

Rediscovering the Lattice-Fluid Theory for Phase Equilibria of Complex Mixtures

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Abstract—Various lattice statistical-thermodynamic theories after E. A. Guggenheim [Guggenheim, 1952] have been proposed with different assumptions on nonrandomness, the explicitness of the solution, and the model parameters. During the last decade, the present authors proposed a general approximation tool to the quasichemical solution of the nonrandom lattice-fluid combinatory and formulated a new rigorous EOS and the improved versions including the unified group contribution extensions and systems with strong association. In this study, developments of those EOSs are discussed with emphasis on the practical utility of each model.

Key words: Lattice Theory, Quasichemical Approximation, Equation of State, Hydrogen Bonding, Complex Mixtures

INTRODUCTION

Most thermodynamic properties of interest in phase equilibria can be calculated from an equation of state (EOS). However, most EOS models do not accurately describe properties of the condensed phase. Alternately, behaviors in the liquid phase are described in terms of excess functions. However, they cannot be applied to pure fluids and have intrinsic limitations at high-pressure.

Thus, until the present time, efforts had been placed on the EOS which is applicable to the liquid phase. Flory opened a new era of EOS theories for condensed phase [Flory, 1970]. Since then, many EOS theories have been proposed. They can be classified as two approaches: radial distribution function theory such as perturbed hard chains and lattice-hole theories. After Guggenheim [Guggenheim, 1952], many lattice-hole models appeared [e.g. Sanchez and Lacombe, 1976; Panayiotou and Vera, 1982 etc.] However, due to the difficulty of explicitly solving the quasichemical approximation in the lattice theory, existing models were obtained with drastic simplifications. The present authors proposed an approximation to the nonrandomness factor to solve the fundamental lattice-hole equation explicitly. By this approximation technique, the authors proposed series of new EOSs such as NLF and MF-NLF EOS in recent years. In this paper, we present a discussion of the historical perspective of the EOSs and the universal group contribution applications to the EOS.

Also, based on Veytsman statistics [Veytsman, 1993] for proton donor-acceptor, the early EOSs were extended to apply to systems with association. Discussion was included for these new extensions with emphasis on phase equilibria of associated mixtures.

BASIC LATTICE-FLUID THEORY

We assume that the partition function can be separated by the physical part and chemical contribution due to the existence of hydrogen bonding,

$$\Omega^c = \Omega_{MLF}^c \Omega_{HB}^c \quad (1)$$

Each contribution is defined below.

1. Physical Combinatory

In a 3-D lattice of the coordination number z , molecules of component i are assumed to occupy r_i sites of the unit cell size V_{if} . They interact with surface area q_i with neighboring segment of r -mers. For linear or branched chains, the number of external contacts $zq_i = (z-2)r_i + 2(1-l_i)$ where l_i is the bulkiness factor.

The configurational part of the nonrandom lattice partition function may be written as follows in the quasichemical approximation,

$$\Omega_{MLF}^c = g_R g_{NR} \exp(-\beta U^c) \quad (2)$$

The random contribution, g_R is written in the Guggenheim-Huggins-Miller approximation,

$$g_R = (N_r! / (N_r! N_i!)) (N_q! / (N_i!))^{z/2} \quad (3)$$

The nonrandom contribution g_{NR} is given by

$$g_{NR} = \frac{[\Pi N_{ii}^0! \Pi (N_{ij}^0/2)!]^2}{[\Pi N_{ii}! \Pi (N_{ij}/2)!]^2 \Pi N_{ij}^{M_{ij}}} \quad (4)$$

Where $N_r = N_0 + \sum N_i r_i$, $N_q = N_0 + \sum N_i q_i$ and N_0 is the number of vacant sites. N_{ij} is the number of i - j segment contacts. The quantities with superscript zero denote the same for random mixing.

N_{ij} is related to N_{ij}^0 in the quasichemical approximation.

$$N_{ij} = N_{ij}^0 \Gamma_{ij} \quad (5)$$

$$\Gamma_{ij}^2 = \Gamma_{ii} \Gamma_{jj} \exp\{\beta(\epsilon_{ii} + \epsilon_{jj} - 2\epsilon_{ij})\} \quad (6)$$

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where β denotes $1/kT$ and ϵ_{ij} is the absolute value of interaction energy. Eq. (5) subject to the mass balance constraints,

$$2N_{ii} + \sum_j N_{ij} = zN_i, q_i (i=1, 2, \dots, c) \quad (7)$$

The 'nonrandomness factor' Γ_{ij} may be obtained from the simultaneous solution of Eqs. (5), (6) and mass balance relations. It can be expressed in an explicit form only for binary mixtures in systems with no vacant sites or pure systems. Once Γ_{ij} is known, the mean potential energy is written as

$$U^c = \sum_{i \geq j} \sum N_{ij} (-\epsilon_{ij}) \quad (8)$$

Sanchez-Lacombe [Sanchez and Lacombe, 1976] initiated the random lattice-fluid EOS with the assumptions of no nonrandomness and 'large z ' approximation. Okada and Nose [Okada and Nose, 1981] included the nonrandomness of molecules and vacant sites as described above. However, the solution requires a numerical procedure. Panayiotou and Vera [Panayiotou and Vera, 1982] and Kumar et al. [Kumar et al., 1986] assumed that vacant sites are random. Therefore, their formulation yields $g_{NR}=1$ for pure systems. However, they used the exact solution on the random vacant site basis for binary mixtures. They should have used numerical procedures for a mixture with more than two components. On this basis, their solution is explicit for general multicomponent mixtures. You et al. [You et al., 1994a, b] obtained a general explicit solution by expanding Helmholtz free energy and by including nonrandom vacant sites.

2. Hydrogen-Bonding Contribution

Some components in the mixture have hydrogen donor groups and/or acceptor groups. The number of hydrogen donor groups of type k in species i is d_k^i and the number of acceptor groups of type l in species j is a_l^j . The total number of donor types is m and the total number of acceptor types is n . Then the total number of donor groups of type l (N_d^l) and that of acceptor groups of type k (N_a^k) are given by

$$N_d^l = \sum_j d_j^l N_j, N_a^k = \sum_i a_i^k N_i \quad (9)$$

We also define the total number of donor-acceptor pair (N_{HB}), unpaired donors (N_{i0}^{HB}) and unpaired acceptors (N_{0i}^{HB}) as functions of the number of i - j hydrogen bond pair (N_{ij}^{HB}).

$$N_{HB} = \sum_i \sum_j N_{ij}^{HB}, N_{i0}^{HB} = N_d^i - \sum_j N_{ij}^{HB} \quad (10)$$

Now Veytsman statistics allows us to write the partition function for the hydrogen bond contribution,

$$\Omega_{HB}^c = \frac{1}{N_{HB}^{HB}} \prod_i \frac{N_d^i!}{N_{i0}^{HB}!} \prod_j \frac{N_a^j!}{N_{0j}^{HB}!} \prod_{i,j} \frac{1}{N_{ij}^{HB}} \exp(-\beta N_{ij}^{HB} A_{ij}^{HB}) \quad (11)$$

where

$$A_{ij}^{HB} = U_{ij}^{HB} - TS_{ij}^{HB} \quad (12)$$

and the superscript HB denotes the property change on a hydrogen-bond formation.

THERMODYNAMIC FUNCTIONS

We maximize $\ln \Omega_{NLF}^c$ with respect to N_{ij} and $\ln \Omega_{HB}^c$ with respect to N_{ij}^{HB} at constant volume and temperature. We assume

N_{ij} and N_{ij}^{HB} are independent in finding the maximum terms. This approximation is similar to that by Sanchez and Panayiotou [Sanchez and Panayiotou, 1993].

For hydrogen bonding contribution the maximization conditions are given by,

$$N_{ij}^{HB} N_{ij} = N_{i0}^{HB} N_{0j}^{HB} \exp(-\beta A_{ij}^{HB}) \\ = (N_d^i - \sum_{k=1}^n N_{ik}^{HB})(N_a^j - \sum_{k=1}^m N_{kj}^{HB}) \exp(-\beta A_{ij}^{HB}) \quad (13)$$

Eq. (13) yields a quadratic equation for N_{ij}^{HB} when applied to a general mixture with a single hydrogen-bonding fluid. When more than one group of donors or acceptors are present, they have to be determined numerically. With N_{ij}^{HB} known, Helmholtz free energy due to the hydrogen-bonding contribution is readily written in the Sterling approximation.

$$\beta A_{HB}^c = -\ln \Omega_{HB}^c = N_{HB} \ln N_{HB} - \sum_i (N_d^i \ln N_d^i - N_{i0}^{HB} \ln N_{i0}^{HB}) \\ + \sum_j (N_a^j \ln N_a^j - N_{0j}^{HB} \ln N_{0j}^{HB}) - \sum_i (N_d^i \ln N_d^i - N_{i0}^{HB} \ln N_{i0}^{HB}) \\ + \sum_j (N_a^j \ln N_a^j - N_{0j}^{HB} \ln N_{0j}^{HB}) \\ + \sum_i \sum_j (\beta N_{ij}^{HB} A_{ij}^{HB} + N_{ij}^{HB} \ln N_{ij}^{HB} - N_{ij}^{HB}) \quad (14)$$

As we mentioned above, Eq. (6) is a set of implicit equations even for a binary mixture. Thus an expansion method was developed to yield an explicit Helmholtz free energy as a sum of the reference athermal term and the residual term.

$$\beta A_{NLF}^c = -\ln \Omega_{NLF}^c = \beta A_{NLF}^{c(A)} + \beta A_{NLF}^{c(R)} \quad (15)$$

$$\beta A_{NLF}^{c(A)} = \sum_{i=1}^c N_i \ln N_i + \sum_{i=0}^c N_i \ln N_i - \sum_{i=0}^c N_i \ln N_i + N_i \\ = \sum_{i=1}^c N_i \ln \rho_i + N_0 \ln(1-\rho) - \frac{z}{2} N_0 \ln \left[1 + \left(\frac{q_M}{r_M} - 1 \right) \rho \right] \quad (16)$$

$$\beta A_{NLF}^{c(R)} = \sum_{i,j} \sum \left(\frac{\partial A_{ij}^c}{\partial \epsilon_{ij}} \right) \epsilon_{ij} + \frac{1}{2} \sum_{i,j} \sum \sum_{k,l} \left(\frac{\partial^2 A_{ij}^c}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right) \epsilon_{ij} \epsilon_{kl} \\ = -\frac{z N_0 \beta}{2} \left[\sum_i \sum_j \theta_{ij} \epsilon_{ij} \right. \\ \left. + \frac{\beta}{2} \sum_i \sum_j \sum_k \sum_l \theta_{ij} \theta_{kl} \epsilon_{ij} (\epsilon_{ij} + \epsilon_{kl} - \epsilon_{ik} - \epsilon_{jl}) \right] \quad (17)$$

where

$$\rho_i = N_i r_i / N, \rho = \sum_i \rho_i, \theta_i = N_i q_i / N_{\varphi}, \theta = \sum_i \theta_i, r_M = \sum_i x_i r_i, \text{ and } q_M = \sum_i x_i q_i.$$

The unit cell size is defined by

$$v_H = \sum_{i=1}^m \sum_{j=1}^n N_{ij}^{HB} / \sum_{i=1}^m N_i r_i \quad (18)$$

Finally, we have the Helmholtz free energy as a sum of the physical and chemical contributions.

$$A^c = A_{NLF}^c + A_{HB}^c \quad (19)$$

Other thermodynamic functions EOS and chemical potential follow from the Helmholtz free energy. We named Eq. (19) as the NLF-HB model. When there is no formation of hydrogen bonding, the NLF model reduces to NLF model.

Kumar et al. [Kumar et al., 1986] obtained an expansion for Γ_{ij} on the vacant site free basis and obtained an expansion for

Helmholtz free energy. A more consistent method of introducing quasichemical nonrandom effects is to include the nonrandom vacant sites. In this case one has to use numerical procedures even for binary mixtures as did Okada and Nose [Okada and Nose, 1981a, b].

We find that lattice-fluid theory-based EOSs have potential application to real fluids and that consistency and explicitness may be improved [Lee and Yoo, 1998].

What we derived by Eq. (17) covers the rigorous second order solution to the quasichemical approximation applicable to mixtures. Although the solution we obtained is explicit and thermodynamic functions based on this solution (NLF) are applicable quantitatively to the phase equilibrium calculations of wide range of complex mixtures including systems with association, Eq. (17) is still quite complex. Therefore, an empirical expansion was derived for $A_{MF,NLF}^c$ from a lattice-fluid based nonrandom multifluid (MF) approximation. The generalized result for nonrandom vacant sites is derived to give

$$\beta A_{MF,NLF}^{c(R)} = \int_0^\beta U^c d\beta = - \left(\frac{zN_g}{2} \right) \sum_{i=1}^c \theta_i \left[\ln \left(\sum_{j=0}^c \theta_j \tau_{ji} \right) + \beta \epsilon_{ii} \right] \quad (20)$$

where

$$\tau_{ij} = \exp[\beta(\epsilon_{ij} - \epsilon_{ii})] \quad (21)$$

We named this approximation as MF-NLF. Summation of Eq. (14), (16) and (20) becomes the MF-NLF-HB model. When there is no association in a mixture, the MF-NLF-HB reduces to MF-NLF model.

Extensive study indicates this approximation is probably as accurate as the NLF-HB theory and computationally more efficient. Details of this model will be omitted here.

MOLECULAR PARAMETERS

We discussed four different EOSs above: NLF, NLF-HB, MF-NLF and MF-NLF-HB. As usual with lattice theories, $z=10$ and $V_H=9.75 \text{ cm}^3/\text{mol}$ are fixed. All we need are r_i and ϵ_{ij} for pure fluids. For systems with hydrogen bonding, additional parameters are necessary (i.e., $U_H^{HB} = -25.1 \text{ kJ/mol}$ and $S_H^{HB} = 2.65 \times 10^{-2} \text{ kJ/mol.K}$) for each hydrogen bond pair. The pure component parameters are fitted to experimental data as a temperature-dependent formula,

$$\epsilon_{ii}/k = E_a + E_b(T - T_0) + E_c(T \ln T_0 / T + T - T_0) \quad (22)$$

$$r_i = R_a + R_b(T - T_0) + R_c(T \ln T_0 / T + T - T_0) \quad (23)$$

For mixtures a binary parameter is introduced for ϵ_{ij} as

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2} (1 - \lambda_{ij}) \quad (24)$$

where λ_{ij} is the binary interaction parameter.

GROUP CONTRIBUTION OF PARAMETERS

The functional group contribution methods, which have a long history, have been powerful tools for predicting properties of pure fluids or mixtures from experimental data on related substances. The lattice theory has widely been used to describe excess pro-

perties. UNIFAC and ASOG are among them. It is noteworthy that the nonrandom contribution represented by Eq. (4) may be evaluated either on a molecular basis or on a group basis [Guggenheim, 1952]. On the group basis, Smirnova and Victorov [Smirnova and Victorov, 1987] developed an implicit lattice-fluid EOS with the bulkiness factor.

High and Danner [High and Danner, 1990] have been working on the group contribution method for polymer systems using Panayiotou and Vera EOS. The present authors proposed a new concept of universal group contribution [Yoo et al., 1997]. The basis is the assumption that group parameters are identical whether molecules are in pure fluids or in mixtures. The group contribution approach is applied to determine the parameters as

$$r_i = \sum_k v_{ik} r_k^G \quad (25)$$

$$\epsilon_{ij} = \sum_{k=1}^G \sum_{l=1}^G \theta_{ik}^G \theta_{jl}^G \epsilon_{kl}^G \quad (26)$$

q_i^G may be determined from r_i^G if we require that r_i and q_i satisfy $zq_i = (z-2)r_i + 2(1-l_i)$, for example.

Although lattice models such as NLF, MF-NLF and their HB versions and group contribution extensions described above are not intended for aromatics and cyclic compounds, the application has been extended to such compounds empirically on the molecular level. However, when applied to the group level closed chains present difficulties in relating q_i^G and r_i^G . Without justifications q_i^G is equal to r_i^G in this work. Two group parameters, r_i^G and ϵ_{ij}^G , are determined from values of temperature-dependent r_i , ϵ_{ij} and λ_{ij} data.

APPLICATIONS AND DISCUSSIONS

Lattice-fluid theories proposed by the present authors are classified as NLF, NLF-HB, MF-NLF, MF-NLF-HB models and GC-NLF and GC-MF-NLF. All of these six types of models are critically and extensively used to calculate various thermodynamic properties of pure fluids such as vapor pressures, vapor- and liquid-densities, and enthalpy of vaporization. Also, these models

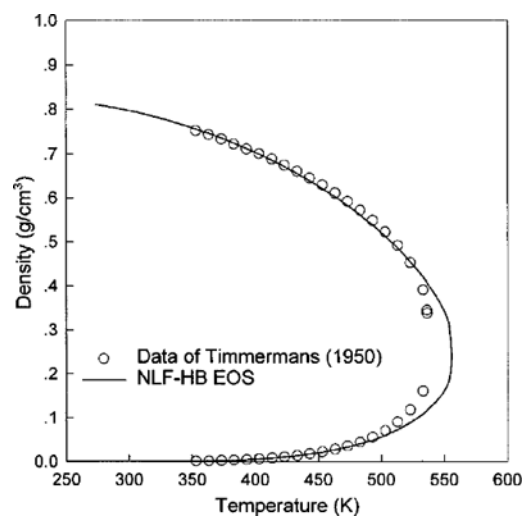


Fig. 1. Calculated saturated temperature-density diagram for pure 1-propanol.

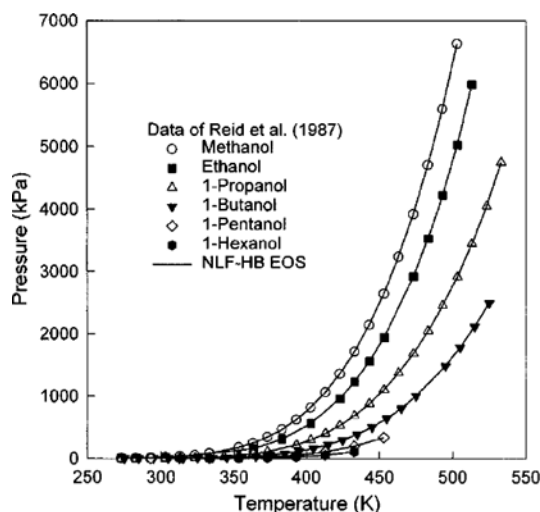


Fig. 2. Calculated temperature-vapor pressure diagram for pure 1-alcohols.

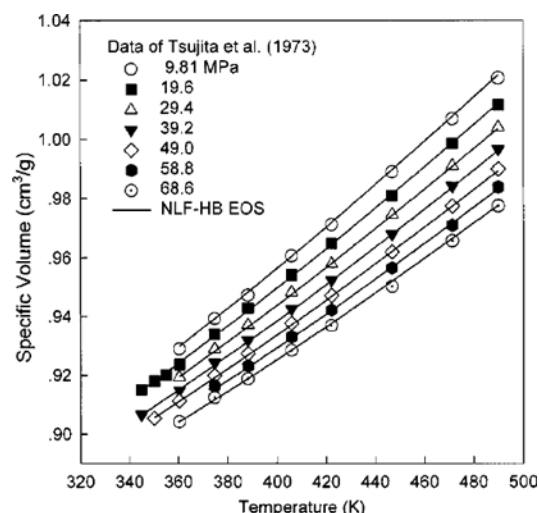


Fig. 3. Calculated temperature-specific volume diagram for PEG.

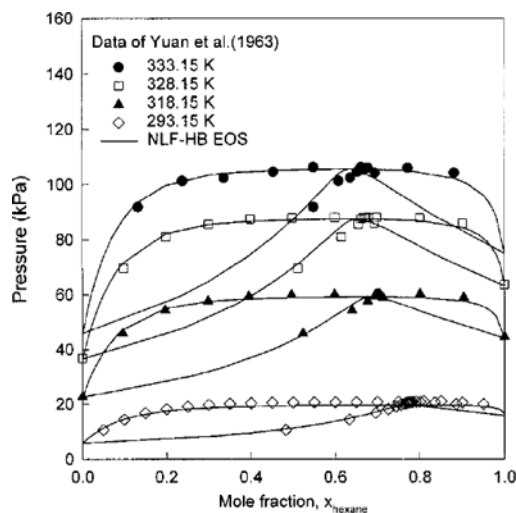


Fig. 4. Calculated isothermal P-x-y equilibria for n-hexane-ethanol system by NLF-HB EOS ($\lambda_{12}=0.030$).

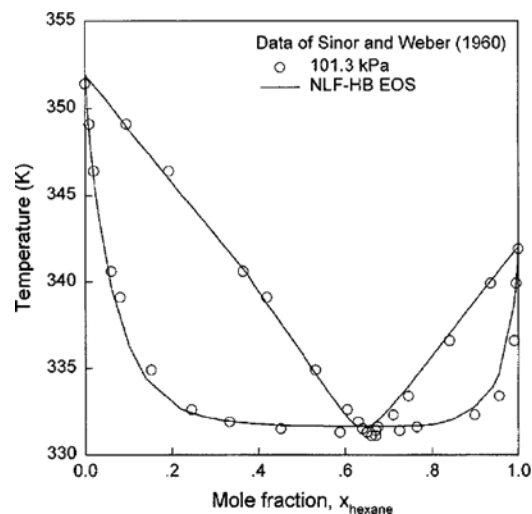


Fig. 5. Calculated isobaric T-x-y equilibria for n-hexane-ethanol system by NLF-HB EOS ($\lambda_{12}=0.030$).

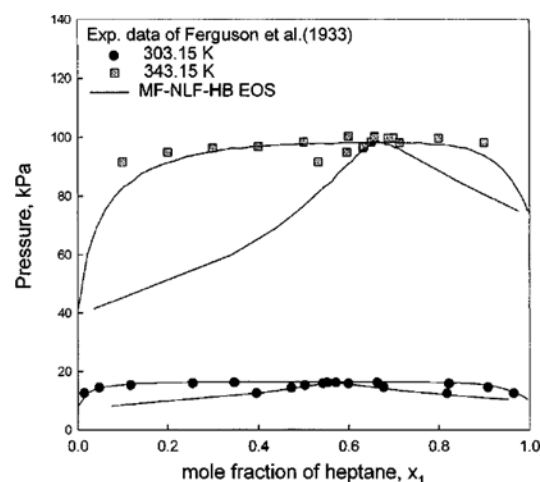


Fig. 6. Calculated isothermal P-x-y equilibria for heptane/ethanol at 303.15, 343.15 K by MF-NLF-HB EOS ($\lambda_{12}=0.357$).

are applied to calculate and predict various types of phase equilibria of mixtures such as VLE, LLE and VSE, density, excess volume, excess enthalpy and critical loci, etc. Tested mixtures including organic compounds and macromolecules with or without the existence of association and details of comparison with data or with other models may be found in the paper cited.

For NLF, MF-NLF and their universal group contribution extensions, extensive comparison with these models and various phase equilibrium data have been made elsewhere [You et al., 1994a, b, 1995, 1997a, b]. Thus, in this work, emphasis was given to an extensive comparison of NLF-HB and MF-NLF-HB models with the data of physical properties of 35 self-associated pure alcohols, and VLE, excess volume and excess enthalpy of 20 mixed hydrocarbon-alcohol systems. Results demonstrated that the two approaches (i.e., NLF-HB and MF-NLF-HB) equivalently fit various experimental data quantitatively enough. We omit here detailed illustration; however, the new lattice-fluid EOSs with the combination of hydrogen bonding theory after Veytsman [Veytsman, 1993] fit associated mixtures well.

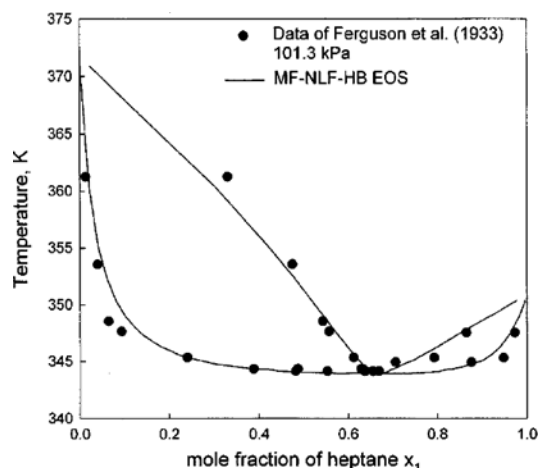


Fig. 7. Calculated isobaric T-x-y equilibria for heptane/ethanol at 101.3 kPa by MF-NLF-HB EOS ($\lambda_{42}=0.357$).

CONCLUSION

Lattice-fluid theories mainly developed by the present authors in recent years were reviewed and compared with data of various pure fluids and binary mixtures. In particular, we found that the new two EOSs with hydrogen bonding contribution can be quantitatively applicable to mixtures by association.

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