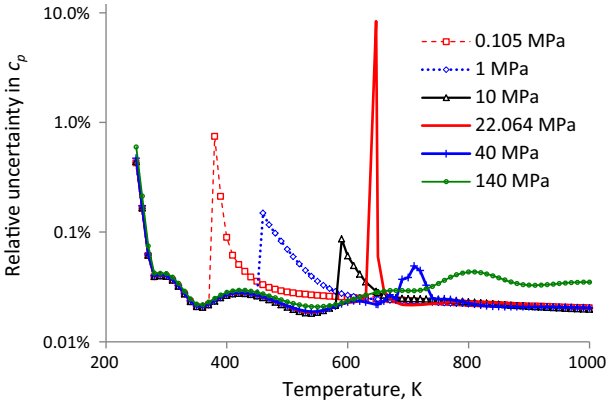

Fig. 8 Uncertainties in c_p calculated using GTC as a function of pressure and temperature. These are considerably less than the corresponding IAPWS-95 uncertainties given in Fig. 3

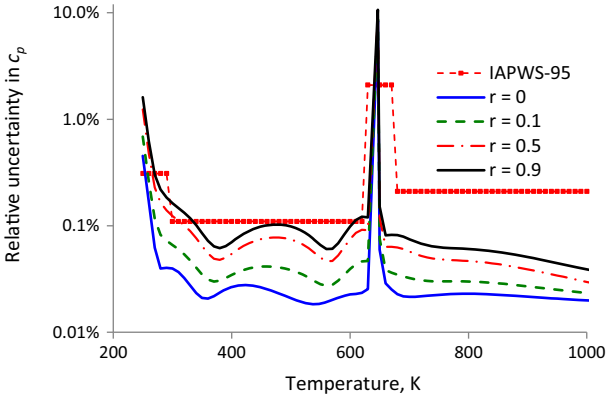

Fig. 9 Comparison of the IAPWS-95 uncertainties at 22.064 MPa with those calculated using GTC and based on different estimates of input data correlation

6 Discussion and Conclusions

Empirical equations can summarize a vast range of measurement data and underlying physics. However, if such equations are merely used to calculate quantities—that is, without any information regarding the uncertainty in those quantities or the covariance of two calculated quantities—then the full power and usefulness of the equations are not being realized. For example, the increasing usefulness and importance of empirical equations, such as TEOS-10 and the many IAPWS reference equations, highlight the need to: (a) be able to adequately characterize the uncertainty (and hence potential error) in the large number of quantities calculated using them; (b) provide a means for the user to readily obtain the uncertainty in the calculated result along with the result itself; and (c) provide a means to pass on the calculated quantity with all covariance information for further processing.

We have shown here how the covariance matrix (or, equivalently, the correlation-coefficient matrix) of the input data can be generated from an appropriate uncertainty budget. The NLF software developed at MSL enables a generalized least-squares fitting routine to propagate this covariance of the measurement data into the parameters of fitted empirical equations. We have further shown how MSL's GTC uncertainty calculator enables simultaneous calculation of the uncertainty, covariance and uncertainty budget for the quantity of interest, without needing to consult tables and interpolate table entries. These two tools can provide the means to unleash the power of empirical equations. GTC can also be a useful tool in post-processing measurement data so it can be published in a form enabling transportability of the measurement covariance. It can also be used to pre-process the measurement data uncertainty budgets to provide measurement data correlation-coefficient matrices suitable for use by NLF and other fitting programs. NLF can also be used to probe and quantify otherwise unrecognized systematic error in measurement data.

It is important to realize that, at this stage, the work described here is still exploratory. For example, it may not be possible to modify the existing IAPWS equations so that they incorporate full parameter covariance while retaining the same parameter values. It should also be noted that the uncertainty propagated using NLF only reflects the uncertainty and correlations in the input data. However, it is not yet clear how to include uncertainties arising from differences between the assumed functional form of the model and the underlying physics. Nevertheless, we suggest that it will be useful for experimenters to provide a suitably formatted uncertainty budget for each measurement. Such budgets would make available all systematic (shared by at least one other measurement) and random (independent) components of uncertainty, each stemming from a single error source. These then can be combined appropriately into measurement correlation-coefficient matrices depending on which measurements are required.

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