Parameter Estimation of BACK Equation of Sate Via Gray-Box Neural Network Models

Ulises I. Bravo-Sánchez[1] *, Florianne Castillo-Borja[1], Ramiro Rico-Martínez[2], and Gustavo A. Iglesias-Silva[2]

[1] Departamento de Ing. Química, Instituto Tecnológico de Aguascalientes, Av. López Mateos 1801 Ote. Aguascalientes, Ags. México. ulisesbs@gmail.com

[2] Departamento de Ing. Química, Instituto Tecnológico de Celaya, Av. A. García Cubas s/n, Celaya, Gto., México

Abstract. Improvement of models for correct estimation of thermodynamic properties have been a topic of many contributions in chemical engineering. In general, parameter estimation is made with a priori formulation of their functionality. In this contribution we adjust model parameters with gray-box models based on neural networks, experimental data and a frame model to be improved. The BACK equation of state (EoS) in used to predict the compressibility factor from Pressure-Volume-Temperature data of n-alkanes. Also, we check the consistency of gray-box models in prediction of properties derived from BACK EoS. The advantage of this approximation is to complement the knowledge of a fundamental model with the capacity of neural networks for pattern recognition. The presence of a frame model guides the optimization of neural networks to find parameters ad-hoc to the model theory.

1 Introduction

Artificial neural networks (ANNs) have been proved to be an excellent tool to recognize data patterns presents, even non linear, in a set of data. However, in systems with many knowledge and research done, use of neural networks can be seen as a forward step in prediction but as a backward step in knowledge. The goal of this contribution is to show a gray-box model formulation based on a deterministic model, neural networks and a set of experimental data to improve the deterministic model. Once the gray-box model formulation has demonstrate a good performance in prediction and has been probed its consistency with fundamental principles, we could use the model with some confidence to extrapolate.

Research in thermo-physical properties of fluids and its modeling has been an area of intensive work. The most successful engineering thermodynamics equations of state are empirical, like Redlich-Wong, Peng-Robinson, Soave and more. In recent years several equation have emerged with a frame work based on fundamental principles. This kind of equations use a better molecular description or information of molecular dynamics. However, simplifications from theory are

* Thanks to: Conacyt SEP-2204-C01-47921

© A. Gelbukh, Á. Kuri (Eds.)
Advances in Artificial Intelligence and Applications
Research in Computer Science 32, 2007, pp. 16–26

Received 18/06/07
Accepted 31/08/07
Final version 22/09/07

made when a model is constructed. Therefore, errors in prediction increased when the model is used in systems different from ones the model has been made. Then, the improvement of prediction of fluid properties still been an active topic in thermodynamics.

In this work, we chose the BACK EoS [6,7] as the frame model to be improved in its parameter functionality. Experimental PVT data for the family of n-alkanes from methane to n-decane are used to predict the compressibility factor (Z). BACK EoS consider two principal deviation effects from ideality, an effect product of repulsive forces and the other from attractive forces. The repulsive term relies in perturbation theory applied to convex bodies and the attractive term comes from an adjusted expansion in series to results of molecular simulation of Argon with a square-well potential. The convex bodies are allowed to have deviation from sphericity by mean of an anisotropy parameter (α), the two remaining parameters are a hard-core-volume related parameter ($\tilde{V}^0$) and the energy potential ($\frac{u^0}{k}$).

Neural networks can be used as a "black box" model. in this kind of model a data vector is feed to the neural net and its parameters are trained to recognize an output data vector. That kind of approximation only assures the best statistical set of neural network parameters to this task without insights of relationships more than existent theory. Extrapolate these models can not be successful at all and just serve to predict the properties of compounds used in training. On the contraries, a "gray-box" model uses the theory existent and just try to complement those fails, therefore the model can be more general. A strategy is necessary to achieve this goal. An iterative procedure is applied to make a diagnosis on which set of variables is the best candidate to drive the modeling without degenerate the frame model (BACK EoS). In the next sections, we present the BACK EoS and the details of the gray-box formulation and finally discussion and concluding remarks.

2 Equation of State Back

Among the vast number of equation of state, in recent years some EoS are emerged with a better fundamental description of fluids with its respective increase on complexity like BACK, PHCST, SAFT, PC-SAFT. The BACK EoS is not excessively complex and is oriented to alkanes; with its original parameters shows good agreement with experimental data until n-butane, and the average deviation increase as the number of carbons increase. Also, deviation from compressibility factor grows with density, that is a common fail in many EoS because are constructed around deviation from ideal gas ($\tilde{V} \rightarrow \infty$), so for specific volumes of liquid the errors are big.

Then, we have two facts that lead us to implement our strategy based on neural networks to improve the parameter estimation of an EoS previously constructed. The BACK as any EoS needs of temperature and specific volume besides its characteristics parameters to calculate the compressibility factor. The

BACK equation[6,7] is an augmented van der Waals EoS of the form:

$$\frac{PV}{RT} = Z = Z^h + Z^a \tag{1}$$

For the repulsive term (Z^h), the equation of Boublik is used:

$$Z^h = \frac{1 + (3\alpha - 2)\xi + (3\alpha^2 - 3\alpha + 1)\xi^2 - \alpha^2\xi^3}{(1-\xi)^3} \tag{2}$$

where α is the anisotropy parameter and ξ is the density of the fluid given by:

$$\xi = 0.74048\frac{\tilde{V}^0}{\tilde{V}} \tag{3}$$

Here $\tilde{V}$ is the specific volume and $\tilde{V}^0$ the molecular hard core volume. The Boublik equation is the result from apply perturbation theory on a fluid with molecules as convex bodies. For the attractive term (Z^a) we use the equation derived by Alder ([14]):

$$Z^a = \sum_{N=1}^{4}\sum_{M=1}^{9} MD_{NM}\left(\frac{u}{kT}\right)^N\left(\frac{\tilde{V}^0}{\tilde{V}}\right)^M \tag{4}$$

where T is the temperature, $(\frac{u}{k})$ is the potential energy and D_{NM} are universal constants.

3 Neural Network Gray-Box Models

The central part of succeed on this parameter estimation approach has to do with the use of the so called gray-box. Our definition of gray-box model involves a deterministic model and one or more neural networks, the topology or connectivity between those elements is defined by the purpose of correction. Once the topology is defined, we construct several gray-box models starting from a model with "minimal knowledge". That means we use the information available in data without take into account the model theory. Therefore, after training the model evolves incorporating information from theory and from observed of analysis to the model itself, to be trained again until the goal is reached.

The kind of neural networks used are feedforward with four layers, also knows as backpropagation neural networks. Each neuron, in feedforward networks, is connected with all the neurons in the previous layer via a weighted connection, which only pass information to all neurons in the next layer, avoiding lateral or recurrent connections. Also each neuron has a bias parameter that contribute to the neuron output. The problem to solve is to find the weights and bias of the neural networks. They are found by solving a least-squares problem using conjugate gradient techniques. Such ANN architecture is the most common and its configuration and training (solution of the least-squares problem) have been described in detail elsewhere (e.g. [15]). The input layer just drives the PVT information to the neural network, two hidden layers functions as the non-linear part of the model and the output layer computes the predicted variables. In our case, the parameter(s) to be included in the fundamental model.

The models based on neural networks and a set of experimental data assures the patter recognition between the input-output vectors [19], but if we do not have an additional strategy then we can not extract relevant information of the system. On the contraries, a "gray-box" model uses the theory existent and just try to complement those fails, therefore the model can be extrapolated with more confidence. A strategy is necessary to achieve this goal. An iterative procedure is applied to make a diagnosis on which set of variables is the best candidate to drive the modeling without degenerate the frame model (BACK EoS).

The scheme of the first gray-box model (named ANN1 for short) is showed in Figure 1. The topology with three neural networks obey to avoid cross interaction among the selected dependency of each EoS parameters and the inputs to the nets. As mentioned previously, first we use information without consider the basis of BACK EoS, therefore in this model we use temperature, specific volume and the number of carbons as independent variables. One neural network uses the number of carbons to recognize the anisotropy factor, because this parameter is only function of molecular geometry and it is considered independent of temperature. In BACK's formulation, $\tilde{V}^0$ is considered temperature dependent, however in this model we use density as input information to the second ANN and finally for $\frac{u}{k}$ parameter the temperature is the independent variable. This

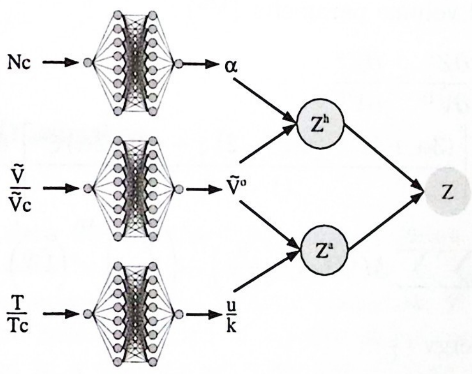

Fig. 1. Scheme of the first gray-box model, ANN1.

model was trained with data of methane, ethane and n-decane to observe if the corrections are consistent for all data. The model is training upon convergence on compressibility factor prediction (Z). The training is via minimization of the square error between the experimental compressibility factor and predicted (energy function, E):

$$E = \sum_{np} \frac{1}{2}(Z_{exp}^{np} - Z_{pred}^{np})^2 \tag{5}$$

where np indexes the training vectors. The neural networks used have one neuron in the input layer (PVT information), one neuron in the output layer (BACK EoS parameter) and eight neurons in each hidden layer. The speed, final value of energy function and values of the final set of weights and thresholds are not as relevant as the values and behavior of the parameters of BACK EoS from the outputs neurons. The training is achieved using the *backpropagation rules*. Such rules are straightforwardly obtained using the chain rule to calculate the derivative of the energy measure with respect to the ANN parameters. For the first model, the derivatives of the energy function with respect of the neural networks parameters ($\boldsymbol{W}$ and $\boldsymbol{\theta}$) required for the backpropagation of the errors, have the general form:

$$\frac{dE}{dW} = -(Z_{exp} - Z_{pred}) \left(\frac{dZ}{dP} * \frac{dP}{dW} \right) \tag{6}$$

where P stands as an EoS parameter. The first part of the derivative $\frac{dZ}{dP}$ can be explicitly calculated from the BACK equation formulation and the second, $\frac{dP}{dW}$, is simply the derivative of one of the network outputs with respect to one of the network parameters. The derivative of compressibility factor with respect of the anisotropy parameter (α) is:

$$\frac{\partial Z}{\partial \alpha} = \frac{3\xi + (6\alpha - 3)\,\xi^2 - 2\alpha\xi^3}{(1 - \xi)^3} \tag{7}$$

For the close-packed volume parameter ($\tilde{V^0}$) :

$$\begin{aligned} \frac{\partial Z}{\partial \tilde{V^0}} &= \frac{\partial Z^h}{\partial \tilde{V^0}} + \frac{\partial Z^a}{\partial \tilde{V^0}} \\ \frac{\partial Z^h}{\partial \tilde{V^0}} &= \left[\frac{(3\alpha + 1) + (6\alpha^2 - 2)\,\xi + (1 - 3\alpha)\,\xi^2}{(1 - \xi)^4} \right] \frac{0.74078}{\tilde{V}} \\ \frac{\partial Z^a}{\partial \tilde{V^0}} &= \sum_N^4 \sum_M^9 M^2 D_{NM} \left(\frac{u}{kT} \right)^N \left(\frac{\tilde{V^0}}{\tilde{V}} \right)^M \left(\tilde{V^0} \right)^{-1} \end{aligned} \tag{8}$$

For the potential energy ($\frac{u}{k}$):

$$\frac{\partial Z}{\partial (\frac{u}{k})} = \sum_N^4 \sum_M^9 MND_{NM} \left(\frac{u}{kT} \right)^N \left(\frac{u}{k} \right)^{-1} \left(\frac{\tilde{V^0}}{\tilde{V}} \right)^M \tag{9}$$

A similar procedure is used for the remaining gray-box models. The second model presented in Figure 2, named ANN2, takes into account more information of BACK theory. We known that both parameters, V^0 and u/k, are function of temperature. Finally, in Table 1 we present the full range of conditions of experimental data used in training and cross validation.

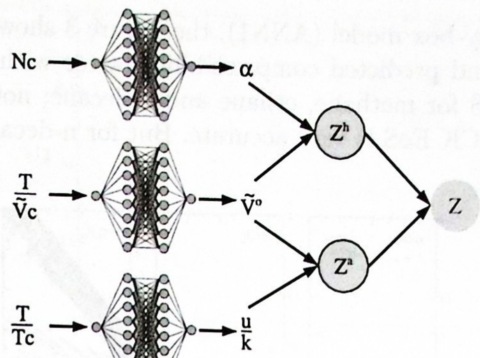

Fig. 2. Scheme of the second gray-box model, ANN2.

	T K	P bar	ρ $\frac{mol}{cm^3} \times 10^3$
CH_4	119.4 – 423.15	16.3 – 291.7	0.0239 – 35
C_2H_6	248.15 – 473.15	11.7 – 410.2	0.0313 – 16
C_3H_8	285.9 – 510.93	1.01 – 689	0.0240 – 13
C_4H_{10}	294.26 – 394.26	1.01 – 8.61	0.0102 – 3
C_5H_{12}	298.15 – 573.15	1.37 – 741	0.0240 – 9.72
C_7H_{16}	285.25 – 313.15	19.3 – 784	0.0670 – 7.95
C_8H_{18}	298.15 – 548	20.2 – 982	0.0352 – 7.48
$C_{10}H_{22}$	294 – 673	15.2 – 1500	0.95 – 4.8

Table 1. Range of pressure, density and temperature for the experimental database [16].

4 Results and Discussion

A set of 2000 PVT data from methane to n-decane, taken from [16], was the database used. All data belongs to one phase (gas or liquid) of pure compounds. Table 1 summarizes the experimental conditions of data. The data are distributed above and below the critical conditions for each compound. This database was divided in a training set with 80% of each compound set and the rest for cross validation. Every gray-box model was trained five times with random initial condition to validate the model. The results showed are representative of these trainings, the goal is the behavior observed not the final values of neural networks parameters or the number of conjugated gradient iterations needed to reach the final error. Even when the parameters of EoS are molecular properties and are knowns for some molecules, in common practice are considered as empirical parameters from a statistical fit of experimental data. Then, the fitting procedure absorbs the errors of model by idealities or simplifications.

For the first gray-box model (ANN1), the Figure 3 shows the comparison of the experimental and predicted compressibility factor with the model and the original BACK EoS for methane, ethane and n-decane; note that for methane and ethane the BACK EoS is very accurate. But for n-decane, were the predic-

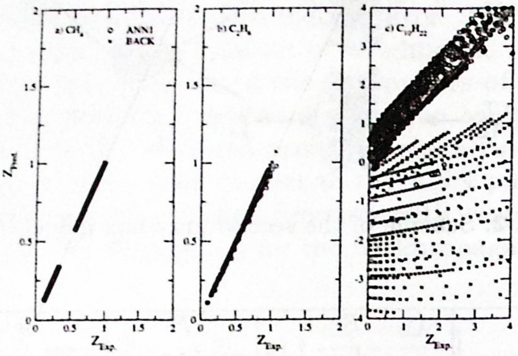

Fig. 3. Comparison of the experimental and predicted compressibility factor with the ANN1 gray-box model (∘) and the original BACK EoS (×) for a) methane, b)ethane and c) n-decane.

tions are extremely worse, with almost every data, the predictions are improved significantly by the addition of neural networks. However, the analysis of the parameters obtained at the outputs of the neural networks is the indicator of succeed for the gray-box model. The anisotropy parameter (α) in Table 2 shows a value below but near unit for methane as was imposed in the original fitting. For ethane, when trained with one isotherm as methane, the α values are greater

	T, K	α_{ANN1}	α_{BACK}
CH_4	180	0.98690	1.0000
C_2H_6	273	0.99579	1.0370
	298	1.04466	
	323	1.02646	
	273, 298, 323	0.97474	
$C_{10}H_{22}$	294, 523, 653	3.29909	1.13490

Table 2. Predicted anisotropy parameter for several training sets with ANN1 gray-box model.

than α for methane; finally for n-decane the α value is too large to the "physical" meaning of the parameter. The close-packed volume parameter ($\tilde{V}^0$), as showed in Figure 4, behaves independent of temperature as the ANN1 model was constructed. all predictions converge to one function in density. However, the search

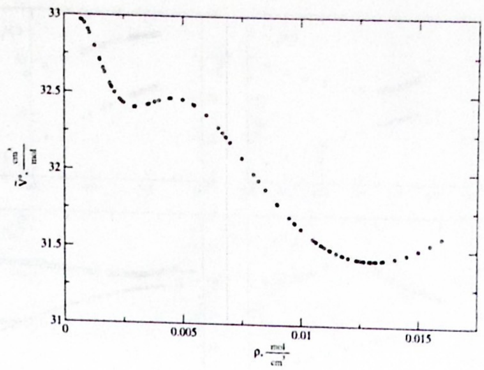

Fig. 4. Packed volume of convex bodies with the gray-box model ANN1 for ethane.

of a function to represent this behavior seems not to be a viable option. That observation comes from the frame of BACK EoS. if we add the density (volume) in the calculus of the close-packed volume parameter that implies a change in the structure of BACK EoS which can degenerate the calculus of another properties derived, such as entropy or enthalpy. For the potential energy ($\frac{u}{k}$) the behavior is smooth and similar to proposed in theory as function of temperature. For the second gray-box model (ANN2), a change in dependency of the second neural network in ANN1 model is made. then we get the ANN2 model. After training, the anisotropy parameter (Table 3) is consistent with the *principle of congruence* which increase its value as the number of carbons increase. However. is to note the high value for α of n-decane which is reflected in the behavior of the two remaining parameters. The close-packed volume parameter ($\tilde{V}^0$), as showed in

	α_{ANN2}	α_{BACK}
C_2H_6	0.9992124	1.037
C_3H_8	1.0164985	1.041
C_5H_{12}	1.0348073	1.0566
$C_{10}H_{22}$	6.128722	1.1349

Table 3. Predicted anisotropy parameter for ANN2 gray-box model.

Figure 5. behaves consistent from methane and n-propane with a tendency to decrease with temperature. From n-pentane the dependency from temperature shows a maxima and for n-decane we found negative values which are "physically" inconsistent. Also, for the potential energy ($\frac{u}{k}$) the behavior is consistent from methane and n-propane. for n-pentane some irregularities are presented and for n-decane, positive values are found but the dependence with temperature is inverted with respect BACK EoS theory. Finally we present, as a consistency test of the ANN2 gray-box model, the calculus of the vapor pressure from BACK

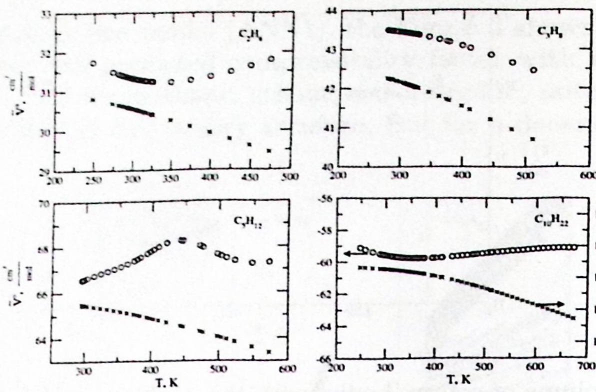

Fig. 5. Comparison of the packed volume of convex bodies with the ANN2 gray-box model (o) and the original BACK EoS (×) for ethane, propane, n-pentane and n-decane.

EoS with the Maxwell's rule of equal areas. This method implies that:

$$P(\tilde{V}^{vap} - \tilde{V}^{liq}) = \int_{\tilde{V}_{liq}}^{\tilde{V}_{vap}} P_{BACK} d\tilde{V} \qquad (10)$$

In Figure 7 we show the agreement of the ANN2 gray-box model to predict the vapor pressure, with some discrepancies for n-decane. Note, the tendency is captured by the model but as the number of carbons increased the errors grows too.

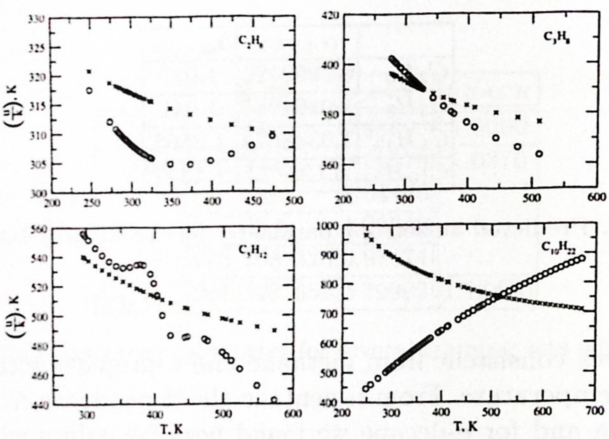

Fig. 6. Comparison of the potential energy with the ANN2 gray-box model (o) and the original BACK EoS (×) for ethane, propane, n-pentane and n-decane.

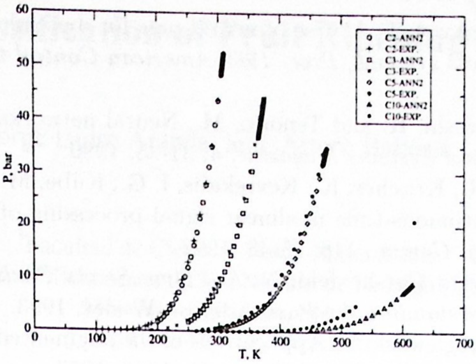

Fig. 7. Comparison of vapor pressure predicted with ANN2 model and experimental data.

5 Summary and Conclusions

We had shown an extended application of gray-box neural network in diagnosis and improvement of BACK EoS prediction of compressibility factor and some insight in its availability to predict derived properties. The strategy followed shows how discriminate a viable set of system variables to fit the parameters of BACK EoS. Additional effort is necessary to substitute the neural(s) network(s) with an empirical compact form that fits the neural networks behavior. This could leads to a better deterministic model with some empirical corrections derived from "what the models needs not what we want to add". However, some issues of this approach has to be mentioned. The optimization of the model is unconstrained and some rigid assumptions of model parameters can not been assured from the beginning. In fact, the three parameters must be always positive and in our approach that condition was suggested to follow by means of scaling the inputs and outputs in some expected range of values. Currently, we are conducting several related and complementary efforts. We are working in refining the models here presented with some insights of improvement. Also, we are looking into the formulation of corrections for more complex equations of state like SAFT for associating compounds (alcohols), where four parameters are needed by the equation. Also, adding constraints in this kind of gray-box models because many physical systems are subjects to constraints.

Acknowledgements

This work has been partially funded by the Mexican Ministry of Public Education(CONACyT: Conacyt SEP-2204-C01-47921 and DGEST).

References

1. A. Bulsari (ed.), *Neural Networks for Chemical Engineers*, Elsevier Science B. V. (1995).

2. Bhat, N. and McAvoy, T. J., Use of neural nets for dynamic modeling and control of chemical process systems, *Proc. 1989 American Control Conference*, 1342-1347, 1989.
3. Chu S. R., Shoureshi, R. and Tenorio, M., Neural networks for system identification, *IEEE Control Systems Magazine*, 4, 31-35, 1990.
4. Rico-Martínez, R., Krischer, K., Kevrekidis, I. G., Kube, M. C. and Hudson, J. L., Discrete- vs. continuous-time nonlinear signal processing of Cu electrodissolution data, *Chem. Eng. Comm.*, 118, 25-48, 1992.
5. Weigend, A. S. and Gershenfeld, N. A., *Time Series Prediction: Forecasting the Future and Understanding the Past*, Addison-Wesley, 1993.
6. Chen, S.S and Kreglewski, A., Applications of the augmented van der Waals theory of fluids, *Ber. Bunsenges. Phys. Chem.*, 81, 1048, 1977.
7. Kreglewski, A., *Equilibrium Properties of Fluids and Fluid Mixtures*, Texas A&M University Press, College Station, Texas, 1984.
8. Normandin A., Grandjean, B. P. A. and Thibault, J., PVT data analysis using neural network models, *Ind. Eng. Chem. Res*, 32, 970-975, 1993.
9. Habiballah W. A., Startzman R. and Barrufet, M. A., Use of neural networks for prediction of vapor-liquid equilibrium K-values for light hydrocarbon mixtures", *SPE Reservoir Engineering*, 121-126, 1996.
10. Sharma, R., Singhal, D., Ghosh, R. and Dwivedi A., Potential applications of artificial neural networks to thermodynamics: vapor-liquid equilibrium predictions, *Comput. Chem. Engng.*, 23, 385-390, 1999.
11. Psichogios D. C. and Ungar, L. H., A hybrid neural network-first principles approach to process modeling, *AIChE J.*, 38, 1499-1511, 1992.
12. Rico-Martínez, R., Anderson, J. S. and Kevrekidis, I. G., Continuous-time Nonlinear Signal Processing: A Neural Network Based Approach for Gray Box Identification, *Proceedings of the 1994 IEEE Workshop on Neural Networks for Signal Processing*, IEEE Publications, 596-605, 1994.
13. Petersen, R., Fredenslund, A. E. and Rasmussen, P., Artificial neural networks as a predictive tool for vapor-liquid equilibrium, *Comput. Chem. Engng.*, 18, S63-S67, 1994.
14. Alder B.J., Young D.A., and Mark M.A., *J. Chem. Phys.*, 56, 3013, 1972.
15. Lapedes, A.S., and Farber, R., Nonlinear signal processing using neural networks: Prediction and system modeling, *Los Alamos Report* **LA-UR 87-2662**, 1987.
16. GERG Technical Monograph, *The GERG databank of high accuracy compressibility factor measurements*, Technical Monograph No. 4, 1990.
17. Simnick, J.J., Lin, H. M. and Chu, C. K., The BACK equation of state and phase equilibria in pure fluids and mixtures, *Equations of State in Engineering and Research*, Advances in chemistry Series, American Chemical Society, 182, 209-233, 1979.
18. Avlonitis, D., Danesh, A., and Todd, A.C., Prediction of VL and VLL equilibria mixtures containing petroleum reservoir fluids and methanol with a cubic EoS, *Fluid Phase Equilibria*, 94, 181-215, 1994.
19. Cybenko, G., Approximation by superpositions of a Sigmoidal Function, *Mathematics of Control, Signals and Systems*, 2, 303-314, 1989.