

A New Nonrandom Lattice Fluid Model and Its Simplification by Two-Liquid Theory for Phase Equilibria of Complex Mixtures¹

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A new rigorous equation of state (EOS) and its simplified version have been proposed by the present authors based on the full Guggenheim combinatorics of the nonrandom lattice hole theory. The simplified EOS, with the introduction of the concept of local composition, becomes similar to the density-dependent UNIQUAC model. However, in the present approach we have a volumetric EOS instead of the excess Gibbs function. Both EOSs were tested for their applicability in correlating the phase equilibria behavior of pure components and complex mixtures. Comparison of both models with experiment includes such systems as nonpolar/nonpolar, nonpolar/polar, and polar/polar hydrocarbons, supercritical systems, and polymer solutions. With two parameters for each pure component and one binary interaction energy parameter, results obtained to date demonstrate that both formulations are quantitatively applicable to complex systems over a wide range of temperatures, pressures, and concentrations.

KEY WORDS: complex mixtures; equation of state; multiphase equilibria; nonrandom lattice theory; polymer solutions; supercritical fluids.

1. INTRODUCTION

Various formulations of thermodynamic theories of solutions can be developed from the framework of the generalized Guggenheim combinatorics

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of lattice statistical mechanics [1, 2]. Indeed, several practical models have originated in this way. The excess function models, such as Flory–Huggins [3, 4], UNIQUAC [5], and various extended versions of these models are based on the rigid lattice description. From a lattice fluid model with holes, a volumetric equation of state (EOS) can be developed. After the work of by Sanchez and Lacombe [6, 7], several EOS-type models have been proposed [8–12]. Recently the present authors have proposed a new approximation to the Guggenheim’s combinatorics and a new rigorous EOS (R-EOS) [13–15]. While maintaining the accuracy of this EOS, we also formulated a simplified EOS (S-EOS) version which is more flexible for use in engineering practice [16]. In this work we present a comparison of the usefulness of both EOSs for the quantitative description of various types of multiphase equilibria for molecularly complex systems.

2. A NEW ELEMENTARY HELMHOLTZ FREE ENERGY

As we have discussed elsewhere [13–16], the configurational part of the nonrandom lattice hole partition function based on the full Guggenheim combinatorics can be written as

$$\Omega^c = g_R g_{NR} \exp(-\beta U) \quad (1)$$

where g_R denotes the random contribution of the Guggenheim combinatorial term and g_{NR} the nonrandom contribution. The potential energy U is equal to $\sum N_{ii}(-\varepsilon_{ii}) + \sum\sum N_{ij}(-\varepsilon_{ij})$. Here ε_{ij} is the absolute value of the interaction energy between molecular segments i and j . When the lattice interchange energy $\Delta\varepsilon_{ij}$ is defined as $\varepsilon_{ii} + \varepsilon_{jj} - 2\varepsilon_{ij}$, the nonrandomness factor, Γ_{ij} is given by $\Gamma_{ij}^2 = \Gamma_{ii}\Gamma_{jj} \exp(-\beta \Delta\varepsilon_{ij})$. An “athermal solution” corresponds to taking $U=0$, and for this solution the nonrandomness factor Γ_{ij} is 1, or $N_{ij}^0 = N_{ij}$. Then the configurational Helmholtz free energy, A^c may be obtained from the relation $\beta A^c = -\ln \Omega^c$ using Eq. (1).

As we discussed elsewhere [13], a new configurational Helmholtz energy based on the full Guggenheim combinatorial term can be derived by expanding A^c around the reference athermal solution in terms of ε_{ij} . The resulting expression of A^c is given by

$$A^c = A^c + \sum_{i \geq j} \sum \left(\frac{\partial A^c}{\partial \varepsilon_{ij}} \right)^0 \varepsilon_{ij} + \left(\frac{1}{2} \right) \sum_{i \geq j} \sum_{k \geq l} \sum \sum \left(\frac{\partial^2 A^c}{\partial \varepsilon_{kl} \partial \varepsilon_{ij}} \right)^0 \varepsilon_{ij} \varepsilon_{kl} \quad (2)$$

When the algebra is done, the following generalized rigorous expression of A^c for multicomponent systems can be obtained from Eq. (2):

$$\beta A^c = \sum N_i \ln \rho_i + N_0 \ln(1 - \rho) - \frac{z}{2} N_q \ln \left[1 + \left(\frac{q_M}{r_M} - 1 \right) \rho \right] - \left(\frac{zN_q}{2} \right) \beta \times \left[\sum \sum \theta_i \theta_j \varepsilon_{ij} + \left(\frac{\beta}{2} \right) \sum \sum \sum \sum \theta_i \theta_j \theta_k \theta_l \varepsilon_{ij} (\varepsilon_{ij} + \varepsilon_{kl} - \varepsilon_{ik} - \varepsilon_{jk}) \right] \quad (3)$$

where $\beta = 1/kT$, $\theta_i = N_i q_i / N_q$, $q_M = \sum x_i q_i$, $r_M = \sum x_i r_i$, $\rho_i = N_i r_i / N_r$, $\rho = \sum \rho_i$, and x_i is the mole fraction of species i . The lattice interaction energy ε_{ij} is defined as $\sqrt{(\varepsilon_{ii} \varepsilon_{jj})(1 - \lambda_{ij})}$, where the λ_{ij} is the binary interaction parameter, and ε_{ij} between holes and molecular species is set to zero. All configurational thermodynamic functions can be formulated from Eq. (3). The first term on the r.h.s. of Eq. (3) is the athermal part $A^{c(A)}$, the second term is due to the random contribution of the potential energy, and the third term represents the nonrandom contribution of the potential energy.

3. SIMPLIFIED VERSION OF HELMHOLTZ FREE ENERGY

We now propose an empiricization based on the same lattice concepts. While retaining the athermal part, we replace the remaining two terms in Eq. (2) by the sum of the “ideal solution” term and “excess” term as

$$A^c = A^{c(A)} + A^{c(IS)} + A^{c(E)} \quad (4)$$

where the athermal part from Eq. (3) is given by

$$\beta A^{c(A)} = \sum N_i \ln \rho_i + N_0 \ln(1 - \rho) - \frac{z}{2} N_q \ln \left[1 + \left(\frac{q_M}{r_M} - 1 \right) \rho \right] \quad (5)$$

The remaining parts in Eq. (4) are obtained based on the following assumptions; holes are randomly placed and the total surface area fraction occupied by molecules is the same whether molecules are in pure state or in mixtures. Then a similar method as used in the derivation of the UNIQUAC model results in the following expressions:

$$-A^{c(IS)} = \frac{zN_q}{2} \theta \sum N_i q_i \varepsilon_{ii} \quad (6)$$

$$-\beta A^{c(E)} = \frac{zN_q}{2} \sum \theta_i \ln \left[\sum \bar{\theta}_i \tau_{ji} \right] \quad (7)$$

where $\tau_{ij} = \exp[\beta \theta (\varepsilon_{ji} - \varepsilon_{ii})]$ and quantities with an overbar denote on a hole-free basis. The summation of Helmholtz free energies given by Eqs. (6) and (7) yields a version of the configurational Helmholtz free energy which

is simplified with respect to Eq. (3). This free energy expression is similar to that of the UNIQUAC model; the main difference is that the combinatorial term here is density dependent.

4. EOS AND CHEMICAL POTENTIALS FOR MIXTURES

From the rigorous and simplified configuration Helmholtz free energy equations given by Eqs. (3), (6), and (7), respectively, expressions for configurational thermodynamic properties can be obtained for each case. Since the volume V is represented by $V = V_H(N_o + \sum N_i r_i)$, both EOSs are obtained from the relation $P = -1/V_H(\partial A^c/\partial N_o)_{T, N_i}$. When the algebra is done, we have the following apparently identical forms of the EOS:

$$P = \frac{1}{\beta V_H} \left\{ \frac{z}{2} \ln \left[1 + \left(\frac{q_M}{r_M} - 1 \right) \rho \right] - \ln(1 - \rho) \right\} - \left(\frac{z}{2} \right) \theta^2 \frac{\varepsilon_M}{V_H} \quad (8)$$

where the ε_M of rigorous case differs from the simplified case as follows:

$$\varepsilon_M^{(R)} = \frac{1}{\theta^2} \left[\sum \sum \theta_i \theta_j \varepsilon_{ij} + \left(\frac{\beta}{2} \right) \sum \sum \sum \sum \theta_i \theta_j \theta_k \theta_l \varepsilon_{ij} (\varepsilon_{ij} + 3\varepsilon_{kl} - 2\varepsilon_{ik} - 2\varepsilon_{jk}) \right] \quad (9)$$

$$\varepsilon_M^{(S)} = \sum \bar{\theta}_j \varepsilon_{ij} + \sum \bar{\theta}_i \frac{\sum \bar{\theta}_k \tau_{kj} (\varepsilon_{kj} - \varepsilon_{ji})}{\sum \bar{\theta}_k \tau_{kj}} \quad (10)$$

Here $\varepsilon_M^{(R)}$ denotes for the rigorous case and $\varepsilon_M^{(S)}$ for the simplified case.

The chemical potential of component i in a mixture for both cases can be obtained from the equation: $\mu_i = N_a(\partial A/\partial N_i)_{T, V} = N_a(\partial A/\partial N_i)_{T, N_o} + r_i N_a V_H P$. Here N_a is Avogadro's number. The resulting equations for both cases are written by

$$\frac{\mu_i}{RT} = \frac{\mu_i^{(A)}}{RT} + \frac{\mu_i^{(R)}}{RT} \quad \text{and} \quad \frac{\mu_i}{RT} = \frac{\mu_i^{(A)}}{RT} + \frac{\mu_i^{(S)}}{RT} \quad (11)$$

where

$$\frac{\mu_i^{(A)}}{RT} = \gamma_i(T) - r_i \ln(1 - \rho) + \ln \left(\frac{\theta_i}{q_i} \right) + r_i \ln \left[1 + \left(\frac{q_M}{r_M} - 1 \right) \rho \right] \quad (12)$$

$$\frac{\mu_i^{(R)}}{RT} = - \frac{z q_i \beta \varepsilon_M \theta^2}{2} \times \left[1 - \frac{r_i}{q_i} - \frac{2 \sum \theta_j \varepsilon_{ji} + \beta \sum \sum \sum \theta_k \theta_l \theta_m \varepsilon_{ik} (\varepsilon_{ik} + 2\varepsilon_{lm} - 2\varepsilon_{kl} - \varepsilon_{il})}{\theta^2 \varepsilon_M} \right] \quad (13)$$

$$\begin{aligned} \frac{\mu_i^{(S)}}{RT} = & -\frac{zq_i \beta \varepsilon_M \theta^2}{2} \left[1 - \frac{r_i}{q_i} - \frac{1}{\theta} \frac{(1 + \varepsilon_{ii})}{\varepsilon_M} \right] \\ & + \frac{zq_i}{2} \left[1 - \ln \left(\sum \bar{\theta}_j \tau_{ji} \right) - \sum \frac{\bar{\theta}_j \tau_{ij}}{\bar{\theta}_k \tau_{kj}} \right] \end{aligned} \quad (14)$$

where $\gamma_i(T)$ is the reference chemical potential, which depends only on temperature.

These general equations for multicomponent mixtures easily reduce to their pure forms since all ε_M become ε_{ii} and τ_{ij} become 1 for a pure fluid. Although not presented here, other thermodynamic properties can be derived for mixtures from both equations for the Helmholtz free energy [13–16]. The critical point for the vapor–liquid phase transition is determined from the classical criticality conditions; $(\partial P/\partial \rho)_T = 0$ and $(\partial^2 P/\partial \rho^2)_T = 0$. Once expressions for the criticality conditions are evaluated, the critical compressibility factor $Z_c = r_1 P_c / T_c \rho_c$ is readily calculated.

5. MOLECULAR PARAMETERS

In formulating both EOSs, the general relation in lattice theory, $zq_1 = zr_1 - 2r_1 + 2$ is used. We also define the characteristic volume V_1^* as $V_1^* = N_a V_H r_1$. Therefore the characteristic volume gives sufficient information for determining r_1 and q_1 . The other molecular parameters are the interaction energy ε_{11} , the coordination number z , and the unit cell volume V_H . We set $z = 10$ and $V_H = 9.75 \text{ cm}^3 \cdot \text{mol}^{-1}$ [13]. Thus, both models require two molecular parameters, V_1^* and ε_{11} , respectively for each pure component.

Based on experimental data, the parameters V_1^* and ε_{11} are determined by regression analysis at each isotherm and readily fitted to the following empirical correlations as a function of temperature for an easy engineering practice.

$$\frac{\varepsilon_{11}}{k} = E_a + E_b T + E_c \ln T \quad \text{and} \quad V_1^* = V_a + V_b T + V_c \ln T \quad (15)$$

Compilations of the estimated values of the coefficients for pure components in Eq. (15) are summarized in Ref. 13 for the R-EOS and in Ref. 16 for the S-EOS for up to 200 pure fluids. They include nonpolar, weakly polar, strongly polar, supercritical, and polymeric substances. Accordingly we have used these values in the illustrations in the next section. Due to the limited space here, the parameters are not tabulated here.

6. COMPARISON OF MODELS WITH EXPERIMENT

Since we discussed the computational aspects and the comparison of both models with experiments elsewhere [13–16], only a few results are given here. For pure systems, both models quantitatively fit the experimental equilibrium properties such as vapor pressures, saturated densities, and heats of vaporization. However, we experience some degree of inaccuracy in fitting such data in the immediate vicinity of the critical point due to the intrinsic nature of the mean field approximation in the configurational lattice partition function. Thus for pure systems, we do not recommend either model for the immediate vicinity of critical region ($(T - T_c)/T_c < 0.1$ and $(P - P_c)/P_c < 0.1$).

The extensive compilations of the binary interaction energy parameters, λ_{ij} , and the range of errors for various types of binary mixtures are reported by the present authors in Refs. 14 and 15 for R-EOS and in Ref. 16 for S-EOS. The types of binary systems we tested are the VLE and VSE of polar mixtures, supercritical systems, and polymer solutions [13–16]. Here we only demonstrate a few comparative results for such systems. In Fig. 1, results calculated from the R-EOS and S-EOS for isothermal vapor–liquid equilibria for the CO₂–methanol system [8] are shown, together with the results computed from the PR-EOS [19], the

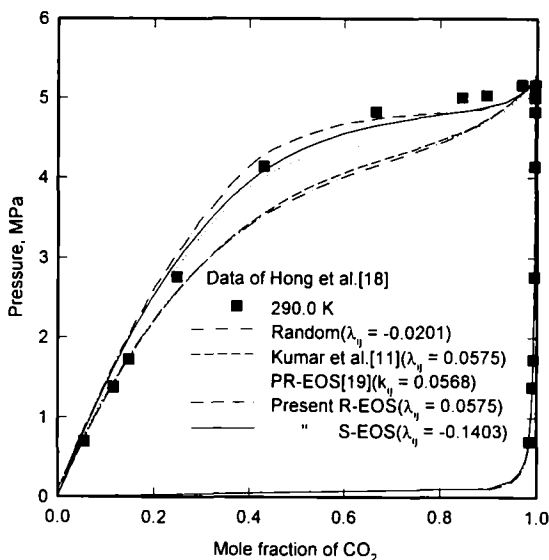


Fig. 1. Comparison of various models for the vapor–liquid equilibria of carbon dioxide–methanol system at 290.0 K.

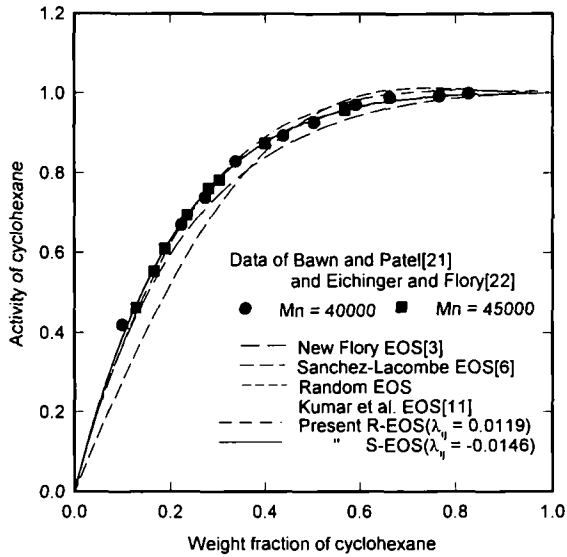


Fig. 2. Comparison of various models for the activities of cyclohexane in polyisobutylene solutions at 298.15 K.

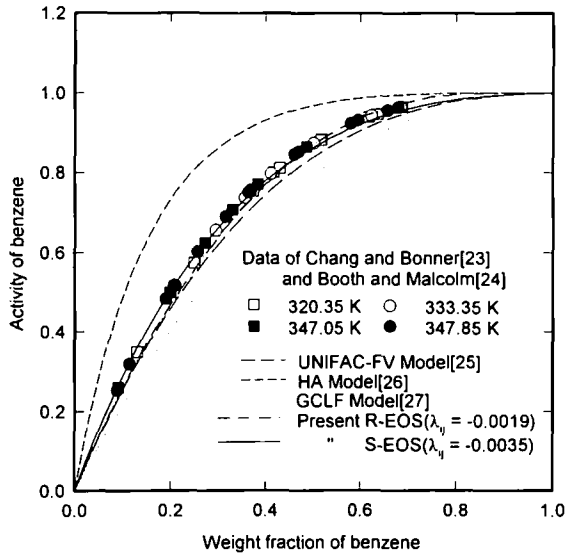


Fig. 3. Comparison of our two models with group contribution models for the activities of benzene in polypropylene solution.

random case [8], and the model by Kumar et al. [11]. This figure shows that the results of the present models fit data better than other models in the same genre and the PR-EOS.

In Fig. 2, calculated results by the R-EOS and S-EOS with activity data of cyclohexane in polyisobutylene solution [21, 22] are compared with the EOSs by Flory [20], Sanchez and Lacombe [6, 7], Kumar et al. [11], and Panayiotou and Vera [8]. While the present models and the Flory-EOS fit the data well, the results of other models show larger errors for this system. We found similar trend for other systems [16]. Finally in Fig. 3 the calculated results for the present EOSs for activities of benzene in polypropylene solution [23, 24] are compared with the existing group contribution methods which are used frequently in engineering practice for polymer systems. They include the UNIFAC-FV [25], HA [26], and GCLF [27] models. The results of the present EOSs fit the data surprisingly well and provide a possibility of reformulating the S-EOS as the group contribution model. Accordingly, an extension of the S-EOS as a group contribution method is under way by the present authors.

In summary, by expanding the Helmholtz free energy from the full Guggenheim combinatorial term of nonrandom lattice hole theory, a new rigorous EOS is developed and its applicability was demonstrated. To make the R-EOS simpler and more versatile, we propose a new modified S-EOS by introducing the local composition concept. Both EOSs were tested for their ability to represent the phase equilibrium behavior of pure components and mixtures. With two parameters for pure each component and one binary interaction energy parameter, results obtained to date demonstrate that both models are quantitatively applicable to a wide range of temperatures, pressures and concentrations.

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