contributions for our system. More work is needed to extract detailed conformational information from our NMR data.

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Approximate Nonrandom Two-Fluid Lattice-Hole Theory. General Derivation and Description of Pure Fluids

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An approximate molecular theory of classical fluids based on the nonrandom lattice statistical-mechanical theory is presented. To obtain configurational Helmholtz free energy and equation of state (EOS), the lattice-hole theory of the Guggenheim combinatorics is approximated by introducing the nonrandom two-fluid theory. The approximate nature in the derivation makes the model possible to unify the classical lattice-hole theory and to describe correctly the configurational properties of real fluids including macromolecules. The theory requires only two molecular parameters for a pure fluid. Results obtained to date have demonstrated that the model correlates quantitatively the first- and second-order thermodynamic properties of real fluids. The basic simplicity of the model can readily be generalized to multicomponent systems. The model is especially relevant to (multi) phase equilibria of systems containing molecularly complex species.

Introduction

Knowledge of phase equilibria is essential for the understanding of various phenomena occurring in nature and industrial processes. Investigation of these equilibria, especially in multicomponent systems, is of importance in numerous branches of science and engineering. In principle a single volumetric equation of state (EOS) is sufficient for des-

cribing configurational properties of fluids. However, despite the long history, formulations of EOSs continue to be a less tractable subject of research in molecular thermodynamics. The traditional quest, over 100 years since the seminal work of van der Waals, for equations representing quantitatively the fluid state has been continued by the industrial needs for accurate process design calculations and, on the other hand, by the rapid advances in computational techniques. Among numerous statistical-mechanical theories for configurational properties, the nearest-neighbor lattice statistical-mechanical theory has been studied extensively after Guggenheim's pioneering work.[1]

Stemming from the generalized Guggenheim combinatory, various formulations of solutions were considered by several investigators.[2] A lattice without vacant sites, called 'rigid lattice', has been the base for liquid models. The well known Flory-Huggins model[3] and the UNIQUAC equation[4] can be regarded as one of models in this genre. However, these models cannot be applied to the configurational properties of pure fluids. One way of obtaining an EOS-type model for configurational properties is via the lattice-hole theories. Sanchez and Lacombe initiated the research in this field.[5] Since then, several models have been proposed.[6~10] The present authors[11] have briefly discussed the existing lattice-hole theories related to the full Guggenheim's combinatory and quasichemical approximation,[1,2] while discussing in detail the unique features of the previous works, their advantages and shortcomings.

The authors proposed a new rigorous approximation to the Guggenheim's combinatory and an elementary EOS.[11] Recently, they also proposed a simplified EOS and conformed its quantitative applicability to the description of configurational properties of fluids. Although the previous formulations by the authors were based on a sound statistical-mechanical basis, a further improvement would be more convenient in practice. Thus, in this work we present our efforts to develop a more generalized but relatively simple approximate theory while retaining accuracy comparable to the previous rigorous theories.[11] The generalized expression is based on the introduction of two-liquid theory[12] to the nonrandom contribution of molecules and holes in the lattice. The basic accuracy and simplicity of the present formalism of the pure fluids suggests a suitable generalization to multicomponent mixtures. Further, the pure fluid theory presented here is sufficiently accurate and applicable to a wide range of temperatures and pressures. Thus, the resulting mixture theory can be applied to a high level of predictive capability. Details of the generalized theory for mixture are presented previously in this journal [Vol. 18, No. 8, 841, 1997].

Derivation of The Helmholtz Free Energy

Partition Function for General Hole-Multicomponent Fluids. We briefly discuss here the nonrandom lattice-hole partition function based on the Guggenheim's combinatorics,[1,11] which is used as a basis for the derivation of the present theory. In a three dimensional lattice of the coordination number z and of the unit cell size, V_H, a molecule of component i occupies r_i sites and interacts with the neighboring molecular segment with effective surface area q_i so that the number of external contacts, zq_i equals zr_i-2r_i+2 for open chain r-mers. The configurational part of the partition function may be written as,

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

where the random part, g_R and nonrandom contribution, g_{NR} is written, respectively

$$g_R = [N_r!/(\Pi N_i!)](N_q!/N_r!)^{z/2} \tag{2}$$

$$g_{NR} = (\Pi N_{ii}^0! \Pi[(N_{ij}^0/2)!]^2)/(\Pi N_{ij}!\Pi[(N_{ij}/2)!]^2) \tag{3}$$

where and $N_r=N_o+\Sigma N_i r_i$ and $N_q=N_o+\Sigma N_i q_i$, N_0, is the number of vacant sites (or holes), N_{ij} is the number of i-j segment contacts, and the quantities with superscript zero denote the same for random mixing. N_{ij} satisfies the mass balance relations, $2N_{ii}+\sum N_{ij}=N_i zq_i$, $2N_{ii}^0+\sum N_{ij}^0=N_i zq_i$ including holes. $N_{ii}^0=zN_i q_i \theta_i$, $N_{ij}^0=zN_i q_i \theta_j/2$ and $\theta_i=N_i q_i/N_q$ and it is related to N_{ij}^0 in the quasichemical approximation[5] expressed $N_{ij}=\Gamma_{ij}N_{ij}^0$, and $\Gamma_{ij}^2=\Gamma_{ii}\Gamma_{jj}\exp(-\beta\Delta\varepsilon_{ij})$ and $\Delta\varepsilon_{ii}=\varepsilon_{ii}+\varepsilon_{jj}-2\varepsilon_{ij}$. $\beta=1/kT$.

The configurational part of potential energy in eq. 1 is written as,

$$U^c = \sum_i N_{ii}(-\varepsilon_{ii}) + \sum_{i>j}\sum N_{ij}(-\varepsilon_{ij}) \tag{4}$$

where is the absolute value of interaction energy between segments i and j. 'Athermal solution' corresponds to taking $U^c=0$ and for this solution $g_{NR}=1$ or $\Gamma_{ij}=1$. One difficulty in the first-order solution or the quasichemical approximation of the Guggenheim's combinatory of nonrandom lattice theory has been that it yields the exact solution only for hole-single molecular species systems. Therefore, the solution for real mixtures has to resort to numerical procedures.[6~10]

Approximate Derivation of Helmholtz Free Energy. The configurational Helmholtz free energy may be obtained from Eq. (1) by the relation

$$\beta A^c = -\ln\Omega^f \tag{5}$$

As recently presented by the authors,[11] the configurational Helmholtz free energy in Eq. (5) can be expanded rigorously in terms of ε_{ij} around the reference athermal solution to give the first-order approximation by

$$\beta A^c = \beta A^{c0} + \beta \sum_{i\geq j}\sum \left(\frac{\partial A^c}{\partial \varepsilon_{ij}}\right)^0 \varepsilon_{ij} + \left(\frac{\beta}{2}\right)\sum_{i\geq j}\sum_{k\geq l}\sum\sum \left(\frac{\partial^2 A^c}{\partial\varepsilon_{kl}\partial\varepsilon_{ij}}\right)^0 \varepsilon_{ij}\varepsilon_{kl} + \cdots \tag{6}$$

where superscript 0 indicates that the expression is evaluated at the reference athermal solution. The first term in the r.h.s. of Eq. (6) denotes the reference athermal part, the second term represents the random part, and the higher terms including the third term, correspond to nonrandom contribution. As we have demonstrated elsewhere,[11] the final expression obtained by Eq. (6) describes quantitatively the configurational properties of real fluids. For hole(0)-single component(1) fluids, all i reduced to 1 and all j reduced to 0. However, the resulting Helmholtz free energy is significantly complex due to its series expansional nature. Thus, to make simple while

preserving comparable accuracy, we introduce the two-fluid theory to the lattice combinatorics. Indeed, it is interesting to see if the approximation presented here describes correctly the configurational properties.

While retaining the athermal part, we may replace the remaining parts in Eq. (6) by the residual part as,

$$\beta A^c = \beta A^{c(A)} + \beta A^{c(R)} \tag{7}$$

where the athermal part, $A^{c(A)}$ is equivalent to a combinatorial contribution in the random array in conjunction to Eq. (6) and $A^{c(R)}$ is due to the residual nonrandom interaction energy. In Eq. (7), the athermal part for hole-single component fluid is given by,[11]

$$\beta A^{c(A)} = \sum_{i=1}^{c} N_i \lambda_i + \sum_{i=1}^{c} N_i \ln N_i - \sum_{i=1}^{c} N_i - N_r \ln N_r + N_r$$
$$= \sum_{i=1}^{c} N_i \ln \rho_i + N_0 \ln(1-\rho) - \frac{z}{2} N_q \ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right] \tag{8}$$

where, $q_M = \sum x_i q_i$, $r_M = \sum x_i r_i$, $\rho_i = N_i r_i / N_r$, and $\rho = \sum \rho_i$. x_i is the mole fraction of species i.

While preserving the athermal part, we replace the residual part with the two-fluid theory[4,12] by using the thermodynamic relation at constant volume and composition,

$$\beta A = \int_{\beta_0}^{\beta} U d\beta + \text{constant} \tag{9}$$

where the internal energy, U_c, is residual part in the nonrandom two-fluid theory. If we take β_0 a very high temperature, the solution becomes a random (ideal) mixture. The constant in Eq. (9) becomes $\beta A^{c(A)}$ and the integral becomes $\beta A^{c(R)}$. Thus, Eq. (9) can be rewritten as,

$$\beta A^{c(R)} = \int_0^{\beta} U^c d\beta \tag{10}$$

Now N_{ij} are evaluated in the two-liquid theory,[12]

$$N_{ij} = \frac{z}{2}\left(N_i q_i \frac{q_j \tau_{ji}}{\sum_{k=0}^{c} \theta_k \tau_{ki}} + N_j q_j \frac{\theta_i \tau_{ij}}{\sum_{k=0}^{c} \theta_k \tau_{kj}}\right) \tag{11}$$

where the nonrandomness factor τ_{ji} is defined as,

$$\tau_{ji} = \exp[\beta(\varepsilon_{ji} - \varepsilon_{ii})] \tag{12}$$

ε_{ji} is the absolute value of the interaction energy between segments of species j and ε_{ji} between holes and molecular species is zero. When the algebra is done as shown in Appendix A, we have for $A^{c(R)}$,

$$\beta A^{c(R)} = -\left(\frac{zN_q}{2}\right)\sum_{i=1}^{c} \theta_i \left[\ln\left(\sum_{j=0}^{c} \theta_j \tau_{ji}\right) + \beta\varepsilon_{ii}\right] \tag{13}$$

The sum of Helmholtz free energies given by Eqs. (8) and (13) yields the complete derivation of the configurational free energy, A^c. There are other expressions for configurational properties such as EOS and chemical potential using standard thermodynamic methods.

EOS and Other Thermodynamic Properties of Pure Fluids

EOS, Chemical Potential and Fugacity Coefficient.

Since the system volume V for hole-single component fluids is represented by $V = V_H(N_0 + N_1 r_1)$, the EOS for pure fluids is obtained from the relation of Eqs. (8) and (13),

$$P = \frac{1}{\beta V_H}\left\{\frac{z}{2}\ln\left[1 + \left(\frac{q_1}{r_1} - 1\right)\rho\right] - \ln(1-\rho) + \frac{z\theta_1^2}{2}\left(\frac{\tau_{01} - 1}{\theta_0\tau_{01} + \theta_1}\right)\right\} \tag{14}$$

where $\theta_0 = 1 - \theta_q$.

The chemical potential, μ_i, and fugacity coefficients, ϕ_i for pure component 1 is

$$\frac{\mu_1}{RT} = \lambda_1(T) - r_1 \ln(1-\rho) + \ln\frac{\theta_1}{q_1} + r_1 \ln\left[1 + \left(\frac{q_1}{r_1} - 1\right)\rho\right]$$
$$+ \left(\frac{zq_i\theta_1}{2}\right)\left\{1 - \frac{r_1}{q_1} - \frac{1}{\theta_0}[\ln(\theta_0\tau_{01} + \theta_0) + \beta\varepsilon_{11}] - \frac{1 - \tau_{01} r/q_1}{\theta_0\tau_{01} + \theta_1}\right\} \tag{15}$$

$$\ln\phi_1 = \ln\left(\frac{f_1}{P}\right) = -r_1\ln(1-\rho) - (1-r_1)\ln\left[1 + \left(\frac{q_1}{r_1} - 1\right)\rho\right]$$
$$- \frac{zq_1}{2}\ln\left[1 - \theta_1\left(1 - \frac{1}{\tau_{01}}\right)\right] + \frac{zr\theta_1^2}{2\rho}\left(\frac{\tau_{01} - 1}{\theta_0\tau_{01} + \theta_1}\right) - \ln Z_1 \tag{16}$$

where f_1 is fugacity and Z_1 is the compressibility factor for pure component 1.

Second Order Properties.

The molar configurational internal energy can be obtained from Eq. (13) by the relation,

$$\frac{\beta U^c}{N_1} = -\left(\frac{T}{N_1}\right)\left(\frac{\partial \beta A^c}{\partial T}\right)_{N_0, N_1} = \frac{zq_1'}{2}\ln\left\{1 + \left(\frac{q_1}{r_1} - 1\right)\rho\right\}$$
$$+ \frac{z}{2}(q_1'\theta_1 + q_1'\theta_0)\{\ln(\theta_0\tau_{01} + \theta_1) + \beta\varepsilon_{11}\}$$
$$+ \frac{z}{2}q_1\left\{\frac{\theta_0\theta_1 q_1'/q_1 + \beta\theta_0(\varepsilon_{11} - \varepsilon_{01} - \varepsilon_{11}')\tau_{01}}{\theta_0\tau_{01} + \theta_1} + \beta(\varepsilon_{11}' - \varepsilon_{11})\right\} \tag{17}$$

where the primed quantities denote derivatives with respect to ln T. For q_1' the following relation is obatined,

$$q_1' = r_1'\frac{(z-2)}{z} = \frac{(V_1^*)}{N_a V_H}\frac{(z-2)}{z} \tag{18}$$

For polymers, experimental data are often reported as the second order thermodynamic functions such as the thermal expansion coefficient, α_1 and the isothermal compressibility factor β_1. They are

$$T\alpha_1 = \frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{T}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P + \frac{T}{V_1^*}\left(\frac{\partial V_1^*}{\partial T}\right)_P$$
$$= \beta P V_H + \frac{z\theta_1^2\beta\tau_{01}(\varepsilon_{11} - \varepsilon_{01} - \varepsilon_{11}')}{2(\theta_0\tau_{01} + \theta_1)^2} \Big/ \left[\frac{\rho}{1-\rho} + \frac{z\rho}{2}\left[\frac{q_1/r_1 - 1}{1 + (q_1/r_1 - 1)\rho}\right]\right.$$

$$+\frac{r_1 z\,\theta_1^3(\tau_{01}-1)(2\tau_{01}-\theta_1\tau_{01}+\theta_1)}{\theta_0\tau_{01}+\theta_1)^2}\Bigg]+\frac{r_1'}{r_1} \tag{19}$$

$$P\beta_1=-\frac{P}{\rho}\left(\frac{\partial\rho}{\partial P}\right)_T=\beta PV_H\left\{\frac{\rho}{1-\rho}+\frac{z\rho}{2}\left[\frac{q_1/r_1-1}{1+(q_1/r_1-1)\rho}\right]\right.$$
$$\left.+\frac{r_1 z\,\theta_1^3}{2q_1\rho}\frac{(\tau_{01}-1)(2\tau_{01}-\theta_1\tau_{01}+\theta_1)}{(\theta_0\tau_{01}+\theta_1)^2}\right\}^{-1} \tag{20}$$

where ε_{11}' and r_1' are derivatives of ε_{11} amd r_1 with respect to ln$T$, respectively.

Critical Conditions and Vapor-Liquid Transition. The critical point for vapor-liquid transition is determined from the well-known classical critical conditions, that is

$$\left(\frac{\partial P}{\partial\rho}\right)_T=0=\frac{1}{\beta V_H}\left\{\frac{1}{1-\rho}+\frac{z}{2}\left[\frac{q_1/r_1-1}{1+(q_1/r_1-1)\rho}\right]\right.$$
$$\left.+\frac{r_1 z\,\theta_1^3}{2q_1\rho^2}\frac{(\tau_{01}-1)(2\tau_{01}-\theta_1\tau_{01}+\theta_1)}{(theta_0\tau_{01}+\theta_1)^2}\right\} \tag{21}$$

$$\left(\frac{\partial^2 P}{\partial\rho^2}\right)_T=0=\frac{1}{\beta V_H}\left\{\frac{1}{(1-\rho)^2}-\frac{z}{2}\left[\frac{q_1/r_1-1}{1+(q_1/r_1-1)\rho}\right]^2\right.$$
$$+\frac{r_1 z(\tau_{01}-1)\theta_1^3}{2q_1\rho^3(\theta_0\tau_{01}+\theta_1)^2}\left[\left(\frac{3r_1\theta_1}{q_1\rho}-2\right)(2\tau_{01}-\theta_1\tau_{01}+\theta_1)\right.$$
$$\left.\left.+\frac{r_1\theta_1^2(\tau_{01}-1)(3\tau_{01}-\theta_0\tau_{01}+\theta_1)}{q_1\rho(\theta_0\tau_{01}+\theta_1)}\right]\right\} \tag{22}$$

Once Eqs. (21) and (22) are evaluated, the critical compressibility factor is readily obtained

$$Z_c=\frac{r_1 P_c}{T_c\rho_c} \tag{23}$$

When r_1=1, Z_c=0.386 and when r_1=∞, Z_c=1/3 for random distribution of molecules and holes.[5,8] Also, when r_1=1, Z_c= 0.323 when the two-fluid nonrandom distribution contribution is taken into account as discussed by the present authors elsewhere.[11] Also, another value of Z_c=0.342 from the hole theory of liquid, which is identical with the quasi-chemical approximation.[13] Since Z_c of most real fluids is less than 0.3, the present theory is still inaccurate at the critical point, however, the present model gives the most improvement with emphasis in practice among the lattice-hole theory in the same genre.

The vapor pressure and the saturated density of vapor and liquid phases in equilibrium at the system temperature and pressure are calculated from the relation,

$$\mu^V(T,P,\rho^V)=\mu^L(T,P,\rho^L) \tag{24}$$

where the superscript V and L denote vapor and liquid phases, respectively. Using this relation, vapor-liquid equilibrium calculation can be carried out in the subcritical region. Eq. (24) shall also be referred to as the binodal condition.

The solution of Eq. (14) must be obtained by numerical methods. The character of the solution can be seen by rewriting the EOS in the form,

$$F(\rho)=\frac{1}{\beta V_H}\left\{\frac{z}{2}\ln\left[1+\left(\frac{q_1}{r_1}-1\right)\rho\right]-\ln(1-\rho)\right.$$
$$\left.+\frac{z\,\theta_1^2}{2}\left(\frac{\tau_{01}-1}{\theta_0\tau_{01}+\theta_1}\right)\right\}-P=0 \tag{25}$$

In general Eq. (25) has three solutions in the subcritical region, as illustrated in Figure 1. The solutions at the lowest and highest value of ρ correspond to minima, and the intermediate solution corresponds to a maximum in Helmholtz free energy. The highest density minima corresponds to a liquid, while the lower density corresponds to a gas.

For the calculation of the heat of vaporization, the intramolecular modes of motion in the two phases can be assumed to be the same. Then, the heat of vaporization, ΔH^{vap} is obatined from the enthalpy of the existing vapor and liquid phases as,

$$\Delta H^{vap}=H^V-H^L=(U^c+PV^V)^V-(U^c+PV^L)^L \tag{26}$$

Determination of the Molecular Parameters

There are apparently four molecular parameters in the present EOS for pure fluids, z, V_H, $V_i^*(=N_AV_Hr_1)$ and ε_{11}. We set z is 10 and N_AV_H equal to 9.75 cm^3mol^{-1} as used in the lattice-hole theories in the same genre.[2,6-8] N_A is Avogadro's number. The specific choice of the lattice parameter (z and V_H) has no significant effect on the capability of the EOS. Thus, to model real pure fluids, we need to determine two molecular parameters r_1 (or V_1^*) and ε_{11}.

In principle any thermodynamic property can be utilized to determine the parameters, V_1^* and ε_{11}. We, also, expect

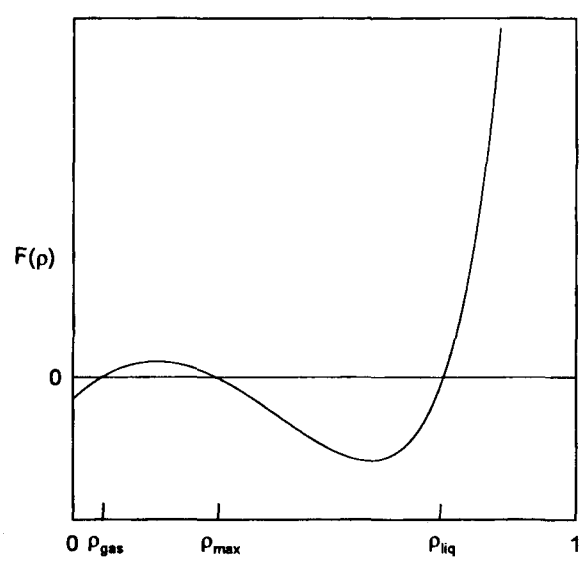

Figure 1. Schematic representation of the solution of the EOS.

Table 1. Numerical values of characteristic volume and energy parameter at 298.15 K for some real fluids

	Energy parameter, ε_{11} (K)	Volume parameter, V^* (cm^3/mol)
Ethane	75.30597	50.00875
1-Butane	90.14383	79.00241
Butene	90.85149	74.59008
Isobutane	85.85598	79.68326
Cyclopentane	107.07006	80.45045
Pentane	93.98580	93.68969
Isopentane	91.76331	86.64576
1-Hexene	97.03353	103.88880
Cyclohexane	108.34441	93.51527
Hexane	96.84253	108.00225
Heptane	98.55286	123.21581
Octane	100.19321	137.49850
Nonane	100.40065	152.59733
Decane	101.40404	151.85464
Undecane	102.48994	181.89423
Dodecane	102.87011	197.11775
Tridecane	104.00080	211.56045
Tetradecane	104.56035	225.34946
Pentadecane	103.97514	241.68011
Hexadecane	103.92734	254.89902
Pentadecane	104.07783	270.54296
Octadecane	104.91673	283.47351
Nonadecane	105.03467	297.84004
Eisosane	106.34487	310.35896
Methanol	193.87737	37.79108
Ethanol	163.58386	53.04182
Butanol	141.53014	82.55258
Cyclohexanol	141.57231	99.53095
Carbon dioxide	85.91302	34.28608
Diethylamine	104.57031	87.98273
Methylcyclopentane	104.14662	95.72049
Phenol	162.35524	83.08802
Water	411.30305	17.79060
Acetone	125.37214	65.30755
Fufural	160.24300	77.88277
Tetrahydrofuran	121.77255	72.02294
Chloroform	121.85711	70.18573
Toluene	118.02728	94.30087
Benzene	119.89117	79.19188
Bipheyl	134.15672	137.24671
Phenathrene	140.72082	155.54797
Benzoic acid	182.15738	101.30545
Anthracene	139.42065	151.69049
Naphthalene	133.60559	114.96641

that the range of molecular species to which the EOS would be applicable is wide and that the parameters for pure fluids are determined by means of different methods depending on the property data available. For fluids in the subcritical region, EOS parameters are determined by using vapor pressure and saturated density. A useful collection of such data is available for organic liquids.[14] For substances for which these data are not availabe, one of the methods Antoine, Miller, Yen-Woods, Rackett, Frost-Kalkwarf-Thodos, or Hankinson-Brost-Thomson is used. These methods

Table 2. Numerical values of characteristic volume and energy parameter at 298.15 K for some common polymers

Polymer	Energy parameter, ε_{11} (K)	Volume parameter, V^*(cm^3/mol)
Polyisobutylene	129.80899	1.00534
Poly(o methylstyrene)	174.58897	.89830
Poly(methyl methacrylate)	186.54804	.78493
Poly(n buthyl methacrylate)	130.38981	.87539
Polyethylene(branched)	125.90716	1.09120
Polyethylene(HMW, linear)	126.19111	1.10371
Polyethylene(linear)	128.03908	1.08934
Polystyrene	153.98175	.87741
Poly(vinyl acetate)	132.63399	.78125
Poly(propylene oxide)	112.62813	.51732
poly(dimethyl siloxane)	99.67046	.89121

for vapor pressure and saturated density are reviewed in the data book.[15] For gases above the critical point, existing pVT data in the literatures[16] can be used.

For polymeric substances whose vapor pressure is extremely low, we can only use appropriate data or correlations for liquid density.[17] Since we cannot determine two parameters from a single property, we need an independent relation which may be provided by atomic group contribution methods.[17,18] In this way, the best fitted values of the two molecular parameters, V_1^* and ε_{11} are obtained at 298.15 K by a standard data regression program and are summarized in Table 1 for some real fluids and in Table 2 for some common polymers, respectively. For versatile use of the model in phase equilibrium calculation for process design purposes, it is desirable to make the two parameters a function of temperature.[6] For polymers, V_1^* s is a specific quantity for one segment. As a result it becomes independent with respect to the molecular weight.

Comparison with Other Lattice Theories and Experiment

Comparison with Other Lattice Theories. The model presented here can be reduced to several well-known theories. First, if we neglect nonrnadom contribution (g_{NR}=1, τ_{ij}=1 N_{ij}=N_{ij}^0) and define reducing parameters, $(z/2)\varepsilon_{11}=P^*V_H=RT^*$, it becomes random form EOS suggested by Panayiotou and Vera,[8] and Kumar *et al.*,[9]

$$\frac{\tilde{P}}{\tilde{T}} = -\ln(1-\tilde{\rho}) + \frac{z}{2}\ln\left[1+\left(\frac{q_1}{r_1}-1\right)\tilde{\rho}\right] - \frac{\theta^2}{\tilde{T}} \qquad (27)$$

where $\tilde{P}=P/P^*$, $\tilde{T}=T/T^*$ and $\tilde{\rho}=V^*/V$.
If we take the large value of z, Eq. (27) becomes the one suggested by Sanchez and Lacombe,[5]

$$\frac{\tilde{P}}{\tilde{T}} = -(1-\tilde{\rho}) + \tilde{\rho}\left(1-\frac{1}{r_1}\right) - \frac{\theta^2}{\tilde{T}} \qquad (28)$$

Since the advantages and shortcomings of Eq. (28) are well-known , we will not elaborate on them here.

If we term the 'holes' as solvent or assign no holes in the mixture form of the configurational Helmholtz free energy

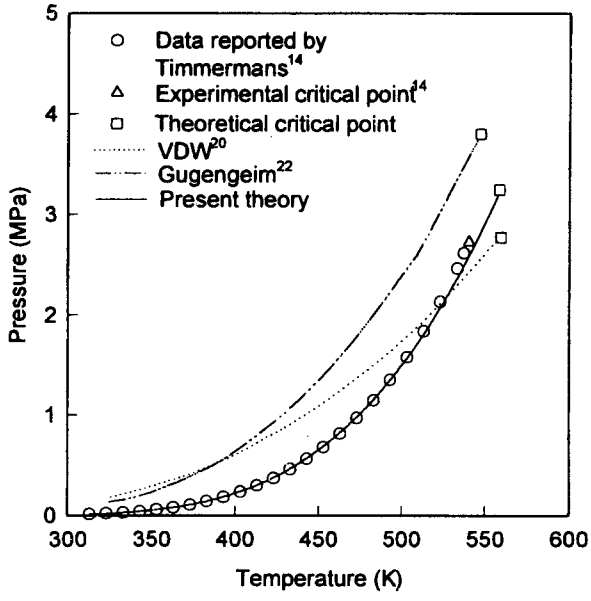

Figure 2. Comparison of experimental vapor pressure data of n-heptane with those calculated by other theories.

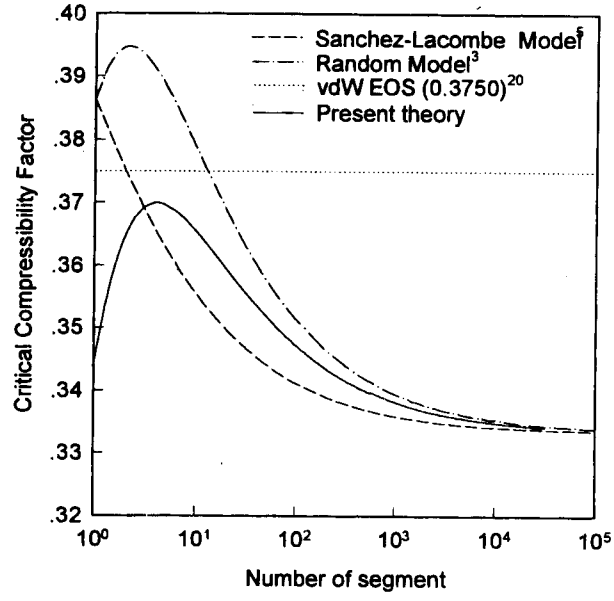

Figure 4. Comparison of various theories for compressibility factor.

expressions in Eq. (8) and (13) with the addition of the bulkiness factor, $l_i=(z/2)(r_i-q_i)-(r_i-1)$, it reduces to the UNIQUAC and UNIFAC-type[19] excess function models[4] which is one of the mixture models used most widely in engineering-oriented usages for liquid mixtures.

In the dilute limit, Eq. (28) is identical with the result one obtains from the Flory approximation[3] for the configurational part of the partition function for a lattice without holes. If we term the vacant site as solvent, make an assumption of a dilute solution, and introduce the definitions; $\tilde{\rho}=\phi_{polymer}$, $\tilde{T}=\chi^{-1}$, $r_1=n_{polymer}$ and $\tilde{P}/\tilde{T}=P_{osm}v_s/RT$, we then recover the Flory equation for the osmotic pressure[3] from Eq. (28). Here $\phi_{polymer}$ is the volume fraction of the polymer, χ is the Flory-Huggins interaction parameter, $n_{polymer}$ is the degree of polymerization, P_{osm} is the osmotic pressure of the solution, and v_s is the molar volume of the solvent. It is obvious that under appropriate approximations and assumptions, the present EOS reduces to the well-known models.

If we expand the present theory in virial form in the limit case of small molecules, *i.e.*, when, r_1 and q_1 become a unity, the EOS in some respects becomes similar to that of van der Waals. However, since these aspects of the lattice-theory based models with van der Waals, lattice gas, hard spere fluids and cell models, and 'c' parameter theories were discussed in detail by Sanchez and Lacombe[5] and by Kumar *et al.*,[9] we omit here further comparative discussions of them. Instead, we compared the present theory with existing theories of van der Waals,[20,21] Guggenheim's hard sphere fluid.[22,23]

Comparisons of pressure and vapor-liquid saturated densities by the present theory, van der Waals' theory, and Guggenheim's hard-sphere theory are shown in Figures 2 and 3 with experimental orthobaric densities of n-heptane. Except near the critical point, the present theory adequately describes pressure and vapor-liquid saturated densities, including the critical point.

In Figure 4 a comparison is made of the van der Waals theory, Sanchez-Lacombe theory, and random lattice theory with the present EOS for the compressibility factor. Among the lattice- model theories, the present theory properly estimates the compressibility factors as a function of segment numbers.

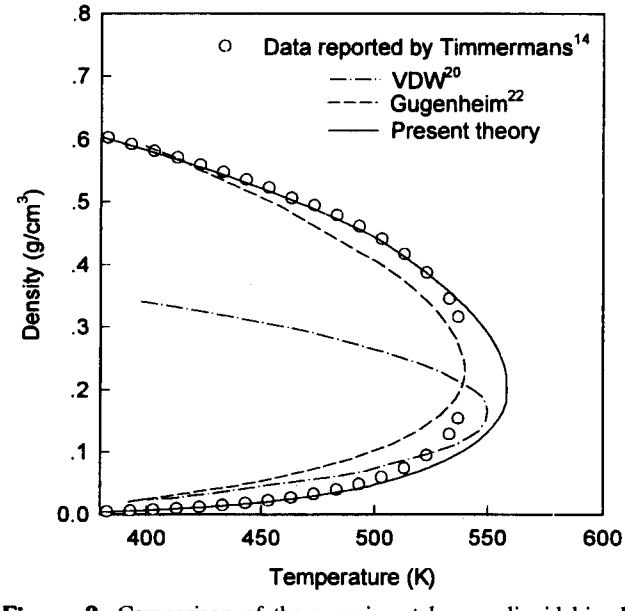

Figure 3. Comparison of the experimental vapor-liquid binodal curve of n-heptane with various theories.

Comparisons with Experiment. The adequacy of

Table 3. Comparison of experimental and calculated values for some first-order thermodynamic properties of n-heptane

Property	T (K)	Experiment	Theory	% error
Heat of vaporization, kJ/mol	371.85	32.45	32.57	+.37
Liquid density, g/cm³	298.15	0.6795	0.6790	-0.07
vapor density, g/cm³	373.15	0.0036	0.0035	-2.78
cohesive energy density, J/cm³	298.15	231.4	226.4	-2.16

Table 4. Comparison of experimental and calculated values for some second-order thermodynamic properties of n-heptane at atmospheric pressure

Property	T(K)	Experiment	Theory	% error
Thermal expansion coedfficient, K^{-1}	298.15	1.2×10^{-3}	1.08×10^{-3}	-10.00
Isothermal compressibility, MPa^{-1}	298.15	1.4×10^{-3}	1.5×10^{-3}	+7.14

the present theory compared with the experiment is given in Table 3 and 4 where calculated and experimental values of first- and second-order thermodynamic properties of n-heptane are illustrated.

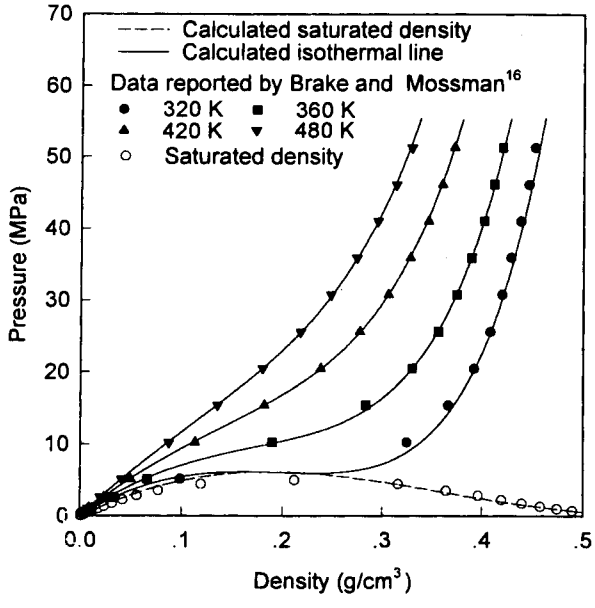

Figure 5. Densities at sub- and super-critical temperatures for pure ethane.

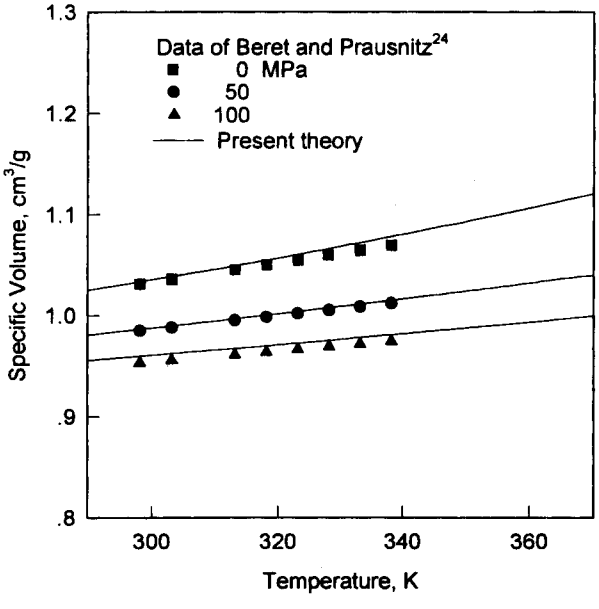

Figure 6. Calculated specific volume of poly(dimethyl siloxane) as a temperature of pressure at various temperature.

As illustrated in Figure 5 and Figure 6, experimental density data for ethane, poly(dimethyl siloxane) were fitted by the present EOS over a wide range of densities. For a wide range of pressure and temperature, the EOS correlates the data quantitatively better than any other self-consistent lattice theory in the same genre.

In summary, an approximate molecular theory based on the lattice model is presented. The theory is relatively simple and versatile. The EOS with only two molecular parameters predicts well the vapor-liquid phase transition of simple fluids and macromolecular fluids. The generalization of the theory to complex mixtures including polymer solutions is relatively straightforward. Details of the various phase equilibria of mixtures are presented in a separate article in this Journal.

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Appendix A. Derivation of the Residual Part of Helmholtz Free Energy

The residual part of the configurational residual Helmholtz free energy based on the two-fluid theory given by Eq. (13) can be derived using the thermodynamic relation at constant volume and composition,

$$\beta A^{c(R)} = \int_0^\beta U^c \, d\beta \tag{A1}$$

$$= \int_0^\beta \left(\sum_i N_{ii}\varepsilon_{ii} + \sum_{i>j}\sum N_{ij}\varepsilon_{ij} \right) d\beta \tag{A2}$$

$$= -\frac{zN_q}{2} \int_0^\beta \sum_i \theta_i \sum_j \frac{\theta_j \tau_{ji} \varepsilon_{ji}}{\sum_{k=0}^{c} \theta_k \tau_{ki}} \, d\beta \tag{A3}$$

$$= -\frac{zN_q}{2} \int_0^\beta \sum_i \theta_i \left[\sum_j \frac{\theta_j \tau_{ji} (\varepsilon_{ji} - \varepsilon_{ii})}{\sum_{k=0}^{c} \theta_k \tau_{ki}} + \varepsilon_{ii} \right] d\beta \tag{A4}$$

$$= -\frac{zN_q}{2} \left[\int_0^\beta \sum_i \theta_i d\left(\ln \sum_{k=0}^{c} \theta_k \tau_{ki} \right) + \int_0^\beta \sum \theta_i \varepsilon_{ii} \, d\beta \right] \tag{A5}$$

where N_{ij} is given by,[12]

$$N_{ij} = \frac{z}{2} \left(N_i q_i \frac{\theta_j \tau_{ji}}{\sum_{k=0}^{c} \theta_k \tau_{ki}} + N_j q_j \frac{\theta_i \tau_{ij}}{\sum_{k=0}^{c} \theta_k \tau_{kj}} \right) \tag{10}$$

Thus we have,

$$\beta A^{c(R)} = -\left(\frac{zN_q}{2} \right) \sum_{i=1}^{c} \theta_i \left[\ln \left(\sum_{j=0}^{c} \theta_j \tau_{ji} \right) + \beta \varepsilon_{ii} \right] \tag{12}$$

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Oxygen Evolution Reaction at Electrodes of Single Phase Ruthenium Oxides with Perovskite and Pyrochlore Structures**

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Single phase ruthenium oxides with perovskite ($ATi_{1-x}Ru_xO_3$ (A=Ca, Sr)) and pyrochlore structure ($Bi_2Ru_2O_7$, $Pb_2Ru_2O_{6.5}$) have been prepared reproducibly by solid state reaction methods and their electrocatalytic activities for oxygen evolution have been examined by Tafel plots. Tafel slopes vary from a low value of 42 mV/decade up to 222 mV/decade at room temperature. The high exchange current densities and high Tafel slopes compared with those obtained from the RuO_2 DSA electrode at the crystalline single phase metal oxide electrodes suggest that they are better electrocatalysts at low overpotentials. A favorable change in the Tafel slope for the oxygen evolution reaction occurs as the ruthenium content increases. Substitution of Ti for Ru in the perovskite solid solutions enhanced their chemical stability by losing marginal electrochemical activity.

Introduction

The oxygen evolution and reduction reactions are of special importance in water electrolyzers, fuel cells, and batteries using air cathodes since slow kinetics of these reactions are the chief cause of efficiency losses.[1] Transition metal oxides possess many of the desirable characteristics for practical electrodes for oxygen evolution.[2] The poor stability of some metal oxides over anodic potential ranges where oxygen evolution takes place is a major problem. Dimensionally stable anode (DSA) materials have been attractive elec-

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**This article is dedicated to Prof. Woon-kie Paik (Sogang University) in commemoration of his 60th birthday.