Modified Guggenheim-Huggins-Miller combinatorial factor and its application to lattice fluid equation of state

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Abstract−The Guggenheim-Huggins-Miller (GHM) combinatorial factor is modified by introducing a factor in the pair probability of a hole-hole pair. The proposed contribution is combined with the expanded quasi-chemical contribution and tested against saturated vapor pressure and liquid density. The proposed model correlates experimental saturated liquid density better than a quasi-chemical nonrandom lattice fluid (QLF) model based on original GHM combinatorial factor. The optimized parameters show a quite different behavior compared with that of the QLF model and the relationships between the parameters of two models are discussed.

Key words: Combinatorial Factor, Equation of State, Guggenheim-Huggins-Miller, Lattice Fluid, Pair Probability

INTRODUCTION

The lattice fluid equation of state provides a simple way to describe the interactions between molecules, such as repulsion or hydrogen bonding [1-3]. These interactions are expressed in terms of a combinatorial factor and generally derived based on the concept of probability and counting because the molecules should be distributed in the given lattice following physical constraints. Several combinatorial factors were proposed for athermal (or repulsive) contribution. Flory and Huggins [4-6] introduced the concept of insertion probability representing the chance of arranging chain molecules in a lattice without overlap and derived an analytic combinatorial factor ignoring chain-connectivity. Later, Guggenheim, Chang and Miller could induce the identical combinatorial factor accounting for the chain connectivity and the effect of molecular shapes [2,7,8]. This approach introduces the pair probability of having adjacent lattice sites occupied by a pair of monomers. Both approaches were mainly applicable to the system of linear chain molecules. For the system of complex structure as well as linear molecules, Freed and coworkers proposed the lattice cluster theory (LCT) which corrects Flory's approach by expanding it in powers of the inverse coordination number [9]. It takes into account the molecular shape, rigidity and multiparticle interaction and is applied to liquid-liquid equilibria of polymer solutions [10].

These combinatorial factors were originally developed for systems of solvent and chain molecules and thus used to calculate excess thermodynamic properties [2]. However, Sanchez and Lacombe found that the introduction of holes (or vacant sites) in the combinatorial factors with attractive contribution leads to predictable vapor-liquid transition [11]. Following their approach, a number of equations of state have been developed based on Flory's [12] or Guggenheim-Huggins-Miller's (GHM) combinatorial factor [13-18]. The

latter is regarded as real improvement over the former since it considers the effect of molecular shape and chain-connectivity. Foreman and Freed, however, found that some basic ideas underlying the GHM combinatorial factor may be incorrect at sufficiently high chain molecule concentrations [19]. For the case of solvent-solvent pair, the pair probability of the GHM framework at a concentrated region was found to imply that all the adjacent sites of the chain molecules are occupied by solvent molecules, an assumption contrary to reality. This problem is also present in the framework of the equation of state where the solvent is replaced with holes.

The objective of this study is to modify the pair probability of the original GHM framework and derive a combinatorial factor based on the modified pair probability to improve physical properties at a high density region. A factor is introduced in the pair probability and its role is discussed by comparison with the QLF model [18] for saturated properties correlations

COMBINATORIAL FACTOR OF GHM FRAMEWORK

The combinatorial factor of the GHM framework represents the number of ways of distributing r-mers and vacant sites (or holes) on a rigid lattice by considering geometric constraints. Its derivation is described in detail in the literature [1] and we only discuss that procedure briefly. Consider a lattice of N_r sites composed of N_0 and N_1 r-mers. Each site has a coordination number, z. In this study, the lattice coordination number, z, was set to 10. For open-chain r-mers, the total number of neighboring pairs with adjacent sites is,

$$qz = (z-2)r + 2 \tag{1}$$

Suppose we have a group of r sites congruent with r-mer. The group may be occupied with holes or r-mer. If an r-mer occupies that group, that probability, p_A, is given by

$$p_A = \frac{N_1 \sigma}{N_r \delta} \tag{2}$$

where σ is the symmetry number of r-mer and δ is the number of ways of arranging an r-mer when one of its ends is fixed at the end

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of the group. If holes occupy that group, the probability is as follows:

$$p_B = \frac{N_0}{N_r} p_c^{r-1} \tag{3}$$

where N_0/N_r represents the probability of occupying the first site of the group with holes and p_c the pair (conditional) probability of occupying the other site of the pair with holes when one site of the given pair is already occupied by holes. Guggenheim assumed the conditional probability as

$$p_c = \frac{zN_0}{zN_0 + zqN_1} \tag{4}$$

where zN_0 and zqN_1 represent the number of ways of occupying the other vacant site with holes and r-mers, respectively. If we define $\alpha = p_A/p_B$, the combinatorial factor of GHM framework is obtained from the following relation:

$$\ln\frac{g(N_1, N_r)}{g(0, N_r)} = -\int_0^{N_1} \ln\alpha\, dN_1 \tag{5}$$

Integration of the right leads to the combinatorial factor,

$$g(N_1, N_r) = \left(\frac{\delta}{\sigma}\right)^{N_1} \frac{N_r!}{N_0!N_r!}\left(\frac{N_q!}{N_r!}\right)^{\frac{z}{2}} \tag{6}$$

where N_q is defined as $N_q = N_0 + qN_1$.

MODIFIED COMBINATORIAL FACTOR

The combinatorial factor of the GHM framework depends on some assumptions simplifying the model derivation [19]. The conditional probability given by Eq. (4) is based on the assumption that the neighboring sites of r-mers, zq, are occupied with holes. This assumption is reasonable in dilute concentrations because r-mers are nearly surrounded by holes. However, such assumption may be far from reality at a concentrated (or high density) region where r-mers have more contact with each other. In this case, the actual number of ways of occupying the other vacant sites with holes and r-mers will be lower than the assumed values, zN_0 and zN_1q. We modify p_B to account for this behavior by introducing factor, τ, as follows:

$$p_B = \frac{N_0}{N_r}\left(\frac{zN_0}{zN_0 + zqN_1}\right)^{\tau(r-1)} \tag{7}$$

The correction factor leads to increases or decreases of p_B when $\tau < 1$ or $\tau > 1$.

The modified combinatorial factor is obtained by integrating the right side of Eq. (5) with Eq. (7) and given as

$$g(N_1, N_r) = \left(\frac{\delta}{\sigma}\right)^{N_1} \frac{N_r!^\omega}{N_0!^\omega N_r!}\left(\frac{N_q!}{N_r!}\right)^{\frac{z}{2}\tau} \tag{8}$$

where $\omega = \tau + (1-\tau)/r$.

The athermal contribution in Helmholtz energy is given as

$$\beta A^{athm} = -\ln g(N_1, N_r) \tag{9}$$

where β is reduced temperature defined as $1/kT$.

Eq. (7) reduces to the original GHM equation (Eq. (5)) when τ is equal to 1.

In this study, we investigate the effect of τ by proposing an equation of state based on the modified combinatorial factor and comparing it with experimental data. As an attractive contribution, the expanded quasi-chemical theory [15] proposed by You et al. was employed,

$$\beta A^{qca} = -\left(\frac{z\beta N_q}{2}\right)\left[\sum_{i=0}^{1}\sum_{j=0}^{1}\theta_i\theta_j\varepsilon_{ij}\right. \\ \left. + \left(\frac{\beta}{2}\right)\sum_{i=0}^{1}\sum_{j=0}^{1}\sum_{k=0}^{1}\sum_{l=0}^{1}\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij} + \varepsilon_{kl} - \varepsilon_{ik} - \varepsilon_{jk})\right] \tag{10}$$

where ε_{ij} is the pair interaction energy between i-j pair, and θ_0 and θ_i are surface area fraction of holes and component i, respectively. The double and quadruple summations represent random and non-random mixing contribution, respectively.

The configurational Helmholtz energy is the sum of athermal and attractive contribution represented by Eqs. (9) and (10), respectively.

$$\beta A^{conf} = N_1\ln\left(\frac{N_1}{N_r}\right) + \omega N_0\ln\left(\frac{N_0}{N_r}\right) - \frac{z}{2}N_q\ln\left(\frac{N_q}{N_r}\right)\tau - \left(\frac{z\beta N_q}{2}\right)\left[\sum_{i=0}^{1}\sum_{j=0}^{1}\theta_i\theta_j\varepsilon_{ij}\right. \\ \left. + \left(\frac{\beta}{2}\right)\sum_{i=0}^{1}\sum_{j=0}^{1}\sum_{k=0}^{1}\sum_{l=0}^{1}\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij} + \varepsilon_{kl} - \varepsilon_{ik} - \varepsilon_{jk})\right] \tag{11}$$

The residual Helmholtz energy is given by,

$$\beta A^{res} = N_1 + \omega N_0\ln\left(\frac{N_0}{N_r}\right) - \frac{z}{2}N_q\ln\left(\frac{N_q}{N_r}\right)\tau - \left(\frac{z\beta N_q}{2}\right)\left[\sum_{i=0}^{1}\sum_{j=0}^{1}\theta_i\theta_j\varepsilon_{ij}\right. \\ \left. + \left(\frac{\beta}{2}\right)\sum_{i=0}^{1}\sum_{j=0}^{1}\sum_{k=0}^{1}\sum_{l=0}^{1}\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij} + \varepsilon_{kl} - \varepsilon_{ik} - \varepsilon_{jk})\right] \tag{12}$$

The pressure and compressibility factor are as follows:

$$\frac{PV_H}{kT} = \left(\frac{z}{2}\right)\ln\left[1 + \left(\frac{q}{r} - 1\right)\rho\right]\tau - \omega\ln(1-\rho) - \frac{z\beta}{2}\varepsilon_M\theta_1^2 \tag{13}$$

$$Z = \frac{r}{\rho}\left(\frac{z}{2}\ln\left[1 + \left(\frac{q}{r} - 1\right)\rho\right]\tau - \omega\ln(1-\rho) - \frac{z\beta}{2}\varepsilon_M\theta_1^2\right) \tag{14}$$

where V_H is a lattice cell volume, ρ is reduced density defined as $rN_1/(N_0 + rN_1)$

and $\varepsilon_M = \frac{1}{\theta_1^2}\left[\sum_{i=0}^{1}\sum_{j=0}^{1}\theta_i\theta_j\varepsilon_{ij}\right.$
$$\left. + \left(\frac{\beta}{2}\right)\sum_{i=0}^{1}\sum_{j=0}^{1}\sum_{k=0}^{1}\sum_{l=0}^{1}\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij} + 3\varepsilon_{kl} - 2\varepsilon_{ik} - 2\varepsilon_{jk})\right] \tag{15}$$

Phase equilibrium calculation requires chemical potential or fugacity coefficients. The configurational chemical potential is obtained from the configurational Helmholtz energy through the following relation:

$$\beta\mu^{conf} = \left(\frac{\partial\beta A^{conf}}{\partial N_1}\right) + rV_H\beta P \tag{16}$$

One obtains the configurational chemical potential given by

$$\beta\mu^{conf} = \omega r\ln\left[1 + \left(\frac{q}{r} - 1\right)\rho\right] - \omega r\ln(1-\rho) + \ln\left(\frac{\theta_1}{q}\right) + \left(\frac{z\beta}{2}\right)q\varepsilon_M\theta_1^2$$
$$\times\left[1 - \frac{r}{q} - \frac{2\sum_{k=0}^{1}\theta_k\varepsilon_{1k} + \beta\sum_{j=0}^{1}\sum_{k=0}^{1}\sum_{l=0}^{1}\theta_j\theta_k\theta_l\varepsilon_{1j}(\varepsilon_{1j} + 2\varepsilon_{kl} - 2\varepsilon_{jk} - \varepsilon_{1k})}{\varepsilon_M\theta_1^2}\right] \tag{17}$$

The fugacity coefficient is readily obtained by the fundamental relations proposed by Neau [20] or Shin and Kim [18, 21].

$$\ln\varphi_1 = (\omega r - 1)\ln\left[1 + \left(\frac{q}{r} - 1\right)\rho\right] - \omega r \ln(1-\rho) - \ln(Z) + \left(\frac{z\beta}{2}\right)q\varepsilon_M\theta_1^2$$

$$\times \left[1 - \frac{r}{q} - \frac{2\sum_{k=0}^{1}\theta_k\varepsilon_{1k} + \beta\sum_{j=0}^{1}\sum_{k=0}^{1}\sum_{l=0}^{1}\theta_j\theta_k\theta_l\varepsilon_{1j}(\varepsilon_{1j} + 2\varepsilon_{kl} - 2\varepsilon_{jk} - \varepsilon_{1k})}{\varepsilon_M\theta_1^2}\right] \quad (18)$$

RESULTS AND DISCUSSION

The proposed equation of state requires four parameters, unit cell volume, segment length, pair interaction energy and τ, to characterize pure components. The newly introduced factor, τ, is assumed to be component-specific. All component parameters are obtained by regressing experimental saturated liquid density and saturated vapor pressure. Although QLF parameters are available in the literature [18], we obtained new parameter sets for comparison because the temperature ranges of the literature are different from our region of interest. Table 1 shows that the proposed model yields a better agreement with saturated liquid density than QLF model. The deviation for saturated liquid density was found to decrease by 5.4 to 42.7% with the present model when compared with the QLF model. The present model reproduces the saturated vapor pressure for four components better than the QLF model and shows a comparable result

for other components. These results indicate that the introduced factor, τ, mainly affects the liquid density rather than vapor pressure.

Table 2 lists the optimized parameters of QLF and the proposed model and gives additional information regarding the role of τ on other parameters of the equation of state. When τ is larger than 1 (for methane, dimethyl ether, acetone), the lattice cell volume (V_H) as well as the pair interaction energy (ε_{11}) increases and segment length (r) decreases compared with the value of QLF parameter. These parameters show opposite behavior when τ is less than 1. It indicates that some relations between the parameters of the two frameworks, the original GHM framework and this work, exist.

Suppose that no attractive contribution exists and segment length is sufficiently large. Then ω goes to τ and thus Eq. (14) is rewritten as follows:

$$Z = \tau\frac{r}{\rho}\left(\frac{z}{2}\ln\left[1 + \left(\frac{q}{r} - 1\right)\rho\right] - \ln(1-\rho)\right) \quad (19)$$

If we denote V_H^* and r^* as unit cell volume and segment length of original GHM framework, the compressibility factor is given as

$$Z^* = \frac{r^*}{\rho}\left(\frac{z}{2}\ln\left[1 + \left(\frac{q^*}{r^*} - 1\right)\rho\right] - \ln(1-\rho)\right) \quad (20)$$

where q^* is calculated from Eq. (1) with r^*. To find the relations between the parameters of two frameworks, we assume that compressibility factors remain unchanged in the two frameworks. As segment length is assumed to be sufficiently large, the ratio q/r is identical

Table 1. Comparisons of QLF and the present model with saturated vapor pressure and liquid density

Component	T range [K]	AARD P^{sat} (%)[a]		AARD ρ^{sat} (%)		Ref
		QLF	This work	QLF	This work	
Methane	91-180	1.073	0.919	1.045	0.712	[22]
Hexane	244-485	1.872	2.029	1.041	0.596	[23]
Decane	320-600	1.984	2.233	1.983	1.143	[24]
2-Methylpropane	187-375	2.559	2.610	0.804	0.730	[23]
Cyclopentane	229-474	2.113	2.159	0.852	0.791	[23]
Dimethyl ether	179-400	1.649	1.553	1.407	1.331	[24-28]
Acetone	253-471	0.956	0.810	0.712	0.577	[23]
Ethyl acetate	253-503	1.974	2.113	0.855	0.539	[23]
Carbon dioxide	217-295	0.119	0.112	0.455	0.360	[29]

[a]AARD $x(\%) = 100/\text{Ndat}\sum|1 - x_i^{calc}/x_i^{exp}|$

Table 2. Optimized parameters for the QLF and the proposed model

Component	QLF			This work				V_H/V_H^*	r^*/r
	V_H^*	r^*	ε_{11}^*/k	V_H	r	ε_{11}/k	τ		
Methane	7.412	4.775	48.618	8.951	3.895	58.724	1.278	1.208	1.226
Hexane	13.167	8.804	109.714	10.209	11.503	84.320	0.740	0.775	0.765
Decane	15.593	11.640	125.256	11.632	15.879	91.857	0.707	0.746	0.733
2-Methylpropane	11.293	7.414	91.410	10.601	7.926	85.549	0.923	0.939	0.935
Cyclopentane	11.201	7.540	114.116	10.644	7.956	108.182	0.938	0.950	0.948
Dimethyl ether	7.590	7.282	90.832	8.527	6.418	102.970	1.167	1.123	1.135
Acetone	8.027	8.384	113.537	9.551	6.927	137.021	1.252	1.190	1.210
Ethyl acetate	8.815	9.900	110.108	7.667	11.481	94.919	0.843	0.870	0.862
Carbon dioxide	4.003	7.543	68.336	3.586	8.547	60.342	0.864	0.896	0.883

to q*/r*. Thus r and r* have the following relation:

$$r = \frac{r^*}{\tau} \qquad (21)$$

The τ also affects the lattice cell volume. If we assume that a closely packed molecular volume is conserved in the two frameworks, $rV_H = r^*V_H^*$, the lattice ice cell volumes, V_H and V_H^*, have the following relation:

$$V_H = \tau V_H^* \qquad (22)$$

Thus one might expect the relation between the parameters of the QLF model based on original GHM combinatorial factor and this work to be as follows:

$$\tau = \frac{r^*}{r} = \frac{V_H}{V_H^*} \qquad (23)$$

Table 2 shows that the three properties, τ, r^*/r and V_H/V_H^*, in Eq. (23) closely agree with each other for all components. It indicates that τ mainly affects the segment length as well as unit cell volume.

Table 2 also reveals that pair interaction energy parameter, ε, is affected by the introduced factor. It shows a similar behavior with cell volume that ε increases and decreases when $\tau > 1$ and $\tau < 1$ respectively. It implies that the present framework shows a more attractive contribution as $\tau > 1$ and more combinatorial contribution as $\tau < 1$, when compared to the original GHM work.

CONCLUSIONS

This paper proposes a modified GHM combinatorial factor. An equation of state was derived from the proposed combinatorial factor and tested against saturated vapor pressure and saturated liquid density for eight components. Compared with QLF, the proposed model shows better agreement with the saturated liquid density and a comparable result for saturated vapor pressure.

Contrary to our expectation for nearly constant τ, it was found to be strongly dependent on components, ranging from 0.707 to 1.278. However, the introduced factor was found to induce new size parameter sets different from those of other lattice fluid equation of state based on the original GHM combinatorial factor.

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NOMENCLATURE

A : Helmholtz energy
g : combinatorial factor
N_0 : number of holes (or vacant sites)
N_1 : number of molecules
N_q : total surface area parameter of the system including holes
N_r : number of total lattice sites
p_A : probability where given r sites is occupied by holes
p_B : probability where given r sites is occupied by a r-mer molecule

P : pressure
q : surface area parameter defined by Eq. (1)
r : segment length of component
V_H : unit cell volume
z : lattice coordination number
Z : compressibility factor

Greek Letters

β : reduced temperature defined by 1/kT
δ : flexibility parameter of molecule
ε_{ij} : interaction energy between pair i and j
θ : surface area fraction
ρ : reduced density or volume fraction
σ : symmetry number of molecule
τ : introduced parameter

Superscripts

ahm : athermal contribution
conf : configurational property
qca : quasi-chemical approximation
* : original GHM framework

Subscripts

0 : vacant sites or hole
i, j, k, l : component index

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