

THERMODYNAMIC PROPERTIES IN THE SERVICE OF PROCESS SIMULATORS

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OBJECTIVES

Illustrate/Distinguish **Service** & **Advice** Roles of Properties in Simulation & Design

Suggest How to Make Properties in **Service**

Efficient

Fast, minimum input, automated

Flexible

Usable in several process applications

Robust

Results reliable for multiple problems

WHY PROPERTIES MODELING?

Competitive Manufacturing Requires

New/Replacement Processes, Products

Economic Efficiency in Time, Effort, Investment

Process Simulators

Allow maximum exploration/optimization

Solve equipment units with Process Models of

Constraint equations (Material/Energy/Fugacity)

Thermo Variables are *Conceptuals* ($h, \phi_p, \gamma_p, \dots$)

Need Data & Property Models to relate *Conceptuals*

to System/Substance *Measurables* ($T, P, \{x\}, \dots$)

USES OF PROPERTY MODELS

Have *Process* simulation & *System* design problems

Simulation (Service)

Design (Advice)

Simulation/Design

Set Design Target

Find Process

Problem

Find System

Alternatives

Feasibility

Fixed compounds
Bounded $T, P, \{x\}$

Constraints

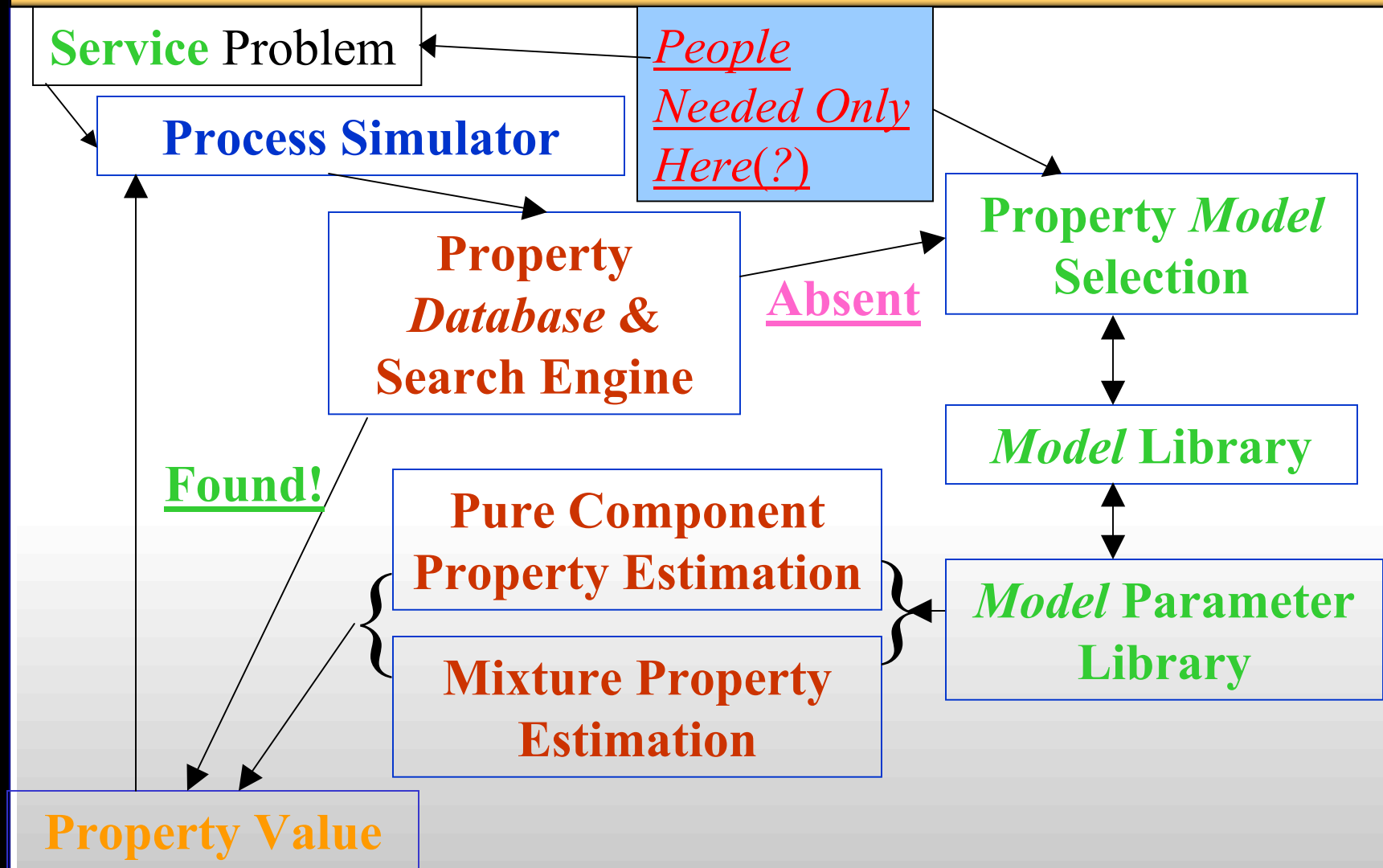
Any compounds
Unbounded $T, P, \{x\}$

Generalized or
System-Specific
Models

Options

Generalized or
Problem-Specific
Models

SERVICE TOOLS FOR PROPERTY PROBLEMS



SERVICE CASES DEPEND UPON KNOWN INFORMATION (DATA/PARAMETERS)

Forward Problems (Service Role)

- Select Appropriate Model

How to be efficient,
reliable, & accurate?

MANY MODELS

Pure Component

P^{Sat}, v^{Sat}, T_c

.....

EoS Models

SRK

PHC

SAFT

.....

Mixing Rules

vdW, G^E

.....

G^E Models

Wilson

UNIQUAC

Electrolyte

NRTL

.....

Group Methods

UNIFAC-I

ASOG

.....

ISSUES FOR SERVICE MODELS

Large model libraries may be needed

Increases application range

Causes model selection/validation uncertainties

Requires many data/parameters

Generalized models may be

Computationally expensive

Unnecessarily complex, especially derivatives

Efficiency/reliability improvements

Simpler models with tuned parameters

generated on-line & validated

Sensitivity analysis of parameters

EXAMPLE: CO₂ & ACRYLIC ACID

VLE separation feasibility & conditions?

Limited pure component, binary data available

Model selection suggests EoS, specifically SAFT

Corresponding states form, no binary parameter

But takes large computational resources

Questions:

Use directly or to set up simpler model?

What is efficient procedure to generate model?

SAFT REFERENCE; SRK APPLICATION

VLE data from SAFT, use to fit SRK k_{12} – fast/reliable

Values passed to Database, Parameter library for use in other applications

Property Estimation Toolbox version

Selected compounds

No	Name	Formula	CASNO	Database
1.	acrylic-acid	C3H4O2	000079-10-7	user.mdb
2.	CARBON-DIOXIDE	CO2	000124-38-9	user.mdb

Phase Equilibrium Model Selected Results

Regression Successful

Data Set: Data Set 1 : SubSet = All Compounds

Plot Type: P-x-y Plot

Regressed Parameters	Value	Unit
k_{ij} (C3H4O2/CO2)	-0.01002727099257	

See the output file for more details.

Graph Control: Gridlines Legend Box

P-x-y Plot

Legend Box

- $y_{exp}(1)$ = Red
- $x_{exp}(1)$ = Red
- $y(1)$ = Green
- $x(1)$ = Green

Pressure (Bar) vs. $x(1), y(1)$

CASE: PARAMETERS UNKNOWN

CapecDB Manager - [CAPECDB MANAGER:2]

File Edit View Database Help

Search by:

- Name
- Formula
- Cas-number

 Type the Search-string: Search CapecDB View Compound

Found Compounds:

Casno	Chemname	Smiles	Formula
000052-52-8	Cyclopentanecarboxylic acid, 1-amino-	O=C(O)C(N)(CCC1)C1	C6H11NO2
000052-67-5	Pencillamine	CC(C)(S)C(N)C(O)=O	C5H11NO2S
000052-68-6	Dipterex	COP(=O)(O)C(O)C(O)C(C)C1	C4H8Cl3O4P
000052-85-7	Phosphorothioic acid, O- 4- (dimethylami	O=S(=O)(N(C)C)c(ccc(C	C10H16NO5PS
000052-86-8	Haloperidol	OC2(CCN(CCCC(=O)O)c1	C21H23ClFNO2
000052-90-4	L-Cysteine	O=C(O)C(N)CS	C3H7NO2S
000053-03-2	Prednisone	C1(=O)C=C2CCC3C4CC	C21H26O5
000053-05-4	Tetrahydrocortisone	C12(C)C3C(=O)CC4(C)	C21H32O5
000053-06-5	Cortisone	CC13CCC(=O)C=C1CCC	C21H28O5
000053-16-7	Estra-1,3,5(10)-trien-17-one, 3-hydroxy-	O=C(C)C(C)C(c1c(cc(O)	C18H22O2
000053-41-8	Androsterone	C1(CO)CC2CCC3C4CCC	C19H30O2
000053-46-3	Methanethine Bromide	c12oc3ccc3c(c1)C(=O)	C21H26BrNO3
000053-70-3	Dibenz(a,h)anthracene	c1c(c1c2)ccc2c2)ccc	C22H14
000053-86-1	Indomethacin	COc1ccc2n(Cc(=O)c3cc	C22H25N3O
000053-89-4	Benziperylon	O=C(NC(=O)c1ccc2)cc	C22H25N3O
000053-96-3	Acetamide, N-9H-fluoren-2-yl-	O=C(Nc(ccc1c1C2ccc	C15H13NO
000054-04-6	Mescaline	NCCc1cc(O)c(C)C(O)C1	C11H17NO3
000054-06-8	Adrenochrome	C12=C(O)C(=O)C=C1	C9H9NO3
000054-11-5	Pyridine, 3-(1-methyl-2-pyrrolidinyl)-, (S)	n(ccc1C(NCC2)C)C2)	C10H14N2

ProPred - NoName

Summary Marrero and Gani Constantinou and Gani Joback and

property Values estimated by using methods included in Pr

Compound Name: 2-amino-4-methyl pentanoic acid
 compound CAS : 000061-90-5
 v (g/mol) : 131.18

Est estimates are suggested for each property according to developers' criteria. See detailed estimates through each of the corresponding pages

Property	Method	Unit	Est. Value	Exp. V
Tm	MG	K	582.55	566.1
Tb	MG	K	510.42	N/A
Tc	MG	K		
Tc	MG	bar		
Vc	MG	cm ³ /mol		
Zc	MG			
Sf[298K]	MG	kJ/mol		
Hf[298K]	CG	kJ/mol		
Sf[298K]	MG	J/(mol*K)		
omega	JR			
Hv[298K]	*****	kJ/mol		
Hv[Tb]	MG	kJ/mol		
Hfus	MG	kJ/mol		
Vm[298K]	*****	cm ³ /mol		
Vm[Tb]	MG	cm ³ /mol		
Sol. Par. [298K]	*****	MPaK		
Refractive Index	*****			
Molar Refraction	*****			
Surf. Tens. [298K]	*****	dyn/cm		
S. T. Temp.	*****	K		
Log(Kov)	CG			
Log(Ws)	CG	Log(mg/L)		
Closed Flash Temp.	*****	K		
Open Flash Temp.	CG			
Hansen Disp. sol.	*****	MPaK		
Hansen Polar sol.	*****	MPaK		
Hansen Hydr. sol.	*****	MPaK		
Dipolar moment	*****	debye		
Dielectric const.	*****			
Henry[298K]	*****	bar* ³ /mo		

G = Marrero and Gani method

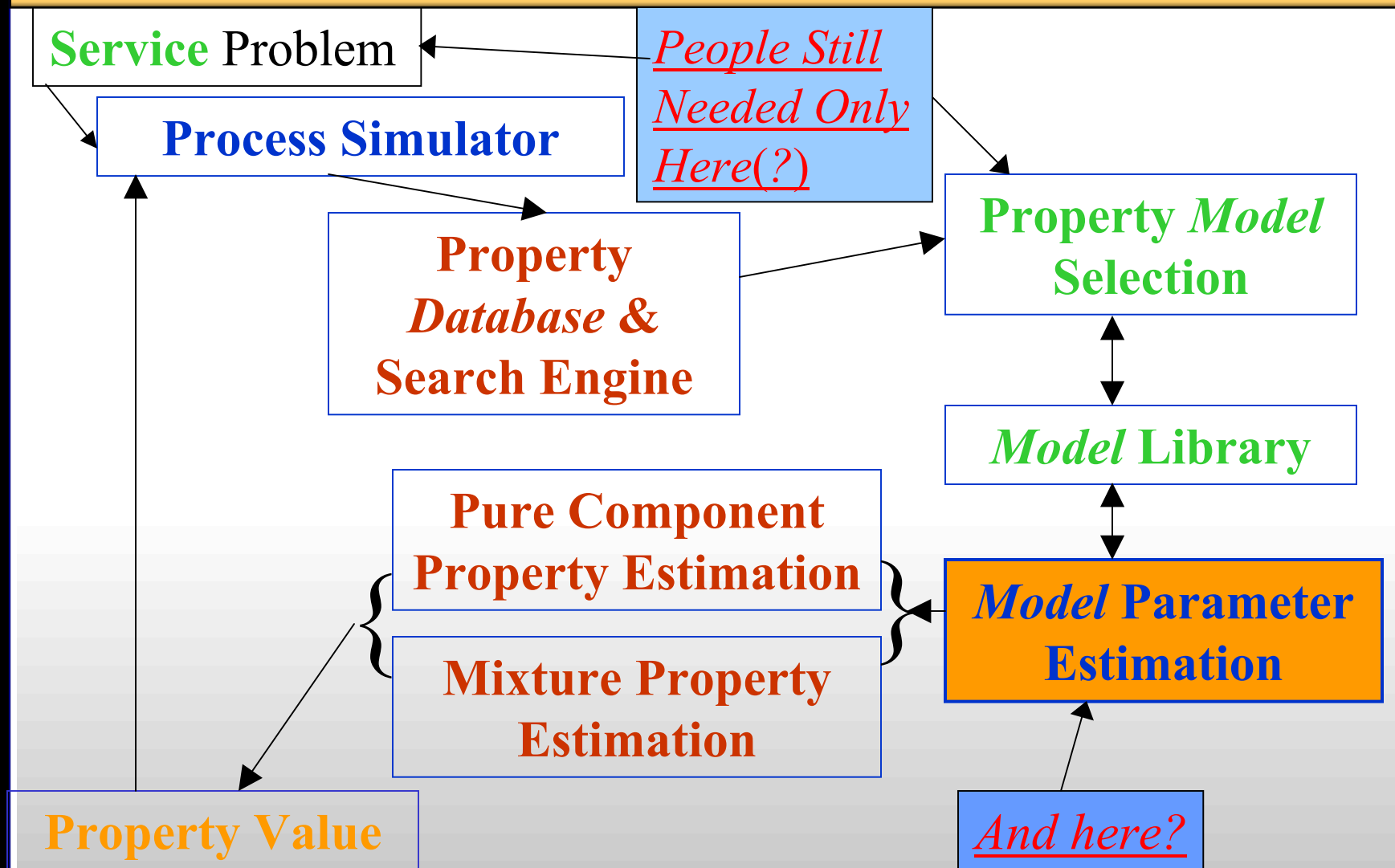
Thermodynamic Diagram

Pressure vs. Enthalpy

P (bar)	H (kJ/mol)	Phase
6.72	77.11	sat. liq.
6.72	7.17	sat. gas
10.00	6.55	gas

Though much information available, no data nor model parameters for case of interest
 Must estimate parameters
 Should be efficient!

SERVICE TOOLS FOR PROPERTY PROBLEMS



EXAMPLE: H₂O/ KCl/EtOH/Ampicillin

Effect of ethanol on solubility of ampicillin

Limited pure/binary/ternary SLE data available
Speciation identified

Model selection suggests Electrolyte NRTL

Most binary parameters known

Questions:

Procedure of greatest efficiency?

Minimum parameters to be fitted?

SYSTEM DEFINITION & PROPERTIES

Comp. No.	Name	Phase	Ion type	Salt type	Other spec.
1	H ₂ O	Vapor / solvent	-		
2	Ampicillin	Liquid / solid	Dipole	Organic	
3	KCl	Solid	-	Inorganic	
4	EtOH	Vapor / solvent	-		
5	H ⁺	Liquid	Cation		
6	OH ⁻	Liquid	Anion		
7	Ampicillin ⁺	Liquid	Cation		
8	Ampicillin ⁻	Liquid	Anion		
9	K ⁺	Liquid	Cation		
10	Cl ⁻	Liquid	Anion		

	Properties name	SLE	Models
Pure Properties	Born radius	*	Data
	Density	*	Racket
	Dielectric constant	*	Correlation
Mixture Properties	Activity coefficient	*	electrolyte NRTL
	Solubility	*	Solubility product

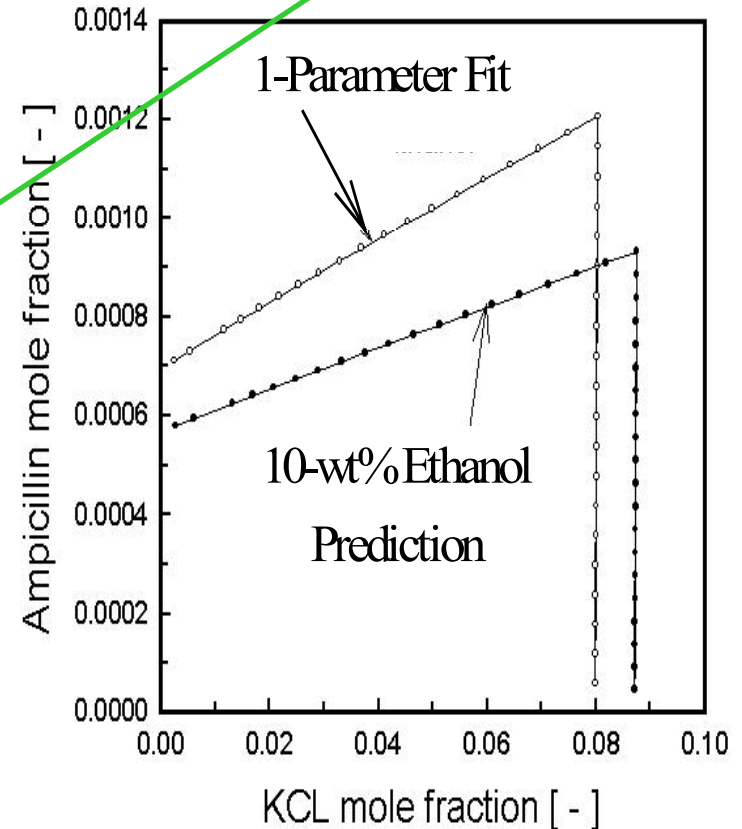
FIT SENSITIVE BINARY PARAMETER(S)

Of 15 parameters in Electrolyte-NRTL H₂O/KCl model,
Ampicillin ternary sensitive to only 1;
Minimizes fitting effort

H ₂ O					
(H, OH)					
(H, Cl)					
(K, OH)					
(K, Cl)					
	H ₂ O	(H, OH)	(H, Cl)	(K, OH)	(K, Cl)

H ₂ O					
(H, OH)					
(H, Cl)					
(K, OH)					
(K, Cl)	*				
	H ₂ O	(H, OH)	(H, Cl)	(K, OH)	(K, Cl)

Fitted



DETERMINATION OF PARAMETER SENSITIVITY

Evaluate sensitivities from

$$\frac{dF}{d\tau_k} = \sum_{j=1}^{N_{EXP}} \frac{dF_j}{d\tau_k} = \sum_{j=1}^{N_{EXP}} \frac{d\left(\sum_{i=1}^{N_p} \left| (p_i^{cal} - p_i^{exp}) / p_i^{exp} \right| \right)_j}{d\tau_k}$$

F = function, p = property value, τ = parameter

Fit only parameters k with large $dF/d\tau_k$

SERVICE DIFFERS FROM ADVICE IN TARGET/KNOWN INFORMATION

Forward Problems (Service Role)

- Select Appropriate Model
- Tune/Re-estimate Model Form/Parameters
- Simplify Model When Possible with Accuracy
- Compute Properties & Derivatives

Automate?

Reverse Problems (Advice Role)

- Select Appropriate Properties & Models
- Estimate Model Parameters
- Compute Properties
- Validate (Data, Theory, Microsimulation)
- Select “Best” System

ISSUES FOR ADVICE MODELS

Must use general models for multiple properties

Data/parameters often unavailable

Unknown accuracy/reliability

Efficiency improved with

Strategy for obtaining information

Experiment/Theory/Microsimulation

On-line model generation/validation

Reliability better via sensitivity-analysis/validation

Some, but not all steps same as service role

MODEL GENERATORS MAY NOT MATCH SERVICE OR ADVICE USER NEEDS

Provide limited testing

Systems – Known substances

Properties – Standard EoS, G^E

Weak Validation – Consistency, limits, multiproperty

Give inefficient formulation

Theoretical basis without computational strategy

Excessive # of parameters

Complex expressions, especially derivatives

Result often correlation with limited prediction

FUTURE PROSPECTS

Properties strategy separate from process simulation?

Advice problem does process once with target
then iteratively finds substances/states

Algorithms for advanced systems need to treat

Simultaneous reactions/mass & heat transfer

Education of generators/users on roles of

Properties & models

Products of model generators

Implementation by model users

CONCLUSIONS

Service & Advice roles exist for properties

Differences in objective, model usage & input

Careful strategies can meet goals to

Maximize productivity

Reduce uncertainty

Elucidate sensitivity

Allow “machines to work & people to think”