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UNIFIED EQUATION OF STATE BASED ON THE LATTICE FLUID THEORY FOR PHASE EQUILIBRIA OF COMPLEX MIXTURES
PART I. MOLECULAR THERMODYNAMIC FRAMEWORK

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Abstract—Consistent calculation of fugacities of fluid mixtures remains as one of the most important subjects in contemporary molecular thermodynamics. In practice, equations of state (EOSs) and g^E-models have been used. However, most EOSs are erroneous for condensed phases at high densities and g^E-models are inapplicable for pressure-sensitive systems. Recently to remedy the shortcomings in both approaches, there has been a surge of new g^E-EOS mixing rules. By equating any set of EOS and g^E-models, the limitations in both approaches could be resolved significantly. However, the self-consistency in the underlying concept of those mixing rules remains controversial. During the last several years, the present authors proposed a new lattice-fluid EOS and its simplification relevant to phase equilibrium calculations. Without employing any g^E-EOS mixing rule and with only two parameters for a pure component and one adjustable interaction energy parameter for a binary mixture, results obtained to date demonstrated that the EOSs are quantitatively applicable to a great variety of phase equilibrium properties of mixtures, especially, for complex and/or macromolecular systems. In the present article we summarize the EOSs and extended the applications to liquid-liquid Equilibria. In part I, we discussed briefly the molecular thermodynamic aspects of general derivation of the EOS and a brief discussion of applying the EOSs to pure fluids while the illustrative application to various real mixture systems is discussed in part II.

Key words: *Theory, Equation of State, Nonrandom Lattice Fluid Theory, Fluid-phase Equilibria, Pure Fluids*

INTRODUCTION

Knowledge of fluid-phase Equilibria of fluids and fluid mixtures is essential for designing, optimizing and performing separation and purification processes. All design methods for chemical processes require quantitative estimates of various phase equilibria. Thus, a vast quantity of literature regarding the molecular thermodynamics of phase equilibria has been generated during the last century. However, the goal of correlating or predicting mixture properties from pure component information remains as the most elusive problem. Difficulty in predicting phase Equilibria of mixtures follows from the inadequate understanding of the intermolecular potential energy plays in fluid. Therefore, to calculate various phase Equilibria, it is necessary to construct empirical or semiempirical models; models are only approximations and, thus, contain parameters that must be obtained empirically.

For any type of phase Equilibria, the thermodynamic function of primary interest is the fugacity (f) which is directly related to the chemical potential (μ) and in principle it can be calculated from the volumetric data, i.e., EOSs. The EOS method uses a homogeneous model for all phases and is equally applicable to pure compounds and mixture properties. However, to apply an EOS to condensed phase, volumetric data must be available over an entire density range from ideal gas state to the condensed phase including a two-phase region and often it is not practical to do so because very little data of this type has been reported. Alternatively, fugacities in condensed phases, i.e., liquid mixtures, are calculated with activity coefficients (γ), which are directly related to excess Gibbs energy (g^E). Activity coefficient models are, however, strongly dependent on composition, weakly on temperature and very weakly on pressure. So, they fail to take into account inherently the effect of pressure and they cannot be applied to pressure-dependent systems such as polymer-supercritical fluid systems.

Furthermore, performance demands on materials, which traditional processing techniques cannot meet, have increased unprecedentedly in recent decades while process design engineers have to deal with more complex systems in which the activity coefficient models are frequently more difficult to apply than EOSs and it is necessary to find appropriate EOSs to model the complex phase behavior of molecular mixtures under a variety of conditions. Thus, during the last decades, motivation of research on developing new EOSs for complex mixtures has been increasing. Also, there has been a surge of new g^E-EOS mixing rules as an *ad hoc* method. In the mixing rule, by equating a set of EOS and g^E-models, the shortcomings in both approaches could be resolved significantly. Especially, by utilizing information of group contribution g^E-models such as UNIFAC, one can make an EOS as predictive and/or g^E-models that can be used in high pressure system. However, the self-consistency in the underlying concept of those mixing rules remains controversial [Huron and Vidal, 1977; Wong and Sandler, 1992].

Recently, based on the nonrandom lattice fluid theory of Guggenheim [1952], the present authors proposed a new EOS and

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its simplified version relevant to a variety of phase Equilibrium calculations [You et al., 1993, 1994a, b, c; Shin et al., 1994a, b, 1995a, b; Yoo et al., 1994, 1995]. Without employing a g^E-EOS mixing rule and with two parameters for pure components and one adjustable interaction energy parameter for binary mixtures, results obtained to date with the new EOSs demonstrated that they are quantitatively applicable to phase Equilibria of mixtures as well as pure fluids. Especially the EOSs are found to be reliably applicable to complex and/or macromolecular systems. In the present articles we summarize the thermodynamic framework related to the general derivation of the EOSs and present results of new extensions of the EOSs to liquid-liquid Equilibria and activities of solvents in polymer solutions. In part I, we briefly discuss the molecular thermodynamic aspects of general derivations of the EOSs. The illustrative applications of various phase Equilibria to real complex mixtures are discussed in part II.

BRIEF REVIEW ON THEORIES OF SOLUTION: THE LATTICE THEORY

The EOS approach for complete determination of phase Equilibria is still often not as promising as the excess function approach because we usually do not have sufficiently accurate knowledge of volumetric properties of mixtures at high densities. Knowledge of volumetric information of mixtures whose molecules differ greatly in size is even more inaccurate because of our inadequate understanding of intermolecular forces and the fundamental structure of condensed states of such systems. Up to the present cubic EOSs have been employed extensively although other new non-cubic EOSs have also been used [Carnahan and Starling, 1972; Peng and Robinson, 1976; Orby and Sandler, 1994]. The cubic EOS, however, proves physically inadequate when size differences between component molecules become large [Kumar et al., 1987]. Thus, alternatively, an EOS based on the perturbed hard chain theory has been developed for modeling polymer solutions whose molecules differ greatly in size [Donohue and Prausnitz, 1975]. The EOSs stemming from the technique of perturbation over the distribution function have been used to model mixtures of hydrocarbons consisting of small and large molecules, however, the apparent complexity and the large number of parameters in these models makes them unattractive for practical purposes. However, with increasing efficient computers and with advances in molecular physics, the perturbation theory of fluids is likely to provide a powerful tool for molecular thermodynamics in the near future [Prausnitz et al., 1986].

The other type of models developed for systems whose molecules differ greatly in size (i.e., polymer-solvent mixtures) is the lattice model approach based on the full Guggenheim combinatory of quasilattice description of fluids [Guggenheim, 1952]. As we discuss in the next section, EOS as well as g^E-models can be modeled in principle from the Guggenheim's quasichemical lattice model which in its original form is restricted to small molecules of essentially the same size. An earlier attempt for developing activity coefficient models stemming from the rigid lattice was made by Flory [1941, 1942], Huggins [1941, 1942] and others [Staverman, 1950; Tompa, 1956] known as the Flory-Huggins equation with χ-parameter. The Flory-Huggins equation for real solution does not provide an accurate description of the thermodynamic properties of such solutions, but there is little doubt that this relatively simple theory contains most of the essential features which distinguish solutions of very large molecules from those of small molecules. Numerous extended works after the Flory-Huggins' pioneering model have appeared [Prausnitz et al., 1986]. The latest developments in this field are attempts to alleviate the shortcomings inherent in these early attempts.

Historically, the most important theory of solutions modeled after the Flory-Huggins equation is the Prigogine-Flory-Patterson's free volume theory, sometimes called 'the new Flory EOS [Prigogine, 1957; Flory, 1970; Patterson, 1969, 1970]. The new Flory theory resorted to the use of the generalized van der Waals theory with the lattice cell theory [Prausnitz et al., 1986; Hirschfelder et al., 1954] in formulating the canonical partition function for r-mer fluids. They obtained an EOS rather than an activity coefficient. The EOS contains three parameters for pure fluids and in addition, two adjustable quantities are necessary for the characterization of a binary mixture. This equation has been applied widely for the thermodynamic properties of polymer solutions [Hirschfelder et al., 1954; Zeman and Patterson, 1972; Zeman et al., 1972; Siow et al., 1972] Also, by combining the residual activity expression derived from the new Flory EOS to the Flory-Huggins equation, the model has been used extensively for obtaining the χ-parameter of various polymer solutions [Eichinger and Flory, 1968]. Also, until the present numerous extended applications and modifications of the new Flory theory have appeared [Bonner et al., 1972; Lee et al., 1972; Beret and Prausnitz, 1975; Panayiotou and Vera, 1980]. Others also have attempted to adapt the lattice cell-theory with different notion for the free volume to obtain different formulations for chain molecular systems [Somcynsky and Simha, 1971; Simha, 1977; Jain and Simha, 1980]. The new Flory EOS and its refinements still need to assume a functional form in *a priori* for the free volume which should be based on an empiricism and adopt an external degree of freedom c parameter, which is basically unknown for real solutions. Also, one needs to know density and pressure dependencies of the c parameter and two mixing parameters in order to apply the EOS polymer solutions. These disadvantages of the theory introduce an additional uncertainty to mixture correlations.

The intrinsic difficulties retained in the new Flory theory have been overcome in a rigorous manner by the lattice-fluid theories based on the nearest-neighbor lattice statistical-mechanical theory named after Guggenheim [Panayiotou and vera, 1981] known as Guggenheim-Huggins-Miller approximation [Guggenheim, 1952]. The lattice fluid theory is used to enumerate the number of possible configurations when r-mers were placed on a three dimensional lattice. Different formulations of solutions can be considered under the framework of the generalized Guggenheim combinatory [Panayiotou and Vera, 1981]. Historically, several pioneering theories of solutions have originated from it. When all the lattice sites are occupied by molecules, we termed it as the 'rigid lattice' and one can derive not only the EOS but the activity coefficient such as the work of Barker [1952] or UNIQUAC [Abrams and Prausnitz, 1975] as discussed in the author's previous papers [You et al., 1993; Shin et al., 1995a]. However Sanchez and Lacombe [1976a, b, 1978], in an attempt to obtain an EOS, assigned the first concept of empty sites called 'holes' into the lattice description. From a regular lattice description with holes an EOS-type model can be formulated. Since the Sanchez-Lacombe's works, several models with this concept have been proposed [Kumar et al., 1987; Kehiaian et al., 1978; Sanchez and Lacombe, 1976a, b; Okada and Nose, 1981a, b; Panayiotou and Vera, 1982; Smirnova and Victorov, 1987].

The present authors, reviewed the existing lattice fluid theories stemming from the full Guggenheim combinatory and the quasichemical approximation [You et al., 1994a, b, c] and discussed in detail the unique features of the previous works done relating to the lattice theory by other investigators, with their advantages and shortcomings. They also proposed a new method of approximation to the Guggenheim combinatory, a new EOS, and its simplified expression. They extensively confirmed the quantitative applicability of the EOSs to the calculation of various phase Equilibria [You et al. 1993, 1994a, b, c; Shin et al., 1994a, b; 1995a, b; Yoo et al., 1994, 1995]. In part I, we briefly summarize the consequences related to the new EOSs and present our recent efforts of extension of the EOSs to the calculations of liquid-liquid Equilibria. While activities of solvents in polymer solutions are discussed in part II.

GUGGENHEIM COMBINATORY AND LATTICE PARTITION FUNCTION

1. Guggenheim Combinatory of Lattice Theory

We briefly summarize here the nonrandom lattice hole partition function based on the full Guggenheim combinatory [Guggenheim, 1952; Panayiotou and Vera, 1981; You et al., 1994a]. In a three dimensional lattice with the coordination number z and of the cell volume V_H, molecules of component i occupy r_i sites and interact with neighboring segment of molecules with effective surface area q_i so that zq_i is the number of external contacts given by

$$zq_i = r_i(z-2) + 2(1-l_i) \tag{1}$$

where l_i denotes molecular bulkiness factor. In the present work we set it as zero as others usually do.

The configurational part of the nonrandom lattice partition function away from the critical point in the mean field approximation may be written as follows,

$$\Omega^c = g_R\ g_{NR}\ \exp(-\beta U) \tag{2}$$

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

$$g_R = \left[\frac{N_r!}{(\Pi N_i!)}\right]\ \left[\frac{N_q!}{N_r!}\right]^{Z/2} N_r^{lN_i} \tag{3}$$

Here N_r and N_q are defined as follows,

$$N_r = N_0 + \Sigma N_i r_{,i} \text{ and } N_q = N_0 + \Sigma N_i q_i \tag{4}$$

where N_0 is the number of holes. The summation is over all molecular species unless specified otherwise. The expression for the nonrandom contribution g_{NR} was also given by Guggenheim,

$$g_{NR} = \frac{\left(\Pi N^o_{ii}!\ \Pi\left[\left(\frac{N^o_{ij}}{2}\right)!\right]^2\right)}{\left(\Pi N_{ii}!\ \Pi\left[\left(\frac{N_{ij}}{2}\right)!\right]^2\right)} \tag{5}$$

where N_{ij} is the number of i−j segment contacts and the quantities with the superscript zero denoting the same for random mixing.

N_{ij} satisfies the mass balance relations,

$$2N_{ii} + \Sigma N_{ij} = N_i z q_i,\ 2N^o_{ii} + \Sigma N^o_{ij} = N_i z q_i \text{ for all i including holes} \tag{6}$$

$$N^o_{ii} = \frac{zN_i q_i \theta_i}{2},\ N^o_{ij} = zN_i q_i \theta_j,\ \theta_i = \frac{N_i q_i}{N_q},\ \theta_o = \frac{N_o}{N_q} \tag{7}$$

$$\phi_i = \frac{r_i N_i}{N_r},\ \phi_o = \frac{N_o}{N_r} \tag{8}$$

where θi and ϕi represent site fractions and segment fractions for component i, respectively and the quantities with subscript zero represent for hole fractions. The N_{ii} defined in Eq. (6) is related to N^o_{ij} in the quasichemical approximation as expressed by Panayiotou and Vera [Guggenheim, 1952; Panayiotou and Vera, 1981].

$$N_{ij} = N^o_{ij}\ \Gamma_{ij} \tag{9}$$

$$\Gamma^2_{ij} = \Gamma_{ii}\Gamma_{jj}\exp(-\beta\ \Delta\varepsilon_{ij}) \tag{10}$$

$$\Delta\varepsilon_{ii} = \varepsilon_{ii} + \varepsilon_{jj} - 2\varepsilon_{ij} \tag{11}$$

where β denotes 1/kT. The nonrandomness factor Γ_{ij} may be obtained from Eqs. (9)-(11) but can be expressed in an explicit form only for binary mixtures.

The potential energy U in Eq. (2) is written as follows,

$$U = \sum_i N_{ii}(-\varepsilon_{ii}) + \sum_{i>j}\Sigma N_{ij}(-\varepsilon_{ij}) \tag{12}$$

where ε_{ij} is the absolute value of interaction energy between segments i and j.

'Athermal solution' corresponds to making U=0 and for this solution $g_{NR}=1$ or $N_{ij}^o = N_{ij}$. The explicit dependence of N_{ij} on the interaction energy parameter was obtained in the quasichemical approximation by Guggenheim for binary mixtures without considering vacant sites or 'holes'.

2. An Elementary Derivation of Helmholtz Free Energy

The expression for the configurational part of the Helmholtz free energy may be obtained using the relations,

$$\beta A^c = -\ln\Omega^c \tag{13}$$

As recently presented in detail by the present authors [You et al., 1993, 1994a, b, c; Shin et al., 1994a, b, 1995a, b; Yoo et al., 1994, 1995], a new configurational Helmholtz free energy can be derived from the full Guggenheim combinatory when l_i is zero by expanding A^c in terms of ε_{ij} around the athermal solution. The resulting expression of A^c is given by:

$$A^c = A^{\infty} + \sum_{i\geq j}\Sigma\left(\frac{\partial A^c}{\partial\varepsilon_{ij}}\right)^o \varepsilon_{ij} + \left(\frac{1}{2}\right)\sum_{i\geq j}\sum_{k\geq l}\Sigma\Sigma\left(\frac{\partial^2 A^c}{\partial\varepsilon_{kl}\partial\varepsilon_{ij}}\right)^o \varepsilon_{ij}\varepsilon_{kl} + \cdots \tag{14}$$

where superscript o indicates that the expression is evaluated at the reference athermal solution. When the algebra is done, a generalized rigorous expression of A^c for a multicomponent system can be obtained from Eq. (14). It is given by

$$\begin{aligned}\beta A^c = {} & \Sigma N_i \ln\ \rho_i + N_0 \ln(1-\rho) - \frac{z}{2}N_q \ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right] \\ & - \left(\frac{zN_q}{2}\right)\beta\left[\Sigma\Sigma\theta_i\theta_j\varepsilon_{ij} + \left(\frac{\beta}{2}\right)\Sigma\Sigma\Sigma\Sigma\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}\right. \\ & \left.\times(\varepsilon_{ij} + \varepsilon_{kl} - \varepsilon_{ik} - \varepsilon_{jk})\right]\end{aligned} \tag{15}$$

where $q_M = \Sigma x_i q_i$, $r_M = \Sigma x_i r_i$ and x_i is the mole fraction of species i. The lattice interaction energy ε_{ij} is the absolute value of the interaction energy between a segment of species i and that of species j, which is assumed as follows,

$$\varepsilon_{ij} = \sqrt{(\varepsilon_{ii}\varepsilon_{jj})}(1-\lambda_{ij}) \tag{16}$$

where the λ_{ij} is the binary interaction parameter. ε_{ij} between holes and molecular species is set to zero. Thus, from Eq. (15) all configurational thermodynamic functions can be formulated.

3. A Simplified Version of Helmholtz Free Energy

Although the formulation of Eq. (15) is self-consistent with a sound theoretical basis, a less complicated model would be more convenient in engineering oriented phase equilibrium calculations. Accordingly, we put our efforts to make the previous expression less complicated while preserving comparable accuracy. As recently presented in detail by the present authors elsewhere [Shin et al., 1994a, b, 1995a, b], the rigorous expression of A^c given by Eq. (15) can be reexpressed as

$$A^c = A^{c(A)} + A^{c(R)} + A^{c(NR)} \tag{17}$$

where the 'athermal' part, $A^{c(A)}$, is equivalent to a combinatorial contribution in the random array, the 'random' part, $A^{c(R)}$, is due to energy of random mixing and the 'nonrandom' part, $A^{c(NR)}$, corrects for effect of nonrandom mixing.

We proposed an empiricization on the same lattice concepts. While retaining the athermal part, we may replace the remaining part by the sum if ideal solution part and excess part as,

$$A^c = A^{c(A)} + A^{c(IS)} + A^{c(E)} \tag{18}$$

where the athermal part is given by Eq. (15),

$$\beta A^{c(A)} = \Sigma N_i \ln \rho_i + N_0 \ln(1-\rho) - \frac{z}{2} N_q \ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right] \tag{19}$$

The remaining parts are obtained using the thermodynamic relation at constant volume and composition,

$$\frac{A}{T} = \int_{1/T_0}^{1/T} U d\left(\frac{1}{T}\right) + \text{constant} \tag{20}$$

as in the derivation of the UNIQUAC model [Wilson, 1964]. The internal energy, U, is the sum of the 'ideal solution' part and the 'excess' part in the frame of the nonrandom two-fluid theories as follows

$$-U^{IS} = \frac{z}{2} \Sigma N_i q_i \theta_{ii}^{(0)} \varepsilon_{ii} \tag{21}$$

$$-U^{E} = \frac{z}{2} \Sigma N_i q_i (\Sigma \theta_{ji}^{(1)} \varepsilon_{ji} - \theta_{ii}^{(0)} \varepsilon_{ii}) \tag{22}$$

where θ_{ji} is the local surface area fraction of component j around the segment of component i and the superscripts (0) and (1) denote the states before mixing and after mixing, respectively.

We introduce two assumptions to simplify the evaluation of Eqs. (21) and (22). The first is that the holes are random as Panayiotou and Vera [1982] assumed in a different context. Then the following relation holds, $\theta^{(1)} = \Sigma N_i q_i / N_q = \Sigma \theta_{ji}^{(1)}$. We have only one molecular species in the pure fluid state. Therefore for each pure species, $\theta_i^{(0)} = \theta_{ii}^{(0)}$. The second assumption is $\theta^{(1)} = \theta_i^{(0)} = \theta$ which implies that the total surface area fraction occupied by molecules is the same whether molecules are in pure states or in mixtures. This assumption becomes exact as the number of holes decreases to zero, in which case $\theta = 1$. Based on these assumptions, dropping the superscripts and rewriting Eqs. (21) and (22), we have

$$-U^{IS} = \frac{zN_q}{2} \Sigma N_i q_i (\theta \varepsilon_{ii}) \tag{23}$$

$$-U^{E} = \frac{zN_q}{2} \Sigma \theta_i \Sigma \overline{\theta}_{ji} [\theta(\varepsilon_{ji} - \varepsilon_{ii})] \tag{24}$$

In writing Eq. (24), we have also defined the surface area fraction on the hole free basis as $\overline{\theta}_i = N_i q_i / \Sigma N_j q_j = \theta_i /,\theta$ and $\overline{\theta}_{ij} = \theta_{ij} /.\theta$ $\overline{\theta}_{ji}$ is then written in the following nonrandom mixing form as discussed by Wilson [1964],

$$\overline{\theta} = \frac{\tau_{ji}\ \overline{\theta}_j}{\Sigma \tau_{ki}\ \overline{\theta}_k} \tag{25}$$

where the nonrandomness factor τ_{ji} is derived as $\tau_{ji} = \exp[\beta\theta(\varepsilon_{ji} - \varepsilon_{ii})]$

Now using Eq. (20) we can convert Eqs. (23) and (24) into corresponding Helmholtz energy expressions.

$$-A^{c(IS)} = \frac{zN_q}{2} \theta \Sigma N_i q_i \varepsilon_{ii} \tag{26}$$

$$-\beta A^{c(E)} = \frac{zN_q}{2} \Sigma \theta_i \ln[\Sigma \overline{\theta}_j \tau_{ji}] \tag{27}$$

The sum of Helmholtz free energies given by Eqs. (19), (26) and (27) yields the complete configurational Helmholtz free energy. The free energy expression is similar to that of the UNIQUAC model. The main difference is that the lattice contains holes now and an EOS can readily be derived from the free energy.

MODELING LATTICE EOS AND CHEMICAL POTENTIAL

From the rigorous and simplified configurational Helmholtz free energy equations given by Eq. (15) and Eq. (18), respectively, expressions for configurational thermodynamic properties can be obtained for each case. Since the volume V is represented by $V = V_H(N_o + \Sigma_i r_{i,})$ both EOSs are obtained from the relation; $P = -1/V_H(\partial A^c/\partial N_0)_{T,N_1}$. When the algebra is done, we have apparently identical form of EOS for both cases as follows

$$P = \frac{1}{\beta V_H}\left\{\frac{z}{2}\ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right] - \ln(1-\rho)\right\} - \left(\frac{z}{2}\right)\theta^2 \frac{\varepsilon_M}{V_H} \tag{28}$$

Where ε_M of rigorous case is differ from the simplified case. They are given by,

$$\varepsilon_M^{(R)} = \frac{1}{\theta^2}\left[\Sigma\Sigma\theta_i\theta_j\varepsilon_{ij} + \left(\frac{\beta}{2}\right)\Sigma\Sigma\Sigma\Sigma\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij} + 3\varepsilon_{kl} - 2\varepsilon_{ik} - 2\varepsilon_{jk})\right] \tag{29}$$

$$\varepsilon_M^{(S)} = \Sigma\overline{\theta}_j\varepsilon_{jj} + \Sigma\overline{\theta}_j \frac{\Sigma\overline{\theta}_k\tau_{kj}(\varepsilon_{kj} - \varepsilon_{jj})}{\Sigma\overline{\theta}_k\tau_{kj}} \tag{30}$$

Here, $\varepsilon_M^{(R)}$ denotes for 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 by the equation; $\mu_i = N_a(\partial A/\partial N_i)_{T,V} = N_a(\partial A/\partial N_i)_{T,N_0} + r_i N_a V_H P$. Here N_a is the Avogadro's number. The resulting equations for both cases are written by,

$$\frac{\mu_i}{RT} = \frac{\mu_i^{(A)}}{RT} + \frac{\mu_i^{(R)}}{RT} \text{ and } \frac{\mu_i}{RT} = \frac{\mu_i^{(A)}}{RT} + \frac{\mu_i^{(S)}}{RT} \tag{31}$$

where

$$\frac{\mu_i^{(A)}}{RT} = \gamma_i(T) - r_i\ln(1-\rho) + \ln\left(\frac{\theta_i}{q_i}\right) + r_i\ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right] \tag{32}$$

$$\frac{\mu_i^{(R)}}{RT} = -\frac{zq_i\beta\varepsilon_M\theta^2}{2}\left[1 - \frac{r_i}{q_i} - \frac{2\Sigma\theta_j\varepsilon_{ij} + \beta\Sigma\Sigma\Sigma\theta_k\theta_l\theta_m\varepsilon_{ik}(\varepsilon_{ik} + 2\varepsilon_{lm} - 2\varepsilon_{kl} - \varepsilon_{il})}{\theta^2\varepsilon_M}\right] \tag{33}$$

$$\frac{\mu_i^{(S)}}{RT}=-\frac{zq_i\beta\varepsilon_M\theta^2}{2}\left[1-\frac{r_i}{q_i}-\frac{1}{\theta}\frac{(1+\varepsilon_{ii})}{\varepsilon_M}\right]$$
$$+\frac{zq_i}{2}\left[1-\ln(\Sigma\overline{\theta}_j\tau_{ji})-\Sigma\frac{\overline{\theta}_j\tau_{ij}}{\Sigma\overline{\theta}_k\tau_{kj}}\right] \tag{34}$$

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 pure fluids [You et al., 1994a; Shin et al., 1995a].

The difference in chemical potential of component i in the mixture and the chemical potential of pure component i at the same temperature and pressure, $\Delta\mu_i/RT$ can readily be derived. Then, the activity coefficient can be obtained by the expression

$$\frac{\Delta\mu_i}{RT}=\frac{\mu_i-\mu_{i,\,pure}}{RT}=\ln a_i=\ln(x_i,\ \gamma_i) \tag{35}$$

The Flory-Huggins χ_{ij} interaction parameter may be directly obtained by the equation

$$\frac{\Delta\mu_i}{RT}=\ln\ \phi_i+\left[1-\frac{r_i}{r_j}\right]\ \phi_j+\chi_{ij}\phi_j^2 \tag{36}$$

One of the advantages inherent to the lattice fluid theory is that the Guggenheim combinatory can readily be extended to r-mers and thus the EOS proposed here can be applied to polymer solutions. Comparisons of the present EOS to experimental data for polymer solutions are discussed in part II of the present article.

THERMODYNAMIC PROPERTIES FOR PURE SYSTEMS

1. EOS, Chemical Potential and Fugacity Coefficient

For pure fluids, the simplified EOS given by Eqs. (28) and (30) reduced to the following expression since all ε_M become ε_{ii} and τ_{ij} become 1 for pure compounds because holes are assumed to be random. Therefore EOS given by Eq. (28) and chemical potential Eq. (31) are simplified as follows.

$$P=\frac{1}{\beta V_H}\left\{\frac{z}{2}\ln\left[1+\left(\frac{q_1}{r_1}-1\right)\rho\right]-\ln(1-\rho)\right\}-\left(\frac{z}{2}\right)\theta_1^2\frac{\varepsilon_P}{V_{H'}} \tag{37}$$

where ε_P of the rigorous case is differ from the simplified case. They are given by,

$$\varepsilon_P^{(R)}=\varepsilon_{11}\left[1-\left(\frac{\beta\varepsilon_{11}}{2}\right)\ \theta_o(2\theta_1-\theta_o)\right] \tag{38}$$

$$\varepsilon_P^{(S)}=\varepsilon_{11} \tag{39}$$

Here, $\varepsilon_P^{(R)}$ denotes for rigorous case and $\varepsilon_P^{(S)}$ for simplified case. Especially for the simplified case, the equation of state becomes identical to the random case of the lattice theory [Panayiotou and Vera, 1982].

The chemical potential for both cases reduced to,

$$\frac{\mu_1^{(R)}}{RT}=\lambda_1(T)-r_1\ln(1-\rho)+\ln\frac{\theta_1}{q_1}+r_1\ln\left[1+\left(\frac{q_1}{r_1}-1\right)\rho\right]$$
$$-\frac{zq_1\beta\varepsilon_P^{(R)}\theta_1^2}{2}\left[1-\frac{r_1}{q_1}-\frac{2\theta_1+(\beta\varepsilon_{11})\theta_o\theta_1(1-2\theta_1)}{\theta_1^2\varepsilon_P^{(R)}/\varepsilon_{11}}\right] \tag{40}$$

$$\frac{\mu_1^{(S)}}{RT}=\lambda_1(T)-r_1\ln(1-\rho)+\ln\frac{\theta_1}{q_1}+r_1\ln\left[1+\left(\frac{q_1}{r_1}-1)\rho\right]$$
$$\frac{zq_1\beta\varepsilon_P^{(S)}\theta_1^2}{2}\left[1-\frac{r_1}{q_1}-\frac{2}{\theta_1}\right] \tag{41}$$

where superscript (R) represent for rigorous case and that of (S) the simplified case. Based on the familiar classical thermodynamic relations, the Fugacity coefficients for pure component 1 for both cases are obtained as

$$\ln\phi_1^{(R)}=-r_1\ln(1-\rho)-(1-r_1)\ \ln\left[1+\left(\frac{q_1}{r_1}-1\right)\rho\right]$$
$$-\frac{z\beta\varepsilon_{11}}{2}\left[\frac{r_1\theta_1^2}{\rho_1}+q_1\theta_1-\frac{q_1}{z}\theta_1\theta_o^2\right]+\frac{r_1z(\beta\varepsilon_{11}^2)}{4\rho}$$
$$\theta_1\theta_o^2(2\theta_1-\theta_o)-\ln Z_1 \tag{42}$$

$$\ln\phi_1^{(S)}=-r_1\ln(1-\rho)-(1-r_1)\ \ln\left[1+\left(\frac{q_1}{r_1}-1\right)\right.$$
$$-\frac{\rho z\beta\varepsilon_{11}\theta_1q_1}{2}\left[1+\frac{r_1\theta_1}{q_1\rho}\right]-\ln Z_1 \tag{43}$$

where Z_1 is the compressibility factor.

2. Second Order Properties

For polymers, experimental data are often reported as a second order thermodynamic functions such as the thermal expansion coefficient α_1 and the isothermal compressibility factor β_1. Here we omit expressions of those properties for the rigorous case are omitted here [You et al., 1993, 1994a, c] and we only show the expressions for the simplified case. The expressions for them are obtained from the simplified EOS as

$$T\alpha_1^{(S)}=\frac{T}{V}\left[\frac{\partial V}{\partial T}\right]_P=-\frac{T}{\rho}\left[\frac{\partial\rho}{\partial T}\right]_P+\frac{T}{V_1^*}\left[\frac{\partial V_1^*}{\partial T}\right]$$
$$=\frac{\beta PV_H+\theta_1^2\left[\frac{\beta\varepsilon_{11}}{2}-\frac{z}{2}-\beta\varepsilon'_{11}\right]}{{}^{P}\left[\frac{\rho}{1-\rho}+\frac{(1-r_1)\theta_1}{q_1}-\frac{\beta\varepsilon_{11}r_1\theta_1^3}{q_1\rho}\right]}+\frac{r_1'}{r_1} \tag{44}$$

$$P\beta_1^{(S)}=-\frac{P}{V}\left[\frac{\partial V}{\partial p}\right]_T=\frac{P}{\rho}\left[\frac{\partial\rho}{\partial P}\right]$$
$$=\frac{\beta PV_H}{{}^{T}\left[\frac{\rho}{1-\rho}+\frac{(1-r_1)\theta_1}{q_1}-\frac{\beta\varepsilon_{11}r_1\theta_1^3}{q_1\rho}\right]} \tag{45}$$

where ε_{11}' and r_1' are derivatives of ε_{11} and r_1 with respect to lnT. They can be determined from the temperature dependence of ε_{11} and V_1^*.

3. Critical Conditions and Phase Transition

The critical point for the vapor-liquid phase transition is determined from the well-known criticality conditions. The criticality conditions are derived from both EOS. Here we only give expressions derived from the case of simplified EOS as follows

$$\left(\frac{\partial P}{\partial\rho}\right)_T=0,\ \left(\frac{\partial^2P}{\partial\rho^2}\right)_T=0 \tag{46}$$

$$\frac{\partial P}{\partial\rho}=\frac{z\varepsilon_{11}}{2V_H}\left\{\frac{1}{1-\rho}+\frac{z}{2}\left[\frac{q_1/r_1-1}{1+(q_1/r_1-1)\rho}\right]-\frac{z\beta\varepsilon_{11}r_1\theta^3}{q_1\rho^2}\right\} \tag{47}$$

$$\frac{\partial^2P}{\partial\rho^2}=\frac{z\varepsilon_{11}}{2V_H}\left\{\frac{1}{(1-\rho)^2}-\frac{z}{2}\left[\frac{\frac{q_1}{r_1}-1}{1+\left(\frac{q_1}{r_1}-1\right)\rho}\right]^2\right.$$
$$\left.-\frac{z\beta\varepsilon_{11}r_1^2\theta_1^4}{q_1^2\rho^4}\left[1-2\left(\frac{q_1}{r_1}-1\right)\rho\right]\right\} \tag{48}$$

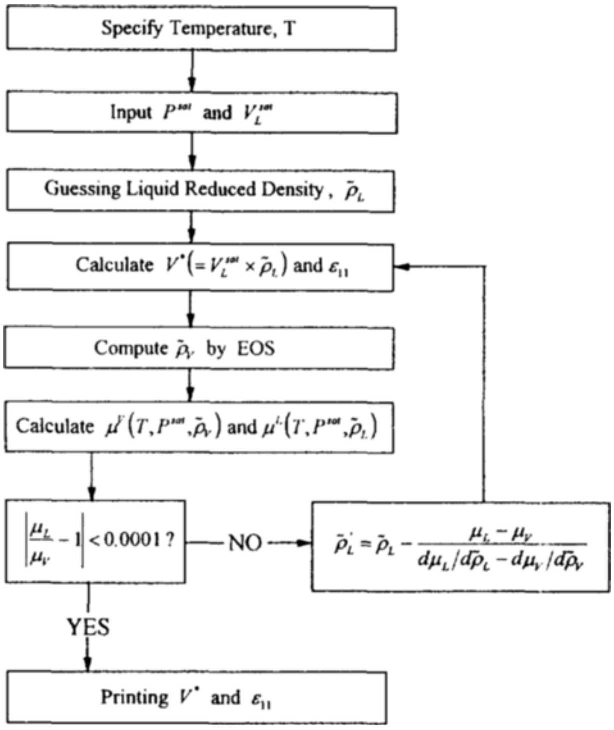

Fig. 1. Algorithm used for the estimation of pure molecular parameters.

Once expressions for the criticality conditions are evaluated, the critical compressibility factor Z_c is readily calculated,

$$Z_c=\frac{r_1P_c}{T_c\rho_c} \tag{49}$$

DETERMINATION OF MOLECULAR PARAMETERS

In formulating both EOSs, the general relation in the lattice theories, $zq_i=zr_i-2r_i+2$ is used by set $l_i=0$. We also define the characteristic volume V_i^* as $V_i^*=N_a V_H r_i$. Therefore the characteristic volume gives sufficient information for determining r_i and q_i. The other molecular parameters are the interaction energy ε_{ii}, the coordination number z, and the unit cell volume V_H. We set z=10 and $V_H=9.75$ cm^{3}mol^{-1} [You et al., 1994a; Shin et al., 1995a]. Thus, both models require two molecular parameters, V_i^* and ε_{ii}, respectively for each pure component i.

Based on various sources of experimental data as discussed elsewhere by the present authors [You et al., 1993, 1994a; Shin et al., 1995b], the parameters V_i^* and ε_{ii} are determined by a regression analysis at each isotherm and readily fitted to the following empirical correlations as a function of temperature for an easy engineering practice.

$$\frac{\varepsilon_{ii}}{k}=E_a+E_bT+E_c\ \ln T \tag{50}$$

$$V_i^*=V_a+V_bT+V_c\ln T \tag{51}$$

Since the range of molecular species to which both the rigorous EOS and the simplified EOS would be applicable are very wide, the parameters V_i^* and ε_{ii} for pure fluids are determined by means of possible different methods depending on the property data available at the temperature of interest. For the gases above the critical point p-ρ-T data are fitted to the model to determine the two parameters for each isotherm by a conventional regression analysis.

Table 1. Basic properties of solids and vapor pressure coefficient of subcooled liquids for pure parameter estimation

Species	T_m [K]	T_b [K]	T_C [K]	P_C [KPa]	Z_C	W	W_{SRK}	V_{HBT} [cm^3/mol]
Benzoic acid	395.6	523.	752.	4560	.25	.62	-	-
Naphthalene	353.5	491.1	748.4	4050	.269	.302	.300	383.4
Biphenyl	342.4	529.3	789.	3850	.295	.372	.363	489.0
Anthracene	489.7	613.1	869.3	3080	.236	.353	-	-
Phenathrene	373.7	613.	873.	3130	.239	.330	.432	571.1
Myristic acid	330.7	-	739.3	1640	-	.952	-	-
Palmitic acid	337.2	-	777.7	1410	-	.975	-	-
Stearic acid	342.5	-	798.8	1230	-	.968	1.231	1343.
Penicillin V	-	733.8	921.7	1720	-	1.168	-	-

Species	VPA	VPB	VPC	VPD	EQS[a]
Benzoic acid	10.5432	4190.70	−125.20	0.	2
Naphthalene	−14.1844	16.6765	−23.538	30.653	1
Biphenyl	−7.6740	1.2301	−3.679	−2.292	1
Anthracene	11.0499	6492.44	−26.130	0.	2
Phenathrene	10.0985	5477.94	−69.390	0.	2
Myristic acid	4.9559	−31.2184	30.481	−43.118	1
Palmitic acid	−4.7425	−11.0978	12.217	−36.926	1
Stearic acid	−4.1199	−13.4943	10.728	−24.567	1
Penicillin V	7.0507	3265.57	142.19	0.	3

a. EQS(1) Miller's Equation

$$\ln\left(\frac{P^{sat}}{P_c}\right)=(1-x)^{-1}[(VPA)x+(VPB)x^{1.5}+(VPC)x^3+(VPD)x^6],\ x=1-\frac{T}{T_c}$$

EQS(2) Antoine's Equation

$$\ln\ P^{sat}=VPA-\frac{VPB}{T+VPC}$$

Where, P^{sat}[bar], T[K]

For liquids and vapors in the subcritical region, parameters are determined using the vapor pressure and the saturated liquid volume wherein the relations of vapor-liquid equilibrium pressure and chemical potential for vapor and liquid phases, i.e., $P^V=P^L$ and $\mu^V=\mu^L$ are used for each isotherm. The algorithm used for estimating the molecular parameters in this way are shown in Fig. 1. In the calculation, substances whose vapor pressure and saturated liquid volume are not available, the method of Frost-Kalkwarf-Thodos or that of Miller is used for vapor pressure and the Hankinson-Brost-Thomson equation or the modified Racket equation is used for the liquid volume. These equations are also used at temperatures below the melting point for the estimation of subcooled liquid properties, which are required in the equilibrium calculation involving solid components. These equations are reviewed in the literature by Reid et al. [1986] and the parameters obtained in the present study for these empirical correlative equations are shown in Tables 1 and 2.

For macromolecular species such as polymers whose vapor pressure is negligible, we can only use data or correlations for liquid density. Since we cannot determine two parameters from a single property, we need an independent relation which may be provided by an atomic group contribution [Bondi, 1968; van Krevelen, 1990; Timmermans, 1950]. Once V_i^* is estimated by this idea the energy parameter ε_{ii} can be determined using the saturated

Table 2. Vapor pressure coefficient and molar volume of solids

Species	Formula	M.W.	V^S[cm^3/mol]	VPA	VPB	VPC	T range[K]
Benzoic acid	C7H6O2	122.12	122.	9.408	4618.1	0.	308.15-343.15
Naphthalene	C10H8	128.17	110.	8.722	3783.0	0.	308.15-353.15
Biphenyl	C12H10	154.21	132.	9.804	4367.4	0.	308.15-343.15
Acridine	C13H9N	179.22	178.	8.721	4740.1	0.	308.15-343.15
Anthracene	C14H10	178.23	142.	9.755	5313.7	0.	308.15-343.15
Phenathrene	C14H10	178.23	151.	8.545	4567.7	0.	308.15-343.15
Myristic acid	C14H28O2	228.38	264.8	18.303	8695.4	0.	308.15-313.15
Palmitic acid	C16H32O2	256.43	300.6	8.304	4099.7	0.	308.15-313.15
Stearic acid	C18H36O2	280.45	335.9	7.019	3703.7	0.	308.15-313.15
Penicillin V	C16H18N2O5S	350.40	231.7	4.814	4430.5	0.	314.85-334.85

where, $\log P^{sat}[\mathrm{Bar}] = \mathrm{VPA} - \dfrac{\mathrm{VPB}}{T[\mathrm{K}] + \mathrm{VPC}}$

Table 3. Coefficients of volume and energy parameter correlations for the simplified EOS

Chemicals	Formula	E_a	E_b	E_c	V_a	V_b	V_c	T range[C]
−Non polar substance								
Pentane	C5H12	100.22	.0309	−2.74	79.21	−.0007	3.48	0-177
Heptane	C7H16	92.66	.0381	−0.97	120.38	−.0050	1.79	0-240
Butene	C4H8	90.66	.0093	−0.470	84.81	.0248	−2.30	0-110
Benzene	C6H6	167.01	.0292	−9.84	19.08	−.0153	11.90	10-200
Styrene	C8H8	115.06	.0237	0.01	26.97	−.0339	15.98	30-240
Ethylbenzene	C8H10	234.54	.0910	−25.43	28.56	−.0334	16.57	0-200
−Weak polar substance								
Diisopropylether	C6H14O	119.57	.0486	−7.04	111.54	−.0101	2.38	0-200
Tetrahydrofuran	C4H8O	128.05	−.0076	−0.93	83.15	.0264	−2.73	0-200
Strong polar substance								
Chloroform	CHCl3	124.20	−.0081	−0.29	69.98	.0194	−0.38	0-210
Acetic acid	C2H2O2	171.43	−.1360	7.81	60.96	.0445	−3.30	30-240
Water	H2O	1394.12	−.2031	−162.56	51.50	.0320	−7.55	0-200
Methanol	CH4O	916.94	.0805	−131.58	−16.36	.0081	9.29	15-220
Ethanol	C2H6O	598.84	.0453	−79.77	61.60	.0299	−2.45	30-110
Propanol	C3H8O	736.17	.1585	−111.64	−51.16	−.0274	22.80	10-244
Butanol	C4H10O	255.40	−.0649	−16.80	33.13	.0004	9.30	0-200
Butanol, tert	C4H10O	142.27	−.1250	3.00	−80.24	−.0680	33.06	20-105
Supercritical substance								
Carbon dioxide	CO2	745.19	.3371	−133.48	−56.87	−.0090	16.92	−27-137
Ethane	C2H6	181.79	.0842	−22.85	−12.99	−.0401	13.46	−27-207
Ethylene	C2H4	162.22	.0696	−19.09	38.17	.0113	0.94	−27-207
Low vapor pressure substance								
Naphthalene	C10H8	97.41	.0114	6.39	10.85	−.0352	20.14	10-217
Palmitic acid	C16H32O2	459.21	.2238	−71.73	206.82	−.0842	17.94	10-200
Stearic acid	C18H36O2	303.20	.1388	−39.50	94.89	−.0840	38.20	10-200
Penicillin V	C16H18N2O5S	41.12	.3746	0.77	519.83	.3269	−76.15	30-150

liquid volume.

The extensive compilations of the estimated values of coefficients for pure components defined by Eqs. (50) and (51) are summarized in references [You et al., 1993, 1994a] for the case of rigorous EOS given by Eq. (37) and (38) up to 200 pure fluids. Also, the values of coefficients in Eq. (50) and (51) for simplified EOS given by Eq. (37) and (39) up to 200 pure components are summarized in reference [Shin et al., 1995b]. Especially the estimated coefficients in reference [Shin et al., 1995b] categorize pure systems as nonpolar, weak polar, strong polar, supercritical and low volatile substances. As a demonstration, the values of coefficients given by Eqs. (50) and (51) for simplified cases for several systems are summarized in Table 3. Also, the estimated coefficients for some illustrative common polymers are shown in Table 4. Accordingly we used these values in the illustrations discussed in part II of the present article.

APPLICATION TO PURE FLUIDS

As far as the case of the rigorous EOS given by Eqs. (37) and (38) is concern, we discussed in detail elsewhere (Table 1 and 2 in reference [You et al., 1994a]), the computational aspects and the exclusive comparisons of the rigorous EOS with experimental data, so we omit here the justification of the theoretical and practical aspects of the rigorous EOS. Here, we briefly illustrate the applicability of the case of simplified EOS given by Eqs. (37) and

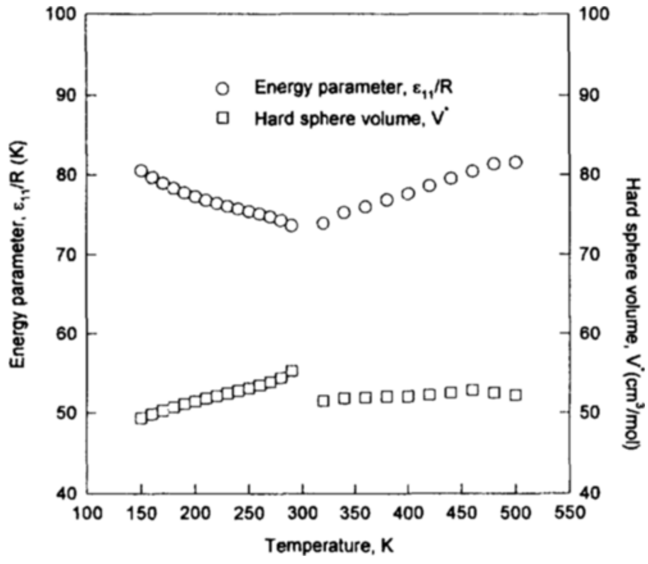

Fig. 2. Discontinuities of pure molecular parameters across the critical region of ethane.

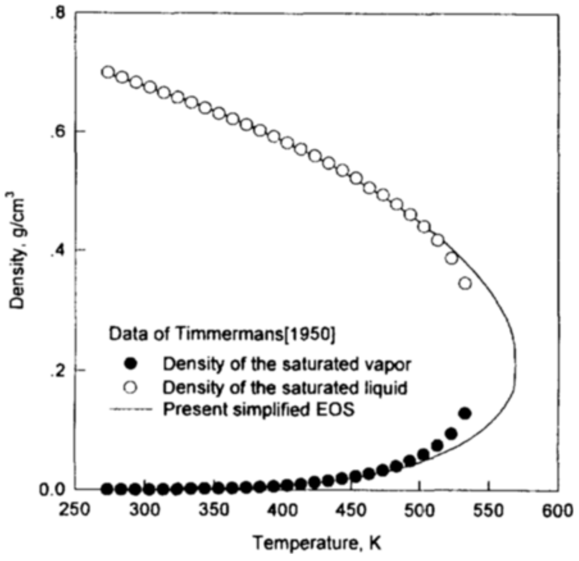

Fig. 4. Calculated saturation density-temperature diagram for heptane in the subcritical region by the simplified EOS.

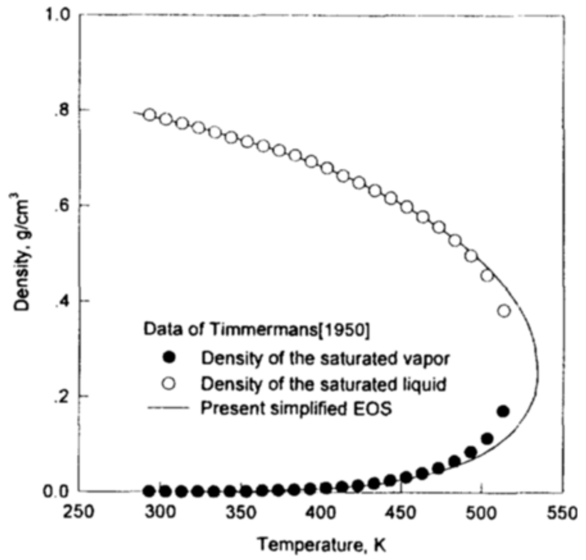

Fig. 3. Calculated saturation density-temperature of ethanol in the subcritical region by the simplified EOS.

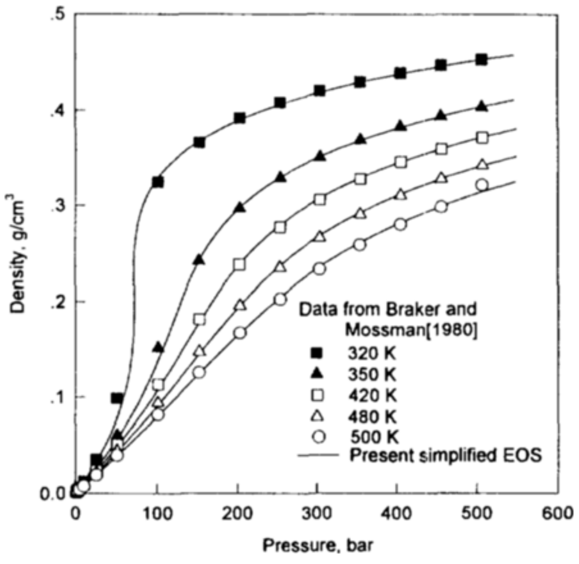

Fig. 5. Calculated isothermal density-pressure of pure ethane in the supercritical region by the simplified EOS.

(39) to pure fluids. Further illustrative applications to the various phase Equilibria of mixtures based on the EOSs presented here are discussed in part II of the present article.

For pure fluids useful at high pressure such as those fluids as used in supercritical fluid technology, the experimental data range from subcritical to supercritical region. In these fluids, we intendedly presented smoothed regression values of parameters in Table 3 despite the existence of discontinuities as illustrated in Figure 2 for ethane. The same discontinuities are observed for other supercritical fluids and light hydrocarbons.

For light substances useful below their critical temperature, comparison of a model to experimental ρ^{sat}-P^{sat}-T data in the subcritical region and ρ-P isotherms in the supercritical region provides reasonable tests for the newly formulated EOS. For a wide range of temperatures and pressures, the simplified EOS was extensively tested. As a result we concluded that the present simplified EOS can quantitatively be used for the calculations of thermodynamic properties of pure components except in the near critical region. As the illustrations show, calculated results of saturation densities for ethanol and heptane are compared with experimental data reported by Timmermans [1950] and they are shown in Figs. 3 and 4, respectively. As one can see in these figures, the error becomes smaller as the pressure is lowered and larger as the critical point is approached. Correlated molecular parameters deviate from the best fitted values near the critical temperature due to the discontinuity in the temperature dependence of parameters and thus introduce large errors in this region.

The other EOSs in the same genre based on the Guggenheim combinatory such as the EOS proposed by Okada and Nose [1981 a, b], Panayiotou and Vera [1982], Kumar et al. [1978] and Smirnova and Victorov [1978], together with the present EOS are based on the mean field approximation to the partition function

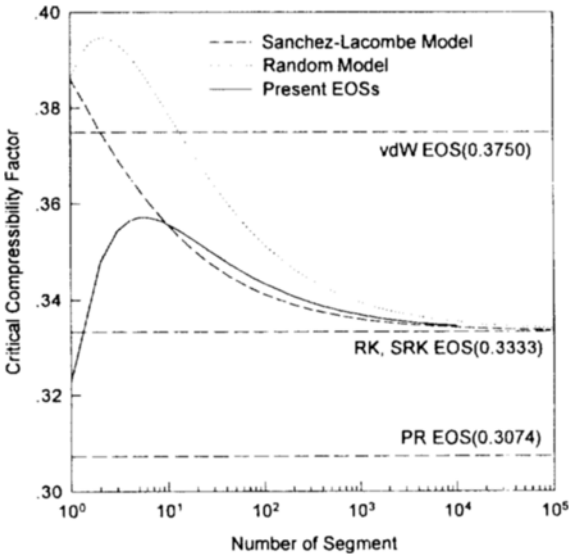

Fig. 6. Dependence of critical compressibility factor as a function of number of segment for equations of state based on the lattice theory.

Table 4. Coefficients of the energy and volume parameter correlations for the simplified EOS for common polymers

Polymer	E_a	E_b	E_c	V*
	K	–	K/lnK	cm^3/g
Polystylene (atatic)	84.318	.1117	0.	.8801
Poly (vinyl acetate)	120.287	−.0035	0.	.7850
Polyisobutylene	95.868	.0624	0.	1.0080
Poly (propylene oxide)	102.436	.0055	0.	.9162
Poly (dimethyl siloxane)	67.001	.0730	0.	.8911
Polyethylene (branched)	92.833	.0710	0.	1.0954
Polyethylene (HMW, linear)	123.201	.0055	0.	1.1077
Polyethylene (linear)	113.946	.0267	0.	1.0951
Poly (o methylstyrene)	91.897	.1022	0.	.9000
Poly (methyl methacrylate)	111.454	.0659	0.	.790
Poly (n butyl methacrylate)	99.633	.0518	0.	.8810
Poly (c hexyl methacrylate)	99.336	.0790	0.	.8400

and from which some inherent uncertainties tend to occur near the critical region. However, as shown elsewhere by the present authors [You et al., 1993, 1994a] for the case of rigorous EOS, the calculated isotherm near the critical point is slightly better than other models in this genre. Almost similar results are also obtained for the simplified case and we omit further illustration for those aspects. As a final illustration, experimental ρ-P isotherm data for ethane [Timmermans, 1950] are compared with the simplified EOS. In the pressure region ranges from 1 to 50 MPa, the EOS correlates supercritical data quantitatively well. Our intention was to find parameters by simple means for use the model EOS in the equilibrium calculations of complex mixtures and in this regards, the parameters shown in Table 3 for ethane are determined mainly with the experimental data below the critical point.

Finally to check the critical behavior of the present EOS, the compressibility factor, Z_c is calculated as a function of segment number, r_i for the EOSs present here by using the criticality conditions given by Eq. (46) together with the EOS proposed by Sanchez and Lacombe [1976a, b, 1978] and random case [Panayiotou and Vera, 1982]. In case of cubic EOSs, Z_c's are the constant values (i.e., 0.375 for van der Waals' EOS, 0.333 for original Redlich-Kwong and RK-Soave EOSs [Soave, 1972, Redlich and Kwong, 1940], and 0.3074 for the Peng-Robinson EOS [Peng and Robinson, 1976]. However, for the case EOSs based on the lattice fluid theories, Z_c's are depend on both the number of molecular segment and the random or nonrandomness of fluids as shown in Fig. 6. For most of real fluids, Z_c's usually stay below 0.30. When we set the segment number as $r_i = 1$, Z_c of Sanchez-Lacombe EOS, which is based on random lattice, is 0.38 while it is 0.323 for the present nonrandom EOSs. When we set r_i infinite, all the EOSs based on the lattice fluid theory converge to 0.333. As a result, we concluded that the EOSs based on the lattice fluid theories whether they take into account the effect of nonrandomness in lattice description, there exists a certain range of uncertainty in the vicinity of the critical point of pure fluids. However, we believe that both EOSs can be used quantitatively for phase Equilibria as we illustrate fully in part II of the present article except the near critical region; $|T-T_c|/T_c<0.1$ and $|P-P_c|/P_c<0.1$. Also, we believe that any further improvement of lattice-fluid EOSs in the critical region should be combined with such nonclassical critical theories as renormalization techniques and scaling laws of critical exponents.

In summary, the characteristic features of the present EOS with other existing EOSs in terms simplicity, versatile applicability, number of parameters and the dependence of parameters on temperature and pressure are summarized in Table 5.

CONCLUDING REMARKS

A new generalized lattice fluid theory which explicitly take into account the nonrandom distribution of holes for pure fluids and fluid mixtures from the full Guggenheim combinatory has been proposed. Also, extendedly, a new simplified EOS has been pro-

Table 5. Comparison of the present EOS with others in the same genre

Model EOSs	No. of pure parameters	Binary parameters	Remarks	Reference
New Flory	v^*_{sp}, T^*, P^*	s_i/s_j, x_{ij}	dependent on T, p	[29]
Lacombe-Sanchez	v^*, ε_{ii}^*, r	ξ_{12}	for each isotherm	[48]
Okada-Nose	v^*, ε_{ii}	δ_i	implicit in Γ	[51]
Panayiotou-Vera	v^*_{sp}, ε^h_{ii}, ε^s_{ii}	κ_{ij}, Q'_{ij}	implicit in Γ	[52]
Random Hole	v^*_{sp}, ε_{ii}	λ_{ij}	inaccurate	[52]
Kumar-Suter-Reid	v^*_{sp}, ε_{ii}	λ_{ij}	inaccurate	[18]
Victorov-Smirnova	v' w_{ij}, h_{ij}, c_{ij}, l_i	-	multiparameters	[53]
Present models	v^*_{sp}, ε_{ii}	λ_{ij}	unified models	

posed and the molecular thermodynamic framework behind the general derivation of the theory is discussed. The simplified EOS presented here was proposed primarily for practical use in the phase equilibrium calculations of complex and/or macromolecular systems at high densities. The simplified EOS as in the case of the rigorous EOS contains two molecular parameters for a pure fluid and one interaction energy parameter for a binary mixture. We present the application to fluid phase Equilibria of various mixtures based on both the EOSs in part II of the present article.

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NOMENCLATURE

A^c : configurational Helmholtz free energy

$A^{c(A)}$: athermal contribution to A^c

$A^{c(R)}$: random contribution to A^{cX}

$A^{c(NR)}$: nonrandom contribution to A^c

$A^{c(IS)}$: 'ideal solution' contribution to A^c

$A^{c(E)}$: 'excess' contribution to A^c

g_R : number of non-degenerate states for the random distribution

g_{NR} : number of non-degenerate states for the nonrandom correction

N_a : Avogadro's number

N_i : number of molecular species i

N_{ij}^0 : number of i-j segment contacts for the random distribution

N_{ij} : number of i-j segment contacts for the nonrandom distribution

N_0 : number of vacant sites or holes

N_r : defined by $N_r=N_0+\Sigma N_i r_i$

N_q : defined by $N_q=N_0+\Sigma N_i q_i$

P : pressure [bar]

q_i : surface area parameter

q_M : mole fraction average of q_i

r_i : segment number

r_M : mole fraction average of r_i

R : universal gas constant [J mol^{-1}K^{-1}]

T : temperature [K]

U^c : configurational internal energy

U^{IS} : 'ideal solution' contribution to U^c

U^E : 'excess' contribution to U^c

V : molar volume [cm^{3}mol^{-1}]

V_i^* : characteristic volume of component i [cm^{3}mol^{-1}]

V_H : volume of a unit cell [cm^3]

x_i : (liquid) mole fraction of component i

y_i : vapor mole fraction of component i

z : lattice coordination number

Greek Letters

α_1 : thermal expansion coefficient

β : reciprocal temperature [1/kT]

β_1 : isothermal compressibility factor

Ω^c : configurational lattice partition function

Γ_{ij} : nonrandomness correction factor for i-j segment contacts

τ_{ij} : nonrandomness factor defined by Eq. (26)

ε_{ij} : interaction energy for i-j segment contacts [J]

ϕ_i : fugacity coefficient for component i

ρ : total segment fraction

ρ_i : segment fraction of component i

μ_i : chemical potential for component i

λ_i : part of chemical potential due to internal degrees of freedom

λ_{ij} : binary interaction parameter for i-j contacts

θ : total surface area fraction

θ_i : surface area fraction of component i

$\bar{\theta}_i$: surface area fraction of component i on the hole free basis

Superscripts

L : liquid phase

sat : saturation state

S : solid phase

V : vapor phase

' : derivative with respect to ln T

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