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A multi-fluid nonrandom lattice fluid model: General derivation and application to pure fluids

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Abstract−A multi-fluid nonrandom lattice fluid model with no temperature dependence of close packed volumes of a mer, segment numbers and energy parameters of pure systems is presented. The multi-fluid nonrandom lattice fluid (MF-NLF) model with the local composition concept was capable of describing properties for complex systems. However, the MF-NLF model has strong temperature dependence of energy parameters and segment numbers of pure systems; thus empirical correlations as functions of temperature were represented for reliable and convenient use in engineering practices. The MF-NLF model without temperature dependence of pure parameters could not predict thermodynamic properties accurately. It was found that the present model with three parameters describes quantitatively the vapor pressure and the saturated density for the pure fluid.

Key words: Multi-fluid, Nonrandom, Lattice, Local Composition, Equation of State

INTRODUCTION

Historically two-liquid theory [Wilson, 1964] and rigid lattice description without vacant sites (or holes) of fluid systems [Guggenheim, 1952] have been widely utilized to formulate various excess Gibbs free energy expressions such as NRTL [Renon and Prausnitz, 1968] and UNIQUAC [Abrams and Prausnitz, 1975]. However, they can be applied only to liquid mixtures at low pressure. To overcome this limitation, various equation-of-state theories have also been proposed by imbedding holes into the rigid lattice description of fluids. One of the well known examples is the EOS after Sanchez and Lacombe [Sanchez and Lacombe, 1976; Lacombe and Sanchez, 1976].

The present authors also recently proposed the multi-fluid nonrandom lattice fluid (MF-NLF) equation of state [Shin et al., 1995; Yoo et al., 1995, 1997] and the MF-NLF model was capable of describing properties for complex systems. However, the MF-NLF model has strong temperature dependence of energy parameters and segment numbers of pure systems; thus empirical correlations as functions of temperature were adopted for reliable and convenient use in engineering practices. If the MF-NLF model neglects the temperature dependence of these parameters, this model cannot predict thermodynamic properties accurately.

In addition, Neau [Neau, 2002] presented a consistent method for phase equilibrium calculation using the fugacity coefficients derived from the Sanchez-Lacombe equation of state. It was pointed out that the configurational chemical potential derived from the configurational partition function does not verify phase equilibrium property.

In this work, a multi-fluid nonrandom lattice fluid model with no temperature dependence of close packed volumes of a mer, segment numbers and energy parameters of pure systems will be presented.

GUGGENHEIM'S COMBINATORY AND THERMODYNAMIC PROPERTIES

The canonical partition function may be written in the classical approximation of statistical thermodynamics [Prausnitz et al., 1999]:

$$Q(N, T, V)=Q^{int}(N, T)Q^{kin}(N, T)Z_N(N, T, V) \tag{1}$$

where Q^{int}, Q^{kin} are the internal and kinetic part of the canonical partition function and Z_N is the configurational partition function.

The expression for the canonical Helmholtz free energy may be obtained from the internal and kinetic part of the Helmholtz free energy and the configurational Helmholtz free energy.

$$\beta A(N, T, V)=\beta A^{int}(N, T)+\beta A^{kin}(N, T)+\beta A^{c}(N, T, V) \tag{2}$$

The configurational Helmholtz free energy A^c may be composed of an athermal part $A^{c,A}$ which is equivalent to a combinatorial contribution in the random array and a residual part $A^{c,R}$ which is due to the residual nonrandom interaction energy.

$$\beta A^{c}=\beta A^{c,A}+\beta A^{c,R} \tag{3}$$

The athermal part of the configurational Helmholtz free energy for a hole-single component fluid is given by,

$$\beta A^{c,A}=\sum_{i=1}^{c}N_i\ln\tilde{\rho}_i+N_0\ln(1-\tilde{\rho})-\frac{z}{2}N_q\ln\left[1+\left(\frac{q}{r}-1\right)\tilde{\rho}\right] \tag{4}$$

where, N_0 and N_i are the number of vacant sites which may be called holes and the number of molecules of species i; r_i and q_i are the segment number and the surface area parameter, respectively.

$$q=\sum x_iq_i,\quad r=\sum x_ir_i,\quad \tilde{\rho}_i=N_ir_i/N_r,\quad \tilde{\rho}=\sum\tilde{\rho}_i,\quad N_q=N_0+\sum N_iq_i \tag{5}$$

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The residual part of the configurational Helmholtz free energy with two-liquid theory is obtained from the thermodynamic relation at constant volume and composition,

$$\beta \mathrm{A}=\int_{\beta_0}^{\beta}\mathrm{U}\,\mathrm{d}\beta+\text{constant} \tag{6}$$

where the internal energy U^c is residual part in the nonrandom two-fluid theory. If β_0 is taken as a very high temperature, the solution becomes a random mixture. The constant in Eq. (6) becomes $\beta\mathrm{A}^{c,A}$ and the integral becomes $\beta\mathrm{A}^{c,R}$. Thus, Eq. (6) can be rewritten as,

$$\beta\mathrm{A}^{c,R}=\int_{\beta_0}^{\beta}\mathrm{U}^c\,\mathrm{d}\beta \tag{7}$$

Now, N_{ij} are evaluated in the two-liquid theory [Wilson, 1964],

$$\mathrm{N}_{ij}=\frac{\mathrm{z}}{2}\left(\mathrm{N}_i\mathrm{q}_i\frac{\theta_j\tau_{ji}}{\sum_{k=0}^{c}\theta_k\tau_{ki}}+\mathrm{N}_j\mathrm{q}_j\frac{\theta_i\tau_{ij}}{\sum_{k=0}^{c}\theta_k\tau_{kj}}\right) \tag{8}$$

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

$$\tau_{ji}=\exp[\beta(\varepsilon_{ji}-\varepsilon_{ii})] \tag{9}$$

Then, the residual part of the configurational Helmholtz free energy with two-liquid theory is given by,

$$\beta\mathrm{A}^{c,R}=-\left(\frac{\mathrm{zN}_q}{2}\right)\sum_{i=1}^{c}\theta_i\left[\ln\left(\sum_{j=1}^{c}\theta_j\tau_{ji}\right)+\beta\varepsilon_{ii}\right] \tag{10}$$

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

From the configurational Helmholtz free energy expression given by Eq. (3), configurational expressions for thermodynamic properties can be obtained. Since the volume is represented by,

$$\mathrm{v}=v^*\mathrm{N}_r=v^*(\mathrm{N}_0+\sum\mathrm{r}_i\mathrm{N}_i) \tag{11}$$

The EOS (equation of state) is obtained from the equation of configurational Helmholtz free energy,

$$\mathrm{P}=\mathrm{P}^c=-\left(\frac{\partial\mathrm{A}}{\partial\mathrm{V}}\right)_{T,N}=-\left(\frac{\partial\mathrm{A}^c}{\partial\mathrm{V}}\right)_{T,N} \tag{12}$$

Obviously, the configurational pressure obtained in this way is the absolute pressure; $\mathrm{P}=\mathrm{P}^c$.

The canonical and configurational chemical potentials are expressed from the canonical and configurational Helmholtz free energy, respectively,

$$\mu_i=\left(\frac{\partial\mathrm{V}(\mathrm{N,T,V})}{\partial\mathrm{N}_i}\right)_{T,V,N_j}$$
$$=\left[\left(\frac{\partial\mathrm{A}^{int}(\mathrm{N,T})}{\partial\mathrm{N}_i}\right)_{T,N_j}+\left(\frac{\partial\mathrm{A}^{kin}(\mathrm{N,T})}{\partial\mathrm{N}_i}\right)_{T,N_j}+\left(\frac{\partial\mathrm{A}^{c}(\mathrm{N,T,V})}{\partial\mathrm{N}_i}\right)_{T,V,N_j}\right] \tag{13}$$

$$\mu_i^c=\left(\frac{\partial\mathrm{A}^c(\mathrm{N,T,V})}{\partial\mathrm{N}_i}\right)_{T,V,N_j} \tag{14}$$

The canonical chemical potentials are not equal to the configurational chemical potentials since A^{int}, A^{kin} are functions of both temperature and number of molecules. The configurational chemical potentials can be used for phase equilibrium conditions in the classical lattice fluid model; thus the Sanchez-Lacombe model leads to an erroneous method for phase equilibrium calculations.

To overcome this problem, phase equilibrium conditions should be calculated by using fugacity coefficients which could be derived directly from the equation of state because the configurational pressure is equal to the absolute pressure. Fugacity coefficients were calculated by derivation of the residual Helmholtz free energy A^r(T, V, N) obtained by integration of the lattice fluid equation of state.

$$\ln\varphi_i=\left(\frac{\partial\mathrm{A}^r(\mathrm{T,V,N})}{\partial\mathrm{N}_i}\right)_{T,V,N_j}-\ln\mathrm{Z} \tag{15}$$

$$\mathrm{A}^r(\mathrm{T,V,N})=-\int_{\infty}^{V}\left(\mathrm{P}-\frac{\mathrm{NkT}}{\mathrm{V}}\right)\mathrm{dV} \tag{16}$$

EOS AND FUGACITY COEFFICIENT FOR PURE FLUIDS

In this work, we present a multi-fluid nonrandom lattice fluid (MLF) model with no temperature dependence of close packed volumes of a mer (v_i^*), segment numbers (r_1) and molecular interaction energy (ε_{11}) of pure systems.

From Eq. (12), we obtain the expression for equation of state for pure components.

$$\frac{\tilde{\mathrm{P}}}{\tilde{\mathrm{T}}}=-\ln(1-\tilde{\rho})+\frac{\mathrm{z}}{2}\ln\left[1+\left(\frac{\mathrm{q}_1}{\mathrm{r}_1}-1\right)\tilde{\rho}\right]-\frac{\theta_1^2}{\tilde{\mathrm{T}}} \tag{17}$$

Here, all the quantities with the tilde (~) denote the reduced variables defined by

$$\tilde{\mathrm{P}}=\frac{\mathrm{P}}{\mathrm{P}^*},\ \tilde{\mathrm{T}}=\frac{\mathrm{T}}{\mathrm{T}^*},\ \tilde{\rho}=\frac{\rho}{\rho^*}=\frac{\mathrm{r}_1\mathrm{N}_1}{\mathrm{N}_r},\ \rho^*=\frac{1}{\mathrm{r}_1\mathrm{v}_1^*} \tag{18}$$

Where the reducing parameters are defined by

$$\mathrm{P}^*\mathrm{v}_1^*=\mathrm{kT}^*=\frac{\mathrm{z}}{2}\varepsilon_M \tag{19}$$

and ε_M, θ_1 are defined by

$$\varepsilon_M=\frac{1}{\beta\theta_1^2}\left[\sum_{i=1}^{1}\theta_i\left(1-\frac{\tau_{0i}}{\sum_{k=0}^{1}\theta_k\tau_{ki}}\right)\right] \tag{20}$$

$$\theta_1=\frac{\mathrm{N}_1\mathrm{q}_1}{\mathrm{N}_q}=\frac{(\mathrm{q}_1/\mathrm{r}_1)\tilde{\rho}}{1+(\mathrm{q}_1/\mathrm{r}_1-1)\tilde{\rho}}=1-\theta_0 \tag{21}$$

The Residual Helmholtz energy, A^r(T, V, N) and fugacity coefficient were calculated given by Eqs. (15)-(16), which has an identical form of the MF-NLF model.

$$\frac{\mathrm{A}^r}{\mathrm{kT}}=\mathrm{N}_1\mathrm{r}_1\left[\left(\frac{1}{\tilde{\rho}}-1\right)\ln(1-\tilde{\rho})\right]$$
$$-\left[\frac{\mathrm{z}}{2}\frac{\mathrm{N}_1\mathrm{r}_1}{\tilde{\rho}}+\mathrm{N}_1(1-\mathrm{r}_1)\right]\ln\left(1+\left(\frac{\mathrm{q}_1}{\mathrm{r}_1}-1\right)\tilde{\rho}\right)+\mathrm{N}_1-\frac{\mathrm{N}_1\mathrm{q}_1\theta_1}{\tilde{\mathrm{T}}} \tag{22}$$

$$\ln\varphi_1=\mathrm{r}_1\frac{\tilde{\mathrm{P}}}{\tilde{\mathrm{T}}}-\frac{\mathrm{zq}_1}{2}\ln\left(1+\left(\frac{\mathrm{q}_1}{\mathrm{r}_1}-1\right)\tilde{\rho}\right)-\ln\mathrm{Z}+\frac{\mathrm{r}_1\theta_1^2}{\tilde{\mathrm{T}}}+(1-\mathrm{r}_1)\theta_1$$
$$-\frac{\mathrm{zq}_1}{2}\left[\ln\sum_{k=0}^{1}\theta_k\tau_{ki}+\beta\varepsilon_{11}+\sum_{l=1}^{1}\frac{\theta_1(\tau_{il}-\tau_{0l}(\mathrm{r}_1/\mathrm{q}_1))}{\sum_{m=0}^{1}\theta_m\tau_{ml}}\right] \tag{23}$$

RESULTS AND DISCUSSION

There are apparently four molecular parameters in this model for pure fluids: z, v_1^*, r_1, ε_{11}. We set z=10 as used in lattice fluid theories of the same genre [Panayiotou and Vera, 1982]. The present model has three pure component parameters without temperature dependence of close packed volumes of a mer (v_1^*), segment numbers (r_1) and energy parameters (ε_{11}) of pure systems. Three pure component parameters have been regressed by using the present EOS and fugacity coefficient from the least-square minimization using differences in calculated and experimental vapor pressure and liquid density data for 80 real fluids.

For each compound, Table 1 lists temperature range, v_1^*, r_1, ε_{11}/k and percent average absolute deviation (AAD %) in vapor pres-

Table 1. Pure molecular parameters for real fluids

Components	v_1^* cm^3/mol	r_1	ε_{11}/k, K	AADP (%)	AADρ (%)	T range, K
Methane	6.867	4.919	47.150	0.570	1.340	100-188
Ethane	7.921	6.066	70.943	0.237	1.976	200-305
Propane	9.153	6.998	82.359	1.164	0.908	190-360
Butane	10.520	7.602	92.752	1.028	0.879	220-420
Isobutane	11.466	8.353	100.128	1.250	0.300	240-450
Pentane	12.524	8.939	106.680	0.883	0.207	283-483
Isopentane	12.924	9.860	110.642	1.719	0.365	273-513
Hexane	13.647	10.511	114.901	1.066	0.301	303-543
Heptane	13.762	11.538	116.985	0.978	0.321	313-553
Octane	14.467	12.114	120.667	1.576	0.432	313-573
Nonane	15.015	12.756	123.456	1.894	0.215	333-523
Decane	15.446	13.448	125.777	1.281	0.507	363-603
Undecane	15.806	14.204	127.553	1.487	0.402	373-633
Dodecane	16.514	14.572	130.468	1.443	0.534	393-653
Tridecane	16.868	14.343	131.121	1.348	0.440	413-653
Tetradecane	17.043	16.006	133.374	1.426	0.662	403-673
Pentadecane	17.163	16.754	134.641	0.800	0.846	413-683
Hexadecane	17.524	17.435	135.567	1.665	0.977	423-683
Heptadecane	17.807	18.056	136.803	1.441	0.864	433-693
Ocatadecane	17.890	18.779	137.907	0.996	0.847	443-703
Nonadecane	18.376	20.930	140.058	0.805	0.942	473-733
Eicosane	18.522	21.653	140.683	0.972	0.861	483-733
Tricosane	19.702	23.677	144.408	0.224	0.513	563-703
Tetracosane	20.500	24.212	146.784	1.507	0.841	543-783
Octacosane	20.473	26.082	146.245	1.742	0.799	563-803
Triacontane	8.236	6.496	90.776	0.237	0.308	253-353
Dotriacontane	10.113	6.686	105.317	1.805	0.240	273-403
Cyclopropane	10.962	7.390	112.713	1.215	0.410	273-423
Cyclobutane	11.923	8.033	118.370	1.680	0.340	273-513
Cyclopentane	13.562	8.163	129.409	1.615	0.276	293-533
Cyclohexane	14.356	8.705	135.335	0.622	0.300	373-473
Cycloheptane	12.308	8.016	114.626	1.596	0.288	280-450
Cyclooctane	13.119	8.697	119.913	1.378	0.173	300-450
Methylcyclopentane	14.264	9.167	124.712	1.878	0.188	323-493
Ethylcyclopentane	14.398	10.179	126.566	1.589	0.248	323-463
Propylcyclopentane	13.714	8.349	121.312	1.738	0.318	293-503
Butylcyclopentane	15.583	8.388	130.046	1.604	0.255	343-523
Methylcyclohexane	15.563	9.390	130.778	1.376	0.229	353-523
Ethylcyclohexane	16.741	9.866	134.146	1.560	1.640	383-443
Propylcyclohexane	17.694	14.676	141.079	0.959	0.303	423-653
Butylcyclohexane	11.298	6.800	95.299	1.405	0.930	273-373
Decylcyclohexane	12.112	7.606	102.324	1.270	0.719	273-423
Butene	12.232	8.790	106.061	0.896	0.339	273-473
Pentene	13.277	9.363	111.657	1.854	1.238	273-473

Table 1. Continued

Components	v_1^* cm^3/mol	r_1	ε_{11}/k, K	AADP (%)	AADρ (%)	T range, K
Hexene	13.775	10.063	115.937	1.586	0.226	303-473
Heptene	10.206	7.829	121.788	1.473	0.266	300-510
Hctene	11.134	8.647	124.959	1.380	0.320	300-530
Benzene	12.388	9.071	129.227	1.814	0.423	310-570
Toluene	13.087	9.844	130.546	1.866	0.532	310-570
Ethylbenzene	13.864	10.463	133.416	1.486	0.321	340-570
Propylbenzene	12.149	9.257	128.919	0.677	0.160	340-573
Butylbenzene	7.916	6.840	91.191	1.340	0.989	253-363
M-xylene	9.891	8.697	98.680	0.762	0.148	273-423
Dimethyl ether	11.994	9.938	100.988	1.010	1.140	293-423
Diethyl ether	7.394	8.707	109.469	0.457	1.244	273-473
Diisopropyl ether	8.802	9.041	113.471	0.761	1.236	293-473
Acetone	9.963	9.593	116.197	1.364	0.520	303-493
Methylethyl ketone	9.646	9.830	115.153	0.980	0.611	303-473
Methyl propyl ketone	7.785	8.822	108.165	1.568	0.441	293-423
Diethyl ketone	8.030	10.440	105.272	1.045	0.174	273-423
Methylacetate	10.809	10.901	115.395	1.020	0.200	333-473
Ethylacetate	5.785	5.167	30.825	1.747	1.512	65-110
Butylacetate	4.523	5.424	36.671	1.319	0.805	70-130
Nitrogen	5.947	4.370	39.027	1.835	1.634	60-140
Oxygen	5.620	5.447	31.743	0.715	0.772	75-121
Argon	6.556	6.137	96.055	1.529	0.990	210-400
Carbon monoxide	8.462	6.463	124.635	0.251	0.712	290-533
Chlorine	11.122	8.404	130.665	1.916	0.561	330-550
Carbon disulfide	11.258	7.665	120.835	1.661	0.319	280-510
Tetrachloroethylene	8.948	7.893	115.520	1.178	0.349	280-510
Carbon tetrachloride	8.485	6.745	117.933	1.777	1.550	300-450
Chloroform	6.637	6.633	95.332	0.246	1.073	255-380
Dichloromethane	14.323	8.278	151.403	1.639	1.234	410-600
Methylchloride	9.467	8.453	119.850	1.035	0.437	270-510
Hexachloroethane	14.375	7.956	145.903	1.405	0.702	360-550
Trichloroethylene	8.498	6.543	97.801	1.548	0.223	250-400
Pentachloroethane	8.277	7.309	102.157	0.822	0.634	260-390
Vinylchloride	11.413	8.276	135.535	1.859	0.424	313-523
Ethylchloride	6.867	4.919	47.150	0.570	1.340	100-188
Chlorobenzene	7.921	6.066	70.943	0.237	1.976	200-305

sure and liquid density. Vapor pressure and liquid density data are from KDB [Kang et al., 2001]. The quality of fit for both vapor pressure and liquid density is as good as can be usually expected for a reasonable, three-parameter lattice fluid equation of state.

The present model is compared with the MF-NLF model, SAFT [Huang and Radosz, 1990] model to calculate the vapor pressure and the saturated density. The MF-NLF model has strong temperature dependence of energy parameters and segment numbers of pure systems, as shown in Fig. 1; thus empirical correlations as functions of temperature were adopted for reliable and convenient use in engineering practices. “6MF-NLF” denotes the MF-NLF model with six adjustable parameters and “2MF-NLF” denotes the MF-NLF model with only two parameters having no temperature dependence. The SAFT model has three pure parameters (segment volume, v^{00}, segment number, m, dispersion energy, u^0/k) in non-associating molecules.

For hexane and benzene components, Table 2 lists percent average absolute deviation (AAD %) in vapor pressure and liquid density. It is shown that the present model is as accurate as the 6MF-NLF and the SAFT models, but the 2MF-NLF model failed to correlate the vapor pressure. Therefore, the MF-NLF model without temperature dependence of pure parameters could not predict thermodynamic properties accurately.

In order to compare three models (present model, 6MF-NLF and SAFT) fairly, we use the same experimental data of vapor pressure and liquid density for the ethane component. Pure parameters and percent average absolute deviation (AAD %) in vapor pressure and liquid density are listed in Table 3 and Fig. 2. It is shown that the present model is slightly better than SAFT model. The 6MF-NLF model is equivalent to the present model, but the 6MF-NLF model

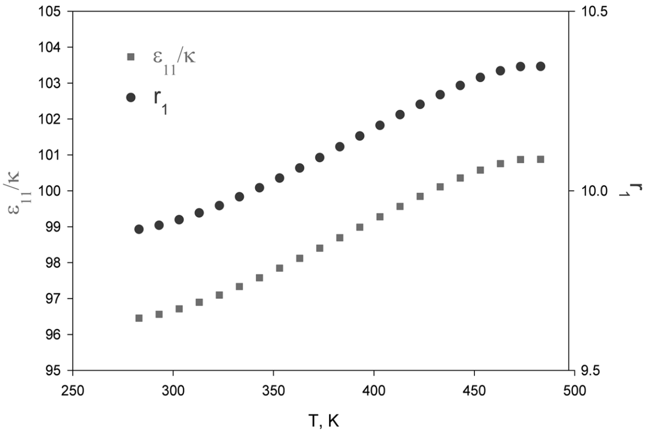

Fig. 1. Temperature dependence of energy parameters and segment numbers of hexane system in the MF-NLF model.

has more adjustable pure parameters than the present model and SAFT model.

Now we focus on the pure parameter behavior according to molar mass. The segment number r_1 increases with increasing molar mass within each homologous series practically linearly. The segment number r_1 is plotted versus molar mass for n-alkanes, n-cycloalkanes, n-alkylcyclopentanes, n-alkylcyclohexanes, and n-alkylbenzenes in Fig. 3. It is reassuring to find that a linear relationship holds for each hydrocarbon. The close packed volume of a molecule $r_1v_1^*$ is a single linear function of the molar mass for all the hydrocarbons, as shown in Fig. 4. Apart from testing these reassuring trends, a practical reason for developing a correlation for $r_1v_1^*$ is to provide the basis for estimating v_1^*, if there are no accurate PVT data available, for a given r_1 and molar mass. A similar molar mass correlation can be developed for the molecular interaction energy ε_{11}/k, which is shown in Fig. 5. Unlike r_1 and $r_1v_1^*$, ε_{11}/k is nonlinear with respect to the molar mass.

For the ease of estimating, r_1, $r_1v_1^*$ and ε_{11}/k have been regressed as simple functions of the mass (MM) for many homologous series.

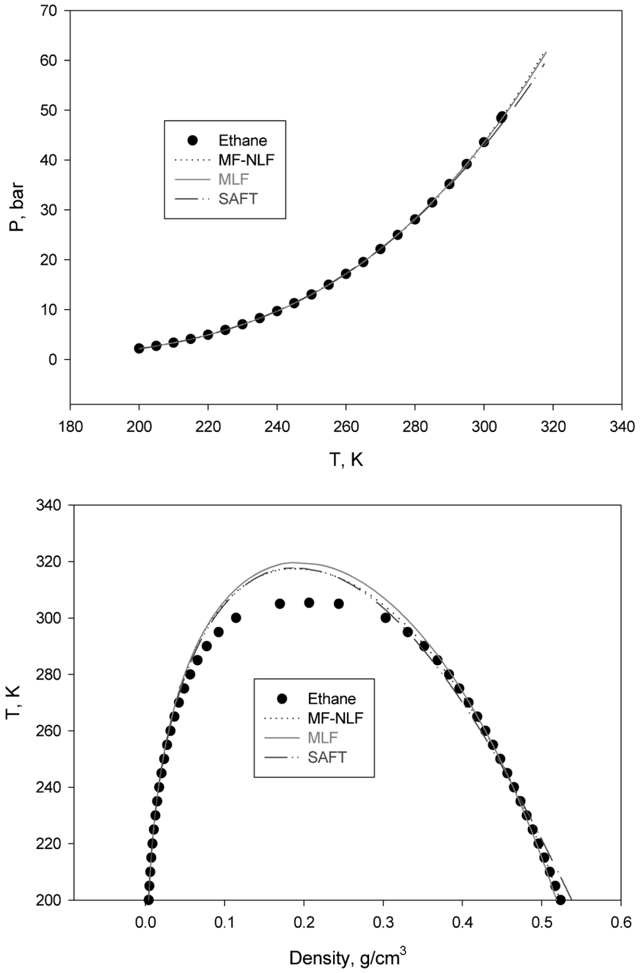

Fig. 2. Calculation results of vapor pressure and liquid density in ethane.

For example,

$$r_1=A^{(1)}+A^{(2)}MM \quad \text{for all hydrocarbons} \tag{24}$$

Table 2. Calculation results of vapor pressure and liquid density in hexane and benzene component

Models	Hexane [283-483 K]		Benzene [300-510 K]	
	AADP (%)	AADρ (%)	AADP (%)	AADρ (%)
2MF-NLF	9.363	2.569	7.593	1.007
$\varepsilon_{11}/k=105.46$, $r_1=10.16$ for Hexane				
$\varepsilon_{11}/k=102.32$, $r_1=10.15$ for Benzene				
6MF-NLF	0.753	0.196	0.756	0.251
MLF (present model)	0.886	0.207	1.473	0.266
SAFT	1.400	2.100	1.176	2.598

Table 3. Calculation results of vapor pressure and liquid density in ethane

Models	AADP (%)	AADρ (%)	Pure parameters	T range, K
MF-NLF	0.382	1.312	$E_a=58.350$, $E_b=-0.061$, $E_c=5.956$ $V_a=72.737$, $V_b=0.043$, $V_c=-6.145$	200-305
MLF	0.237	1.976	$v_1^*=7.921$, $r_1=6.066$, $\varepsilon_{11}/k=70.943$	200-305
SAFT	0.796	2.146	$v^{00}=11.044$, $m=2.426$, $u^0/k=166.515$	200-305

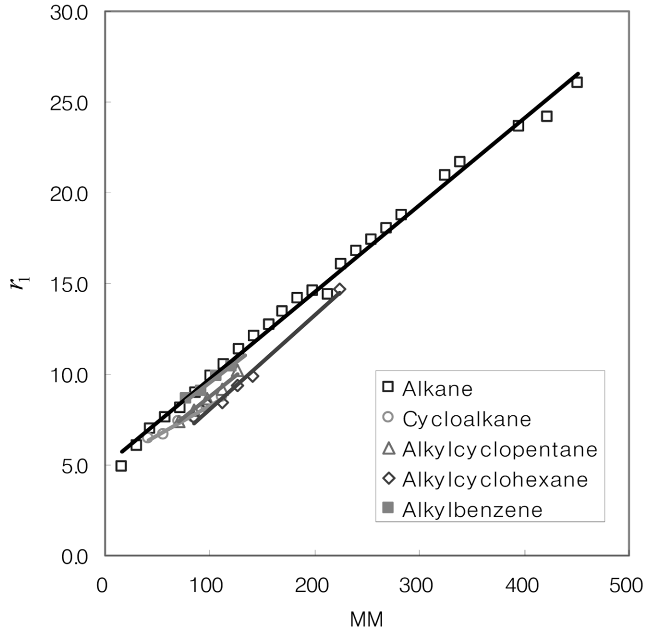

Fig. 3. Segment number r_1 for hydrocarbons, as linear functions of molar mass.

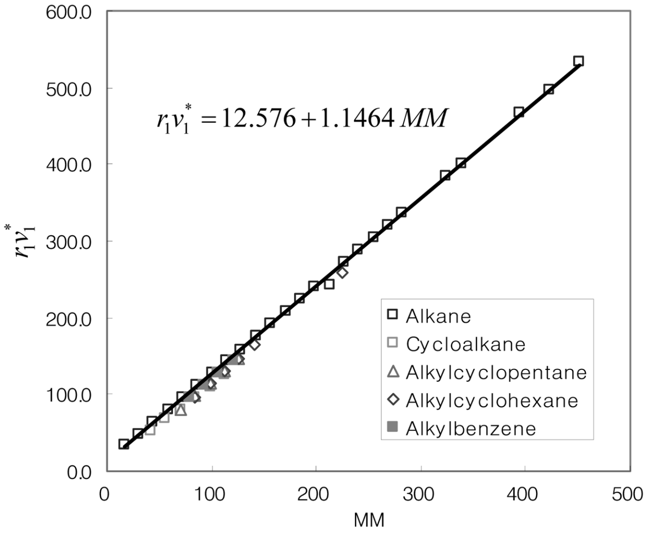

Fig. 4. Close packed volume $r_1v_1^*$ for hydrocarbons, as single linear functions of molar mass.

$$r_1v_1^*=12.576+1.1464MM \quad \text{for all hydrocarbons} \tag{25}$$

$$\varepsilon_{11}/k=A^{(1)}+A^{(2)}\ln(MM) \quad \text{for n-alkanes} \tag{26}$$

$$\varepsilon_{11}/k=A^{(1)}+A^{(2)}MM \quad \text{for other hydrocarbons} \tag{27}$$

We note that Eq. (27) is only a linear approximation that is valid up to the MM of a corresponding n-alkane; for higher MM values, we set ε_{11}/k to be the same as that for a corresponding n-alkane. The solid lines and curves shown in Figs. 3-5 have been predicted from Eqs. (21)-(24). Specific values for the regression coefficients $A^{(i)}$ are reported in Tables 4 and 5. In this way, we have a useful method for estimating all the equation of state parameters for pure fluids where no accurate data are available and, especially, for poorly defined pseudo-components where only average molar mass and average aromaticity are available.

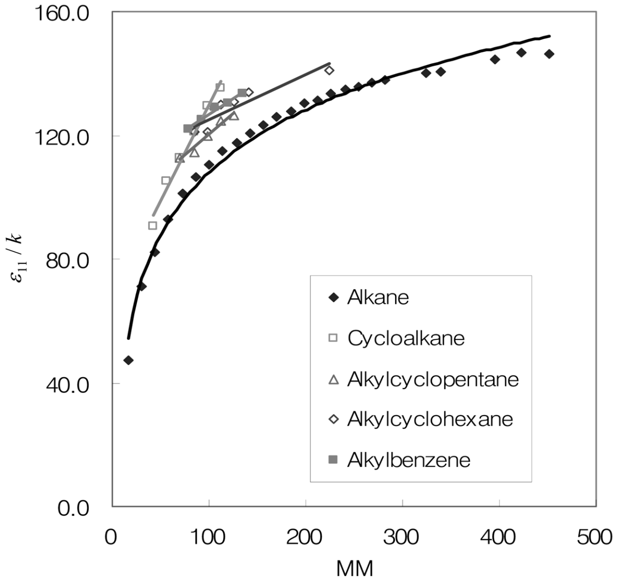

Fig. 5. Molecular interaction energy ε_{11}/k for n-alkane and other hydrocarbon, as smooth but nonlinear function of molar mass.

Table 4. Correlation of the segment number r_1 for hydrocarbons

Systems	$A^{(1)}$	$A^{(2)}$	MM Range
n-Alkynes	4.9458	0.0479	16-451
Cyclohexanes	5.0416	0.0319	42-112
n-Alkylcyclopentane	3.9795	0.048	71-126
n-Alkylcyclohexane	3.0314	0.051	84-224
n-Alkylbenzene	5.0257	0.0451	78-134

Table 5. Correlation of the molecular interaction energy ε_{11}/k for hydrocarbons

Systems	$A^{(1)}$	$A^{(2)}$	MM Range
n-Alkynes	−26.604	29.226	16-451
Cyclohexanes	68.088	0.618	42-112
n-Alkylcyclopentane	93.252	0.2694	71-126
n-Alkylcyclohexane	111.1	0.1423	84-224
n-Alkylbenzene	106.31	0.2045	78-134

CONSLUSIONS

A multi-fluid nonrandom lattice fluid (MLF) model with three molecular parameters (close packed volumes of a mer, segment numbers, and molecular interaction energy) is presented. The MF-NLF model was capable of describing properties for complex systems, but has strong temperature dependence of energy parameters and segment numbers of pure systems. The MF-NLF model without temperature dependence of pure parameters could not predict thermodynamic properties accurately. It was found that the present model with three parameters describes quantitatively the vapor pressure and the saturated density for a pure fluid.

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NOMENCLATURE

A : Helmholtz free energy
$A^{(i)}$: regression constants in Eq. (26), (28), (29)
c : number of the component
f : fugacity
k : Boltzmann's constant
N : number of molecule
N_r : defined by Eq. (8)
N_q : defined by Eq. (5)
m : effective number of segments with the molecule for SAFT model
MM : molar mass
P : pressure
P^c : configurational pressure
Q : canonical partition function
q : surface area parameter
r : number of segments per molecule
T : temperature
u^0 : dispersion energy of interaction between segments for SAFT model
V : volume
v : molar volume
v_1^* : close packed volume of a mer
v^{00} : segment volume for SAFT model
z : lattice coordination number
Z : compressibility factor
Z_N : configration partition function

Greek Letters
β : reciprocal temperature (1/kT)
Γ_{ij} : quasi-chemical nonrandomness factor
ε_{ij} : molecular interaction energy
ε_M : defined by Eq. (17)
φ : fugacity coefficient
ρ : molar density
ρ^* : close packed molar density
μ : chemical potential
τ_{ij} : nonrandomness factor
θ : surface area fraction

Superscripts
a : athermal solution properties
c : configurational properties
r : residual properties
~ : reduced properties
* : characteristic properties

Subscripts
i : component i
0 : vacant sites or holes
int : internal part
kin : kinetic part

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