

Consistency in the prediction of derived properties from cubic equations of state improved through hybrid models of neural networks

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This paper shows how the use of hybrid models (or gray box) based on equations of state and neural networks can be consistent in predicting derived properties of fluids like enthalpy, internal energy, entropy, Gibbs energy. That can be achieved through neural network functionality on the parameters of the equations. A hybrid model combines a rigorous and well-known model with an empirical and/or adaptable model. These hybrid models are formulated to solve a multivariate optimization of the PVT behavior for the alkane series, from methane to n-octane, in recognition of the compressibility factor. The temperature dependence of b parameter improves the liquid description. The derived properties show the appropriate behavior only shifted in density and temperature without losing the structure of the equation of state.

Introduction

The use of artificial neural networks (ANN) in chemical engineering has been very popular because they allow recognize systems highly nonlinear and multivariate, this is useful when the knowledge of the system is null or the problem is too complex for modelling with fundamental principles (Kahrs and Marquardt, 2008). Neural networks generally are used as classifiers or as predictive model without any associated model than the network itself (Sharma et al., 1999). Therefore a model based on neural networks is considered universal if a complete database is considered to assure the whole system is recognized. Many models based on neural networks are reported with optimal configuration. Therefore in the literature are models of neural networks with optimal structure for the case study, the variables reported besides the input and output variables are the number of neurons in each layer and the value of the connections between them. We have used hybrid neural network models with theoretical equations of state (EoS) like SAFT and BACK (Bravo et al., 2002). However, the use of simpler equations like cubic equation of state remains in common use. The motivation of the hybrid models based on neural networks is to take advantage of the knowledge of the

system reflected in the structure of the equation of state and use neural networks to overcome its limitations.

Methodology

Cubic equations of state, starting with the van der Waals equation, contain two parameters (a and b), where the parameter a is a measure of the forces of attraction between molecules and b is a measure of the effective size of the molecule. Usually these parameters are related to the critical properties of substances. We present only results for van der Waals and SRK equations (Table 1) for being, the first equation simpler and less accurate and the second because of its greater use.

Table 1. Expressions for van der Waals and Soave-Redlich-Kwong equations of state.

Cubic EoS	a	b
vdW $Z = \frac{1}{1-b\rho} - \frac{a\rho}{RT}$	$a = \frac{27}{64} \frac{(RT_c)^2}{P_c}$	$b = \frac{1}{8} \frac{RT_c}{P_c}$
SRK $Z = \frac{1}{1-b\rho} - \frac{a\rho}{RT(1+b\rho)}$	$a(T) = 0.42748 \frac{R^2 T_c^2}{P_c} \varphi_r^2$ $\varphi_r = \left[1 + \varphi \left(1 - \sqrt{T_r} \right) \right]$ $\varphi = 0.48 + 1.574\omega - 0.176\omega^2$	$b = 0.08664 \frac{RT_c}{P_c}$

1.1 Derived properties

A residual property is a property expressed relative to its ideal gas value at the same temperature and pressure. Where M is every molar property of the system and g^i denotes ideal gas.

$$M^R \equiv M(T, \rho) - M^{gi}(T_{ref}, \rho^{gi}) \quad (1)$$

Table 2. Derived properties based on compressibility factor transformations.

Residual property	Expression
Internal Energy	$\frac{U^r}{RT} = -T \int_0^\rho \left(\frac{\partial Z}{\partial T} \right)_\rho \frac{d\rho}{\rho}$
Enthalpy	$\frac{H^r}{RT} = Z - 1 + \frac{U^r}{RT}$
Entropy	$\frac{S^r}{R} = -T \int_0^\rho \left(\frac{\partial Z}{\partial T} \right)_\rho \frac{d\rho}{\rho} - \int_0^\rho (Z-1) \frac{d\rho}{\rho} + \ln(Z)$
Gibbs free energy	$\frac{G^r}{RT} = \int_0^\rho (Z-1) \frac{d\rho}{\rho} + Z - 1 - \ln(Z)$
Helmholtz free energy	$\frac{A^r}{RT} = \int_0^\rho (Z-1) \frac{d\rho}{\rho} - \ln(Z)$

1.2 Neural networks

A neural network model is composed of processing units called neurons, which are distributed in layers and a connectivity pattern determined by the type of neural network. The neural network training is based on minimizing an energy function, which is the square error between experimental and predicted variables for a set of input-output data (Equation 2). More details on neural network fundamentals can be found elsewhere (van der Smagt P. P., 1993).

$$E = \min \frac{1}{2} \sum_{i=1}^{np} [Z_i^{Exp} - Z_i^{ANN}]^2 \quad (2)$$

1.3 Hybrid or gray-box models

A gray box model consists of a rigorous model that provides the framework for the description of the system and an empirical model that adjusts the parts that are not considered in the rigorous model (Bravo et al., 2002; Simon et al., 2006; Kahrs and Marquardt, 2008). In this paper, the gray box models consist of an equation of state and one or more neural networks. The neural networks are designed to predict the parameters a and b of the equation in the output layer with Temperature and Carbon number in the alkane molecule as inputs to the networks. These parameters are needed, in addition to temperature and density, to predict the compressibility factor $Z(T,r;a,b)$. The training of the gray box model is based on learning the Z behavior for the database presented. The advantage of hybrid models on the empirical models is their ability to apply interpolation and extrapolation, and the possible generality that can be obtained from the correlation of the parameters obtained by neural networks. Several gray box models were trained with different configuration of the number of neurons in the intermediate layers and the output layer parameters (a , b) of the equation of state. The number of neurons in the intermediate layers was varied based on experience among 8, 10 and 12. Each model was trained at least three times with various seeds for the random number generator to initialize the values of the weights and thresholds of neural networks.

Results

The hybrid models are developed to minimize the compressibility factor predicted by the cubic equation of state through recognition by the neural network of the parameters a and b of the equation, depending on the variables provided in the input layer.

Figure 1 shows the correlation among the experimental data with the prediction of van der Waals equation of state and by ANN-vdW hybrid model. There is a considerable improvement in prediction with the hybrid model. The interesting on implementing hybrid models is the analysis of the functionality for the parameters from neural networks and also to observe the consistency of the hybrid models in predicting the derived properties.

Figure 2 shows the comparison between the parameters defined in Table 1 for vdW EoS and those obtained by ANN-vdW model as function of temperature for each one of the alkanes. There can be seen that the parameter a has a tendency to grow with the number

of carbon and decrease with temperature, this feature is similar to that used in other cubic equation of state. Furthermore, the parameter b defined constant in the vdW EoS has a decreasing dependency on temperature and increasing with the number of carbons on molecule. This variation of the parameter b shifts the uncertainty of the vdW EoS and allows predict with more precision the liquid region.

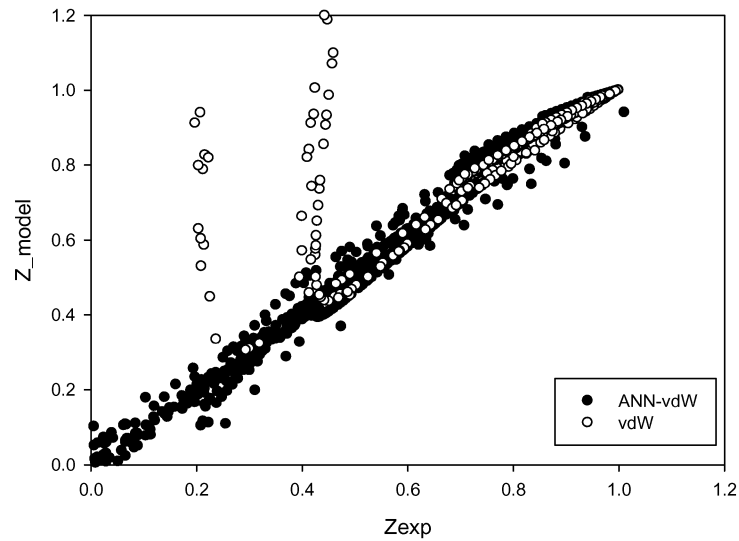


Figure 1. Correlation among the experimental compressibility factor and calculated with EoS-vdW and ANN-vdW.

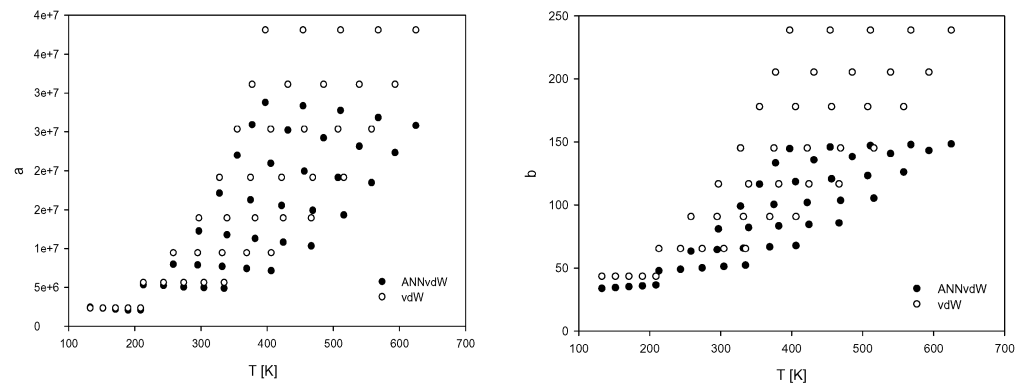


Figure 2. Parameters a y b from ANN-vdW hybrid model and vdW EoS.

For ANN-SRK hybrid model, the corrections on Z and a and b parameters are not as drastic as for the vdW EoS. Now, with the trained neural networks and the proper

transformation of the EoS, the derived properties are calculated (see Table 2). Residual enthalpy is important in energetic calculus; in Figure 3 the prediction with the four models is presented for an isotherm of propane. At low densities, the predictions for all models are equivalent (gas region) and it is clear that vdW EoS has a short range in density that is extended in the ANN-vdW model; for the SRK EoS both models are similar. Figure 4 shows the Gibbs energy for n-heptane, again the vdW EoS is limited in liquid region and both ANN hybrid models tend to correct these region.

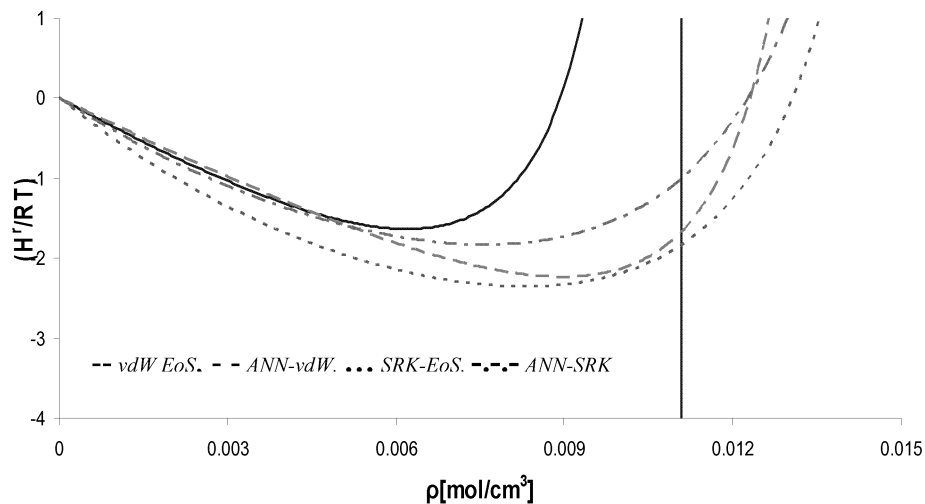


Figure 3. Residual enthalpy from vdW-EoS, ANN-vdW, SRK EoS and ANN-SRK models for propane at 481 K.

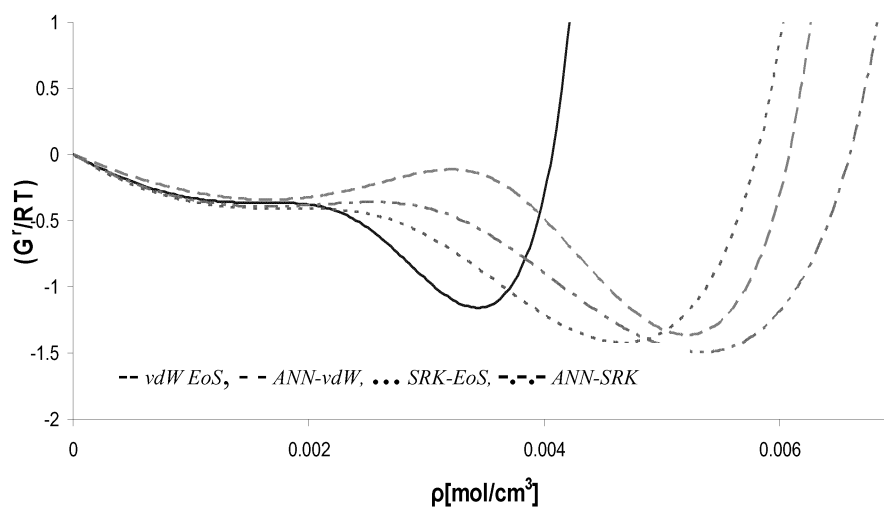


Figure 4. Residual Gibbs energy from vdW-EoS, ANN-vdW, SRK EoS and ANN-SRK models for n-heptane at 540 K.

Conclusions

The hybrid models based on artificial neural networks and cubic equations of state shows consistency for the calculus of derived properties. The structure of the EoS is not altered by the calculus of parameters via neural networks. The ANN behavior for a and b parameters are smooth functions and can be correlated in compact functions to replace the neural network from the model. Therefore, the hybrid models can be seen as alternative to improve fundamental models.

References

- Bravo-Sánchez U. I., Rico-Martínez R., Iglesias-Silva G. A., 2002, Improvement of the Empiricism in the BACK Equation of State via Hybrid Neural Networks, Ind. Eng. Chem. Res. (41), 3705-3713.
- Chouai A., Laugier S. Richon D., 2002, Modeling of thermodynamic properties using neural networks Application to refrigerants, Fluid Phase Equilibria. 199, 53-62.
- Kahrs O., Marquardt W., 2008, Incremental identification of hybrid process models, Comput. & Chem. Eng. (32), 694-705.
- Sharma, R., Singhal, D., Ghosh, R., Dwivedi, A., 1999, Potential applications of artificial neural networks to thermodynamics: vapor-liquid equilibrium predictions, Comput. & Chem. Eng. (23), 385–390.
- Schmitz J. E., Zemp R. J., Mendes M. J., 2006, Artificial neural networks for the solution of the phase stability problem, Fluid Phase Equilibria. (245), 83-87.
- Simon L. L., Fischer U., Hungerbühler K., 2006, Modeling of a Three-Phase Industrial Batch Reactor Using a Hybrid First-Principles Neural Networks Model, Ind. Eng. Chem. Res. (45), 7336-7343.
- van der Smagt P. P., 1993, Minimisation methods for training feedforward neural networks, Neural Networks. (7), 1-11.