INFERENCE OF MIXING RULES FOR THERMODYNAMIC EQUATIONS OF STATE USING NEURAL NETWORKS

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***Abstract*— The Artificial Neural Networks (ANNs) have proven to be a valuable tool for many applications. For modeling, the ANNs can be used to extract *ad-hoc* models that substitute for the lack of a first-principles formulation. The ANN is expected to capture the underlying characteristics of the system and thus can be used to predict, for example, the evolution of the dynamical response of a system. In this contribution we illustrate the use of ANNs for the construction of "gray-box" models: The purpose is not to replace the need for a fundamental model, but rather complement it. The illustration is based in the ANN-inference of mixing rules for a thermodynamic equation of state (EOS). The application of the ANNs within the framework of an EOS substantially increases the potential for applications allowing the estimation of thermodynamic properties different that the ones used for the training of the ANN.**

***Keywords*— Neural Networks, Gray-box, Thermodynamic Equations of State.**

I. INTRODUCTION

Over the last couple of decades the artificial neural networks (ANNs) have proven to be a valuable tool for many applications, such as system identification, fuzzy control, etc. For many of these applications, the ANNs are used to extract *ad-hoc* models that substitute for the absence of a fundamental model (Bhat and McAvoy, 1989; Chu *et al.*, 1990; Rico-Martínez *et al.*, 1992; Weigend and Gershenfeld, 1993). The justification for this approach may be born in the lack of a complete understanding of the phenomena, thus hindering our abilities to formulate such fundamental model. Under these circumstances the neural network methodologies may be used as the basis to gain a better understanding of the phenomena under study. Along this direction, in this contribution we present an ANN gray-box approach for the inference of mixing rules of thermodynamic equations of state (EOS).

Since the early 1970's, there is increasing awareness in the Chemical Process Industries for the efficient use of costly feed-stocks and the elimination of waste. This has lead to the implementation of complicated optimization programs that often require of accurate and extensive knowledge of thermodynamical properties over a wide range of operating conditions. For many systems of interest, accurate predictions of thermodynamical properties of mixtures are not available. ANNs have been successfully used in some instances to construct *empirical* EOS (Normandin *et al.*, 1993; Habiballah *et al.*, 1996). These empirical EOS can be used to predict thermodynamic properties, but their abilities to extrapolate outside the range of the training data used for its construction is limited. Furthermore, the empirical EOS can only be used for the estimation of the property for which they were trained (e.g. estimation of equilibrium constants or compressibility factors), thus greatly limiting their application.

In recent years, several fundamental EOS have been proposed to describe thermodynamic properties of pure fluids with excellent results. However, many of these EOS fail to have similar success when applied to mixtures, thus hindering their application for plant optimization purposes. One of the reasons for the lack of success of the EOS for mixtures is the use of tentative or simplified set of mixing rules. The formulation of such mixing rules can be complicated and is often based on empirical fits or previously derived results for simpler EOS (Hall *et al.*, 1993; Luengo-Ortiz and Starling, 1997).

Here we illustrate how ANN methodologies can be used to improve the predictive capabilities of EOS by inferring "empirical" mixing rules. Our example makes use of the BACK EOS, which has shown excellent predictive properties for pure fluids, and reasonable predictive properties for mixtures based on a somewhat empirical set of mixing rules. In the procedure, the BACK equation for pure fluids is coupled with an ANN that is trained to infer the *best statistical fit* of the mixing rules, using experimental data from binary mixtures for training. The resulting "gray"-model can be used to estimate other ther-