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Light years away from a thermodynamic model?

- Model Discrimination and Validation -

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Thermodynamic data: production, exploitation and impact on process design
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Overview

1. Introduction
   Sensitivity Analysis

2. Goodness of Fit
   Model Discrimination
   Predictive Power 1

3. Goodness of Parameter

4. Defining Model Validation 1

5. Predictive Power 2

Sensitivity Analysis

Unscaled dimensionless

$$S_i := \frac{\Theta_i}{f(X,\Theta)} \left(\frac{\partial f(X,\Theta)}{\partial \Theta_i} \right)_{\Theta_{j \neq i}, X}$$

Standardized and unscaled dimensionless

$$\tilde{S}_i := \frac{\Theta_i}{s(f(X,\Theta))} \left(\frac{\partial f(X,\Theta)}{\partial \Theta_i} \right)_{\Theta_{j \neq i}, X}$$

$X = (x_1, x_2 \ldots x_L)^*$ $x_i \in [x_{i,min}, x_{i,max}]$ $s = \text{stddev}$

$\Theta = (\Theta_1, \Theta_2 \ldots \Theta_{Np})^*$ $\Theta \in \Re^{Np}$ (* means the transpose of a vector or a matrix)

Sensitivity Analysis

Jacobian matrix (design matrix)

$$J(X,\Theta) = -\begin{pmatrix} \frac{1}{s_1}\left(\frac{\partial f(X,\Theta)}{\partial \Theta_1}\right)_{\Theta_{j\neq 1},X_1} & \cdots & \frac{1}{s_1}\left(\frac{\partial f(X,\Theta)}{\partial \Theta_{Np}}\right)_{\Theta_{j\neq Np},X_1} \\ . & & . \\ . & & . \\ . & & . \\ \frac{1}{s_M}\left(\frac{\partial f(X,\Theta)}{\partial \Theta_1}\right)_{\Theta_{j\neq 1},X_M} & \cdots & \frac{1}{s_M}\left(\frac{\partial f(X,\Theta)}{\partial \Theta_{Np}}\right)_{\Theta_{j\neq Np},X_M} \end{pmatrix}$$

M = number of measurements

Sensitivity Analysis

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Parameter error propagation for a what-if scenario

$$cov(X, \Theta) = \left(J(X, \Theta)^{*} \cdot J(X, \Theta)\right)^{-1}$$

parameter variance-covariance matrix

$$e_{\%}(\Theta_i) = \frac{\sqrt{cov(X, \Theta)_{ii}}}{\Theta_i} 100\,\%$$

expected error of parameter Θ_i

$\left(^{*} \text{ means the transpose of a vector or a matrix} \right)$

2. Goodness of Fit

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How to test the power of the most frequently used statistical criteria?

- Simulation of measurements with a true and a false model.

- Evaluation or analysis of the simulated measurements.

- Answer to the question: Which assesment numbers are useful for model discrimination and predictive power ?

Choice of Model

Simulation with a heuristic vapor pressure equation. Compound: water (from triple point up to critical point (1))

$$p_{true} := p_c \exp\left\{ \mathring{\Theta}_1 \left(1 - \frac{T_c}{T}\right) + \mathring{\Theta}_2 \ln\left(\frac{T}{T_c}\right) + \mathring{\Theta}_3 \left[\left(\frac{T}{T_c}\right)^2 - 1\right] \right\} = f\left(T, \mathring{\Theta}\right)$$

$$p_{false} := p_c \exp\left\{ \Theta_1' \left(1 - \frac{T_c}{T}\right) + \Theta_2' \ln\left(\frac{T}{T_c}\right) + \Theta_3' \left[\left(\frac{T}{T_c}\right) - 1\right] \right\} = f\left(T, \Theta'\right)$$

(1) VDI-Wärmeatlas, 11th edition 2013, Springer Vieweg

Choice of Noise

Realistic simulation assumptions: inhomogeneous variance

$$\varepsilon_i \sim \mathcal{N}\left(0, \sigma_i^2 \mid \sigma_i\right) = v \cdot f\left(T_i, \Theta\right) \qquad v = 0.002 \ \left(rel.\, error\right)$$

$$Y_i = f\left(T_i, \mathring{\Theta}\right) + \varepsilon_i \qquad Y_i = \text{simulated vapor pressure measurements}$$

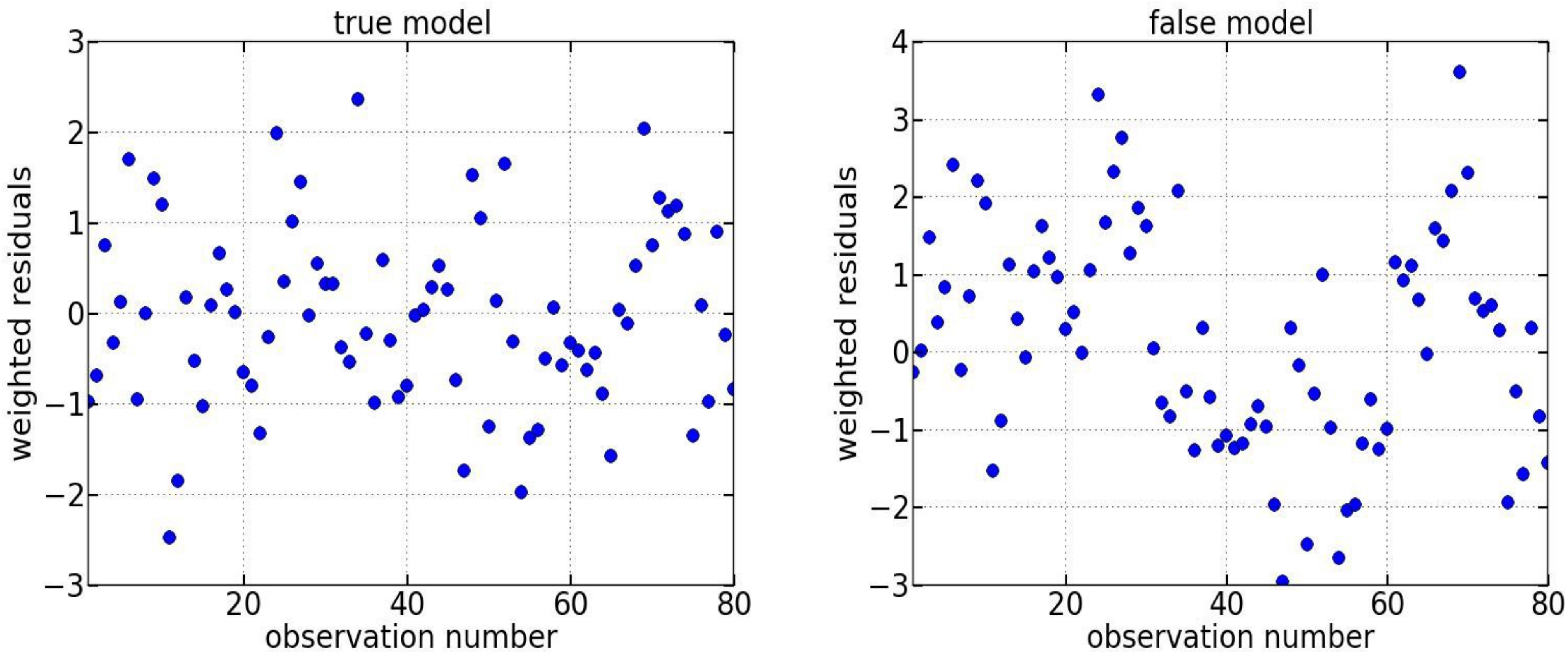
$$\mathcal{E}\left(Y\right) = f\left(T, \mathring{\Theta}\right)$$

Parameter estimation: Levenberg-Marquardt (Least-Squares)

Choice of Noise

Plot of Weigted Residuals vs. Measurement Number

for the True and the False Model



2. Goodness of Fit Quantities

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#	Test quantity	Equation
1	SWS	$SWS := \sum_i \left(\frac{Y_i - \hat{Y}_i}{s_i} \right)^2$
2	χ_r^2	$\chi_r^2 := \frac{SWS}{M - Np}$
3	$P_\alpha^{(\chi)}$	$P_\alpha^{(\chi)} = 1 - P(\chi_t^2 > \chi_c^2) = \alpha$
4	$AAD\%$	$AAD\% = 100 \sum_i \left\vert \frac{Y_i - \hat{Y}_i}{Y_i} \right\vert$

2. Goodness of Fit Quantities

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#	Test quantity	Equation
5	Model bias 1	$\text{Bias 1} = 100 \sum_i \frac{Y_i - \hat{Y}_i}{Y_i}$
6	Model bias 2	$P_\alpha(H_0\!: (Y = a\hat{Y} + b) \wedge (a=1) \wedge (b=0))$
7	$PRE\ SWS$	$PRE\ SWS := \sum_i \left(\frac{Y_i - \hat{Y}_i(\hat{\Theta}_k)}{s_i} \right)^2 \quad (1)$
8	$P_\alpha^{(\chi)}(PRE\ SWS)$	$P_\alpha^{(\chi)} = 1 - P(\chi_t^2 > \chi_c^2) = \alpha$

(1) $k =$ class number

2. Goodness of Fit Quantities

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#	Test quantity	Equation / Explanation
9	Model Bias 2 for $\hat{Y}_i(\hat{\Theta}_k)$	$P_\alpha(H_0\colon (Y = a\hat{Y} + b) \wedge (a = 1) \wedge (b = 0))$

Remark: The R^2 test for non-linear regression is meaningless.

See D.A. Ratkowsky, Handbook of Nonlinear Regression Models. Marcel Dekker, Inc. New York and Basel, 1990. p. 44

2. Goodness of Fit Quantities

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Bias Test 2

Hypothesis: $$Y = \hat{Y}$$

2. Goodness of Fit Quantities

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Bias Test 2

Hypothesis: $Y = \hat{Y}$

$Y = a \cdot \hat{Y} \qquad if \ a = 1$

2. Goodness of Fit Quantities

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Bias Test 2

Hypothesis:

$$Y = \hat{Y}$$

$$Y = a \cdot \hat{Y} \qquad if \;\; a = 1$$

$$Y = a \cdot \hat{Y} + b \qquad if \;\; b = 0$$

2. Goodness of Fit Quantities

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Bias Test 2

Hypothesis: $Y = \hat{Y}$

$$Y = a \cdot \hat{Y} \qquad if \ a = 1$$

$$Y = a \cdot \hat{Y} + b \qquad if \ b = 0$$

H_0 Hypothesis $P_\alpha\left(H_0 : \left(Y = a\,\hat{Y} + b\right) \wedge \left(a = 1\right) \wedge \left(b = 0\right)\right)$

2. Goodness of Fit – Predictive Power 1

e.g. 3-fold cross validation test

N^0: number of run (randomized) $\hat{Y}^1$: predicted response in class 1

$\hat{Y}^0$: calculated for all data points $\hat{R}_i^1$: predicted residual i in class 1

N^0	N^1	N^2	N^3		$\hat{Y}^0$	$\hat{Y}^1$	$\hat{Y}^2$	$\hat{Y}^3$		remarks
1	1	1	1		$\hat{R}_1^0$	$\hat{R}_1^1$				for prediction
2	2	2	2		$\hat{R}_2^0$	$\hat{R}_2^1$				for estimation
3	3	3	3		$\hat{R}_3^0$	$\hat{R}_3^1$				
4	4	4	4		$\hat{R}_4^0$		$\hat{R}_4^2$			
5	5	5	5		$\hat{R}_5^0$		$\hat{R}_5^2$			
6	6	6	6		$\cdots$		$\hat{R}_6^2$			
7	7	7	7		$\cdots$			$\hat{R}_7^3$		
8	8	8	8		$\cdots$			$\hat{R}_8^3$		
9	9	9	9		$\hat{R}_9^0$			$\hat{R}_9^3$		

2. Goodness of Fit - Results

#	Test quantity	True model	False model	Model dis-crimination
1	SWS (1)	79	162	o
2	χ_r^2	1.03	2.1	o
3	$P_\alpha^{(\chi)}$ %	42	$<< 10^{-3}$	+
4	$AAD\%$ (2)	0.15	0.22	-

+ apprioptiate o appropriate if f and database are equal for both models

- not appropriate

(1) $\chi_c^2 = \chi^2_{1-\frac{\alpha}{2}, f} = 103$ (2) remember: assumed rel. error for measurement 0.2 %

2. Goodness of Fit - Results

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#	Test quantity	True model	False model	Model discrimination
5	Model bias 1	-0.02	0.014	- (1)
6	Model bias 2			
	$P_{\alpha/2}(b=0)$ %	29	<< 10^{-3}	+
	$P_{\alpha/2}(a=1)$ %	22	<< 10^{-3}	+

+ appriopriate   - not appropriate

(1) sensitive for residual structure ! → indicator for bias → residual plot

2. Goodness of Fit - Results

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#	Test quantity	True model	False model	Model dis-crimination
7	$PRE\ SWS$	85.8 (1)	719 (2)	o
8	$P_{\alpha}^{(\chi)}(PRE\ SWS)$	23	<< 10^{-3}	+
9	Model Bias 2 for $\hat{Y}_i(\hat{\Theta}_k)$			
	$P_{\alpha/2}(b=0)$ %	29	<< 10^{-3}	+
	$P_{\alpha/2}(a=1)$ %	22	<< 10^{-3}	+

(1) $\chi^2_{crit} = \chi^2_{1-\frac{\alpha}{2},f} = 103$ (2) remember: PRE SWS for all data points and false model: 162

3. Goodness of Parameter

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Questions:

- How trustworthy are estimated parameter values?

- What kind of powerful parameter test methods exist?

- Which criteria must be fulfilled for model validation?

- How can model validation be defined?

3. Goodness of Parameter

Practical example:

- Modeling Peng Robinson Equation of State (PR) with geometric mean mixing rule for the gas phase.

- System CH_4 (1) / H_2O (2) with 168 measured data for gas phase.
  L.L. Joffrion and P.T. Eubank; FPE **43** (1988) 263.

- Independent variables: $T[K],\ \rho^*[mol/m^3],\ \ y_2 : 0.1,\ 0.25,\ 0.5$
  dependent variable: $p[Pa]$ measured pressure
  overall error ~ 0.2 %

3. Goodness of Parameter

Which parameter are selected in the PR EoS?

$$B(T, y, \Theta) = \sum_i \sum_j y_i y_j b_{ij} (1 - \kappa_{ij} \Theta_1)$$

$$A(T, y, \Theta) = \sum_i \sum_j y_i y_j \sqrt{a_{ii} a_{jj}} (1 - \kappa_{ij} \Theta_2)$$

$$\kappa_{ij} = \kappa_{ji} := \begin{cases} 1 & if \quad i \neq j \\ 0 & if \quad i = j \end{cases}$$

→ Analysis of the estimated parameter $\hat{\Theta}_1, \hat{\Theta}_2$

3. Goodness of Parameter

#	Test quantity	Equation / Explanation
10	$\mathcal{R}_{cov}$	$\mathcal{R}_{cov} = \mathcal{R}ank(cov(X, \Theta))$
11	$cond_{\lambda}$	$cond_{\lambda} = \dfrac{\lambda_{max}(cov(X, \Theta))}{\lambda_{min}(cov(X, \Theta))}$
12	$e_{\%}(\Theta_i)$	$e_{\%}(\Theta_i) = \dfrac{\sqrt{cov(X, \Theta)_{ii}}}{\Theta_i} 100\,\%$ (1)
13	$P_{\alpha}^{(\chi)}(var(\Theta))$	$P_{\alpha}^{(\chi)} = 1 - P(var(\Theta) > \chi_c^2) = \alpha$

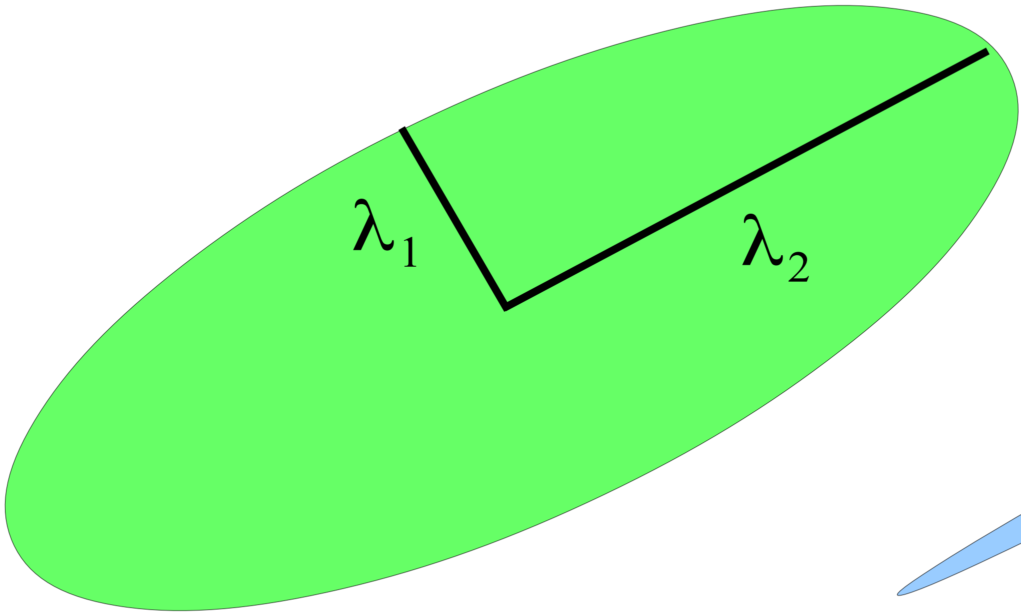
(1) better: exact confidence region based on F statistic (appendix)

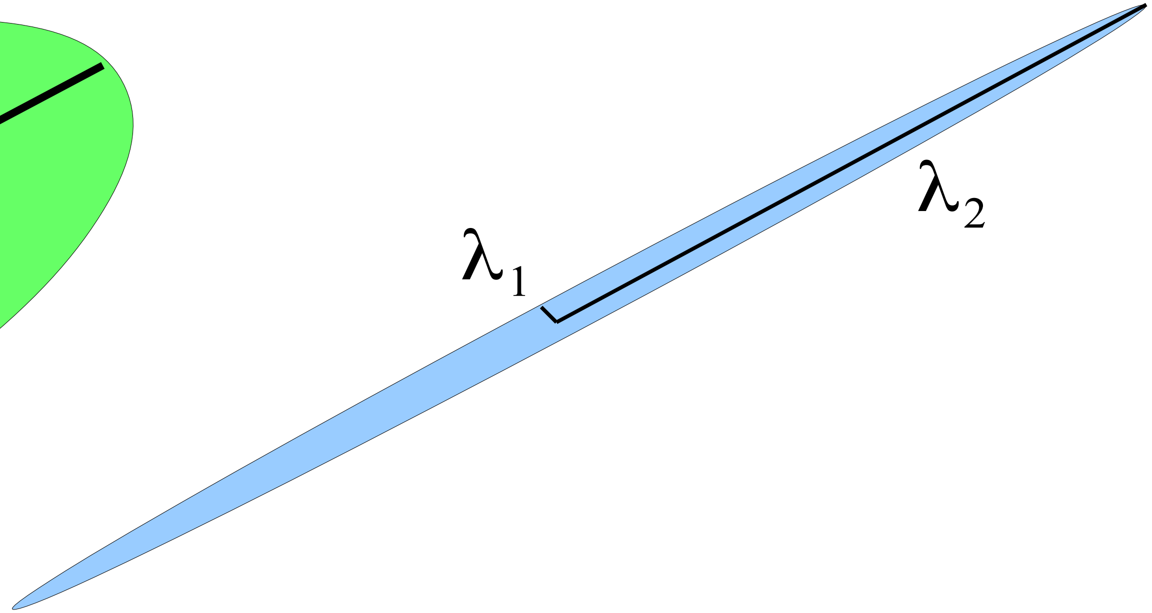
Explanation of the condition number

$$cond_{\lambda} = \frac{\lambda_{max}(cov(X,\Theta))}{\lambda_{min}(cov(X,\Theta))}$$

Well conditioned

poorly conditioned





Generally: the eigenvalues λ_i are variances of the orthogonal main axis of a hyper ellipsoid

3. Goodness of Parameter

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#	Test quantity	PR	Model Acceptance
10	$\mathcal{R}_{cov}$	2	+ (1)
11	$cond_{\lambda}$	600	(2)
12	$e_{\%}(\Theta_i)$	12.2 6.4	
13	$P_{\alpha}^{(\chi)}(var(\Theta))/\%$	0.2 19.5	- +

The model is not accepted

(1) necessary but not sufficient. (2) sensitiv indicator for parameter insufficiency

4. Model Validation – Definition

Selection criterion: quantities with statistical constraints

#	Test quantity	Goodness of Fit	Model Discrim	Pred. Power 1	Goodness of Param.	Model Validation 1
3	$P_{\alpha}^{(\chi)}$ %	+	+			+
6	Model bias 2	+	+			+
8	$P_{\alpha}^{(\chi)}(PRE\ SWS)$		+	+		+
9	Model Bias 2 for $\hat{Y}_i(\hat{\Theta}_k)$		+	+		+
10	$\mathcal{R}_{cov}$	(+)			+	+
13	$P_{\alpha}^{(\chi)}(var(\Theta))$				+	+

5. Predictiv Power – Definition

Predictive Power 1

$$Y = f(X, \hat{\Theta})$$

$$X = (x_1, x_2 \ldots x_L)^*$$
$$Y = (y_1, y_2 \ldots y_Q)^*$$
$$\hat{\Theta} = (\hat{\Theta}_1, \hat{\Theta}_2 \ldots \hat{\Theta}_{Np})^*$$

X independent variables

Y dependent var. (observation)

Predictive Power 2

(→ EoS development)

$$Z = g(X, \hat{\Theta})$$

$$X = (x_1, x_2 \ldots x_L)^*$$
$$Z = (z_1, z_2 \ldots z_I)^*$$

The dependent vari-able Z is not used for parameterizing $\hat{\Theta}$

5. Predictive Power 2

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Predicted quantity: heat capacity $C_{P,M}$ (1) for vapor and for NH_3

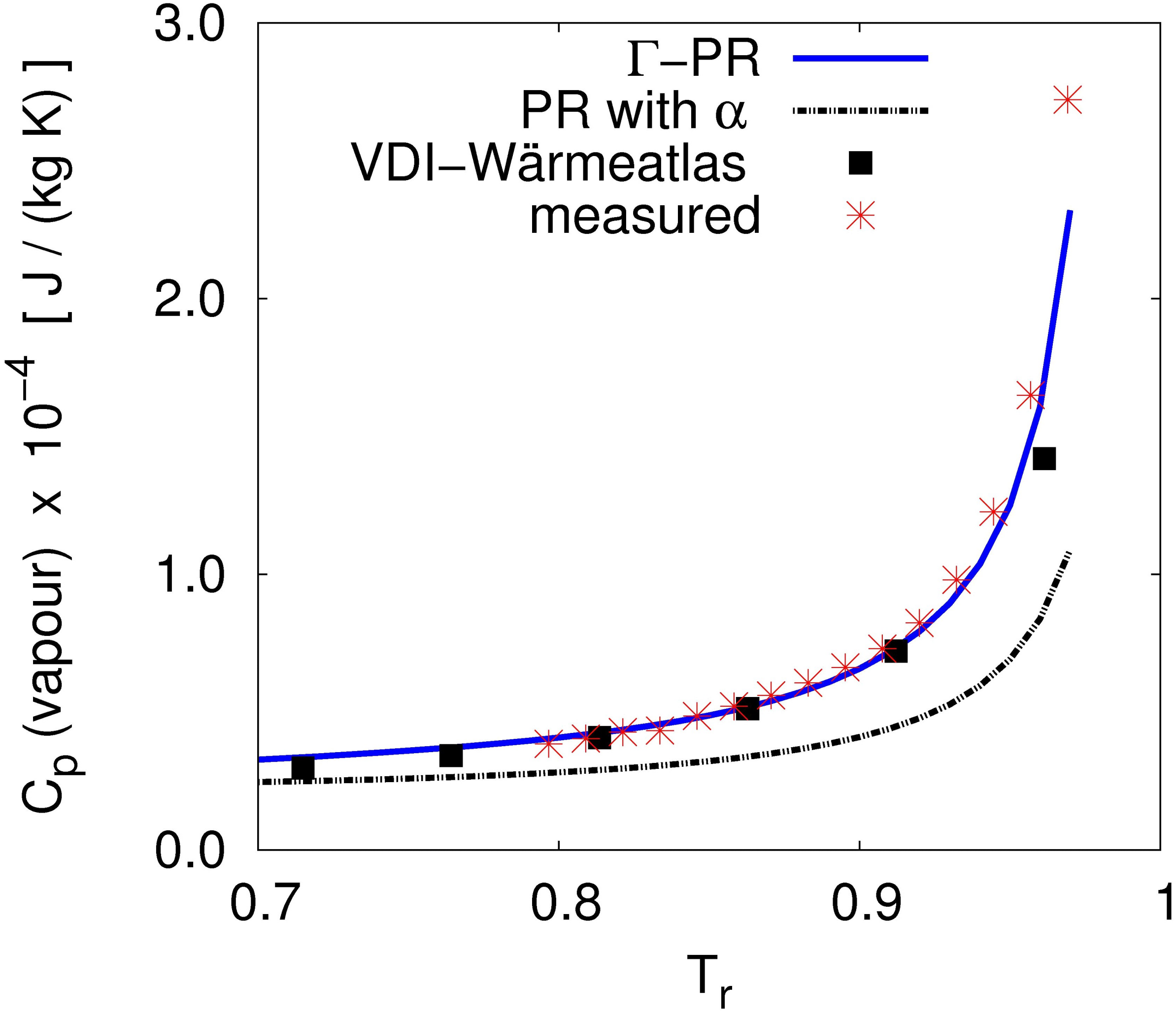
$\Gamma - PR$ Calibration of $\hat{\Theta}$ based on pVT data (2) only

$$\boldsymbol{C}_{\boldsymbol{p},\boldsymbol{M}}(\boldsymbol{T}) = C_{p,id}(\boldsymbol{T}) - T \cdot \int_{\upsilon}^{\infty} \left(\frac{\partial^2 p_M}{\partial T^2} \right)_V dV - R - \boldsymbol{T} \cdot \frac{\left(\frac{\partial p_M}{\partial T} \right)_{\upsilon}^2}{\left(\frac{\partial p_M}{\partial V} \right)_{\boldsymbol{T}}}$$

$(1)\ M = \Gamma - PR$ or $PR(\alpha_{Soave})$ (2) VDI-Wärmeatlas, 11th edition 2013, Springer Vieweg

4. Predictive Power 2

$$\Gamma - PR \quad \text{versus} \quad PR \text{ with Soave correction}, \alpha$$



A. Kud, S. Körkel, S. Maixner,
Chem. Eng. Sci., 65 (2010) 4194

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Appendix

Goodness of Fit - Results

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Example: PR Equation of State

#	Test quantity	Ideal Gas	Virial Equ.	PR
1	$SWS \quad (1)$	5000	267	119
2	χ_r^2	30 (2)	1.6	0.72
3	$P_\alpha^{(\chi)} \quad \%$	0	< 10^{-4}	99
4	$AAD\,\%$	0.65	0.23	0.15

$(1) \quad \chi^2_{crit} = \chi^2_{1-\frac{\alpha}{2},f} \approx 197$

(2) One unit is one „statistical light year“

Goodness of Fit - Results

Example: PR Equation of State

#	Test quantity	Ideal Gas	Virial Equ.	PR (1)
5	Model bias 1 (2)	-0.61	0.22	0.08
6	Model bias 2			
	$P_{\alpha/2}(b=0)$ %	0	0	29
	$P_{\alpha/2}(a=1)$ %	0	0	3

(1) Goodness of fit: model accepted. Goodness of parameter: model refused

(2) sensitive for residual structure ! → indicator for bias → residual plot

Goodness of Parameter

$$J(X,\Theta) := -\frac{1}{s_{i=1,2...M}}\left(\frac{\partial f(X,\Theta)}{\partial \Theta}\right)_{X_{i=1,2...M}}$$

$$cov(X,\Theta) = \left(J(X,\Theta)^{*} \cdot J(X,\Theta)\right)^{-1}$$

$$cov(X,\Theta) = \begin{pmatrix} cov(X,\Theta)_{11} & ... & cov(X,\Theta)_{1\mathrm{Np}} \\ . & & . \\ . & & . \\ . & & . \\ cov(X,\Theta)_{Np1} & ... & cov(X,\Theta)_{NpNp} \end{pmatrix}$$

$$s(X,\Theta_i) = \sqrt{cov(X,\Theta)_{ii}}$$

Goodness of Parameter

The exact conficence region of parameter

$$F\left(N_p, M-N_p, \alpha\right) = \frac{\left[Y-f\left(X,\hat{\Theta}\right)\right]^{*} \mathcal{P}\left(X,\hat{\Theta}\right)\left[Y-f\left(X,\hat{\Theta}\right)\right] / N_p}{\left[Y-f\left(X,\hat{\Theta}\right)\right]^{*}\left[I-\mathcal{P}\left(X,\hat{\Theta}\right)\right]\left[Y-f\left(X,\hat{\Theta}\right)\right] / \left(M-N_p\right)}$$

$$\mathcal{P}\left(X,\hat{\Theta}\right) = J\left(X,\hat{\Theta}\right)\left[J\left(X,\hat{\Theta}\right)^{*} J\left(X,\hat{\Theta}\right)\right]^{-1} J\left(X,\hat{\Theta}\right)^{*}$$

Ratkowsky, Handbook of Nonlinear Regression Models. Marcel Dekker, Inc. New York and Basel, 1990. p. 36

PR and SRK EoS

$$p_{PR}(T, \upsilon, y, \Theta) := \frac{R\,T}{\upsilon - B(y, \Theta)} - \frac{A(T, y, \Theta)}{\left(\upsilon + \delta\, B(y, \Theta)\right) \cdot \left(\upsilon + \varepsilon\, B(y, \Theta)\right)}$$

Sensitivity Analysis

Simulation results for the PR EoS

Sensitivity index	Θ_1	Θ_2
S_I	0.037	0.022
$\tilde{S}_I$	18.3	11.1

Fundamental theorem in statistic for the probability P

$$P\left(X \leqslant c\right) + P\left(X > c\right) = 1$$