A Lattice Model Based on Molecular Clusters for Supercritical Fluids

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Abstract
A semi-empirical fluctuation term is presented to improve a classical equation of state (EOS) for volumetric properties in the critical region. The term is based on the two assumptions: (1) The Helmholtz energy is individually divided into classical and long-range density fluctuation contribution (2) All molecules form cluster near the critical region due to long-range density fluctuation. To formulate such molecular cluster, we extended the Veytsman statistics originally developed for the cluster due to hydrogen bonding. The probability function in the statistics is modified to represent the characteristics of long-range density fluctuation vanishing far from critical region. The proposed fluctuation contribution was incorporated into the Sanchez-Lacombe EOS and the combined model with 6 adjustable parameters has been tested against experimental VLE data. The combined model is found to well represent flatten critical isotherm for methane and top of the coexistence curve for the tested components. The prediction results for caloric data are in good agreement with the experimental data.

1. Introduction
The advance in chemical industrial process engineering requires thermodynamic model to describe various properties over a wide range of temperature and pressure. When the point of interest is far from critical point, classical equations of state [1-3] can be easily applied to calculate and predict physical properties. However, such equations of state often fail to satisfactorily reproduce physical properties near the critical region where a singular behavior in thermodynamic properties is observed [4]. The reason lies that classical equations of state are based on mean field approximation which neglects long-range density fluctuation near the critical point [5].

Several strategies [6-11] were proposed to overcome the deficiency of classical equations of state in describing physical properties near the critical point. These strategies can be classified as empirical and theoretical based. Renormalization group theory and crossover theory are good examples of the theoretical based approach [10-12]. The former is based on the phase-space cell approximation [13-14] as well as the Hamiltonian in White's work [15-16] and the latter founded on classical Landau expansion [170 around the critical point. These approaches have been extended to diverse frameworks such as cubic [10,18], hard-sphere [19,20] and lattice [21] and showed a good representation of the thermodynamic properties over a wide range of temperature and pressure. However, these approaches imply some disadvantages. Renormalization group theory requires numerical integration, indicating that EOS cannot be explicitly expressed. Crossover theory requires several parameters to fit experimental data due to its phenomenological and the signification of long-range density fluctuation has not been clarified [22].

The purpose of this study is to develop a different approach, an explicit alternative formulation of long range density fluctuation in terms of molecular cluster. The molecular clusters are found between molecules forming hydrogen bonding as well as polar fluids and modeled by well-known thermodynamic models such as chemical theory [23], Wertheim's theory [24,25] and Veytsman statistics [26]. However several researches showed that even non-hydrogen bonding molecules can form clusters (or aggregates) near the critical region. Pfund and co-workers [27] showed by small angle x-ray scattering (SAXS) that aggregates of xenon increases near the critical density. Tucker and Maddox [28] could show by molecular simulation that clustering between particles occurs around a critical point. The concept of molecular cluster near the critical region was first introduced in property calculation by Heideman and Prausnitz [23]. They modeled clustering of argon by
chemical theory and showed an improved representation of critical isotherm with their EOS. However no further development was done for non-hydrogen bonding molecules.

To develop this approach, the employed hydrogen bonding theory is required to be flexible enough to describe the clustering near the critical density since such theories were originally developed to account for the clustering at high density region. Hence, Veytsman statistics is used and extended because this statistics provides a probability function which determines the region where clustering is dominant. Lee et al.[29] concluded in their work that Veytsman statistics is enough flexible to account for other type of cluster such as intra-molecular hydrogen bond. We propose a modified probability function which becomes only significant near the critical density and temperature.

2. Thermodynamic Model

It is assumed that both quantities, long-range density fluctuation and molecular cluster, are exactly matched to each other. Let us denote $\Omega$ as classical configurational partition function. If we assign $\Omega_{\text{oc}}$ as partition function solely accounting for clustering effect, the correct total configuration partition function, $\Omega_{\text{t}}$, can be factorized as

$$\Omega_{\text{t}} = \Omega_{\text{oc}} \Omega_{\text{mc}}.$$  \hspace{1cm} (1)

The $\Omega_{\text{oc}}$ has two boundary conditions. As it is associated with the number of ways to distribute clustered molecules, it has a value of 1 at the region far from critical point and reaches some maximum value near the critical region.

$$P = -kT \frac{\partial \ln \Omega_{\text{t}}}{\partial \rho_a},$$  \hspace{1cm} (2)

where $k$ is Boltzmann constant and $\rho_a$ is molar density. We denote $P_c$ and $P_{mc}$ as pressures corresponding to $\Omega_{\text{oc}}$ and $\Omega_{\text{mc}}$ and these pressures have following relation by equation (2),

$$P_{\text{oc}} = -kT \frac{\partial \ln \Omega_{\text{oc}}}{\partial \rho_a} = -kT \frac{\partial \ln \Omega_{\text{mc}}}{\partial \rho_a},$$  \hspace{1cm} (3)

Equation 3 enables us to find the effect of clustering on P-$\rho$ isotherm. Suppose that the temperature of the system is close to critical temperature and clustering effect is most dominant at $\rho_c$ critical density. This indicates that $\Omega_{\text{mc}}$ has a maximum at $\rho_c$. The logarithmic $\Omega_{\text{oc}}$, $\ln(\Omega_{\text{oc}})$, has a similar behavior with $\Omega_{\text{mc}}$, nearly constant far from critical point and convex at $\rho_c$. Thus, its derivative with respect to density are positive convex between 0 and $\rho_c$ and negative concave between $\rho_c$ and $\rho_{mc}$, hard-core density. It means that molecular cluster effect makes a negative pressure correction at lower density than $\rho_c$ and positive pressure correction at higher density than $\rho_c$. Thus $P_{\text{oc}}$ becomes lower than $P_c$ between 0 and $\rho_c$ and higher between $\rho_c$ and $\rho_{mc}$.

The proposed clustering effect is able to flatten the classical pressure isotherm provided that $P_c$ satisfies flowing constraints,

$$P_{c}(T, \rho_c) = P_c$$  \hspace{1cm} (4)

Veytsman statistics was proposed to account for n-mer cluster due to association. Before extending Veytsman statistics to molecular cluster due to long-range density fluctuation, we briefly discuss the basic formalism of the statistics. In the case of pure hydrogen bonding components with single type of donor and acceptor, the number of ways of distributing $N_{HB}$, hydrogen bonding pairs between donor and acceptor, among $N_i$ molecules is,

$$P_a = \frac{(N_{a})(N_{d})}{(N_{a} - N_{HB})(N_{d} - N_{HB})} \frac{1}{N_{HB}^2}$$  \hspace{1cm} (5)

where $a, d$ is the number of donor and acceptor per molecule respectively. Equation 3 assumes that the donors and acceptors of hydrogen bonding pairs are not necessarily to be adjacent with each other. As hydrogen bonding occurs between donors and acceptors nearby, the exact number of ways of distributing $N_{HB}$ pairs between donor and acceptor is defined as,

$$P_{HB} = \frac{1}{N_i} \frac{3a}{r} \frac{3d}{r} = \frac{\rho}{r^2} \frac{3a}{3d}$$  \hspace{1cm} (6)

where $P_{HB}$ is the probability that donor and acceptor are located in the vicinity with respect to each other and thus hydrogen bonding occurs. Panayiotou and Sanchez[31] proposed $P_{HB}$ as,

$$P_{HB} = \frac{1}{N_i} \frac{3a}{r} \frac{3d}{r} = \frac{\rho}{r^2} \frac{3a}{3d}$$  \hspace{1cm} (7)

where $N_i$ is total number of lattice sites composed of $N_c$ holes and $N_i$ r-mers, $r$ is segment length of pure component, $\rho$ is reduced density or volume fraction defined as $rN_i/N_c$ and $S_{HB}$ is entropy loss resulting from hydrogen bonding formation. Equation 7 indicates that hydrogen bonding contribution is negligible at low density and significant at high density region. The canonical partition function of hydrogen bonding contribution is,

$$\Xi_{HB} = \mathcal{E}_{HB} e^{-\frac{E_{HB}}{kT}}$$  \hspace{1cm} (8)

where $E_{HB}$ is hydrogen bonding energy. The last exponential term in the right affects the dependence of
hydrogen bonding to the temperature. As clustering due to long-range density fluctuation is assumed to be negligible at the region far from critical point, the probability for such clustering is proposed as,

$$P_{\infty} = \frac{\rho^m}{\rho_{\infty}^m} (1-\rho)^n \chi$$  \hspace{1cm} (9)

where $\chi$ represents temperature dependence of $\rho_{\infty}$ and the exponent m and n represent the rate of rise and fall of $\rho_{\infty}$ in low and high density region respectively. They all have positive values. The proposed probability function satisfies following boundary condition: it become negligible at low and high density region because $\rho$ and $1-\rho$ lead the eq 9 to zero as $\rho \rightarrow 0$ and 1 respectively. Equation 7 has a maximum at the density $\rho^* = m/(n+m)$.

For $\chi$, a similar relation proposed by Krasak and Deiters [7] was found to be appropriated

$$\chi = C_0 e^{-\beta(N+N_p)} \hspace{1cm} (10)$$

where $T_r$ is reduced temperature defined as $T/T_c$, $H_1$ is a universal constant ($H_1 = 200$) and $C_0$ is component-specific adjustable parameter. This Gaussian function satisfies two boundary conditions with respect to temperature: clustering effect is significant at near-critical temperature and negligible at both low and high temperature region.

To derive a partition function for molecular cluster near the critical region, we made two assumptions. First, the number of donor and acceptor per molecule, a and d, were set to 1 to enable multiple cluster formation. Second, we assumed no interaction energy upon clustering formation between molecules. Thus the partition function is given as

$$Q_{\infty} = \frac{\rho^m}{\rho_{\infty}^m} (1-\rho)^n \chi \frac{(N_1)(N_2)}{(N_1-N_{\infty})(N_2-N_{\infty})} \frac{1}{N_1 N_2} \hspace{1cm} (11)$$

where $N_{\infty}$ is the number of clustered molecules due to long-range fluctuation. Equation (11) is maximized with respect to $N_{\infty}$ to give following constraint,

$$N_{\infty} = \left( N_1 - N_{\infty} \right)^2 \rho^{x-1} (1-\rho)^n \chi$$ \hspace{1cm} (12)

The Helmholtz energy of clustering effect is given as

$$\beta \Delta_{\infty} = -\ln Q_{\infty} \hspace{1cm} (13)$$

where $\beta$ is reciprocal temperature defined as $1/KT$.

Contributions to pressure and configurational reduced chemical potential due to molecular cluster are

$$P_{\infty} = \frac{1}{V_r \beta N_1} \left( \rho_{\infty} - \rho \right)$$ \hspace{1cm} (14)

$$\mu_{\infty} = \frac{N_1}{N_2} + 2(1 - \frac{N_{\infty}}{N_1}) \hspace{1cm} (15)$$

where $V_r$ is specific cell volume of lattice. The $N_{\infty}/N_1$ is positive root of equation (12) given as

$$\frac{N_{\infty}}{N_1} = \frac{2\Delta+1-\sqrt{1+4\Delta}}{2\Delta} \hspace{1cm} (16)$$

where $\Delta = \rho^m(1-\rho)^n \chi$.

The proposed contribution for molecular cluster is derived in the framework of lattice fluid. In the present study, we apply the proposed contribution to the Sanchez-Lacombe EOS. The basic Sanchez-Lacombe EOS has the form

$$P_{\infty} = \frac{1}{V_r \beta} \left[ (1-\rho) \ln(\rho) - \beta \rho \right] \hspace{1cm} (17)$$

$$\frac{\mu_{\infty}}{kT} = \frac{\rho_{\infty} V_r \beta}{\rho} + \frac{1}{\rho} \left( \frac{1}{\rho} \ln(\rho) - \beta \rho \right) \hspace{1cm} (18)$$

where $\epsilon$ is molecular interaction energy and subscript SL is abbreviation of Sanchez-Lacombe. The overall equation of pressure and chemical contribution are

$$P_r = P_{\infty} + P_{\text{exp}} \hspace{1cm} (19)$$

$$\frac{\mu_r}{kT} = \frac{\mu_{\infty}}{kT} + \frac{\mu_{\text{exp}}}{kT} \hspace{1cm} (20)$$

3. Results and Discussion

For pure fluids, the present model requires 3 classical parameters for description: the cell volume ($V_r$), segment number (r), and pair interaction energy ($\epsilon$). Besides these parameters, 3 parameters, m, n and $C_0$ are also required to describe the clustering effect. Although these parameters are empirically defined, we will discuss the connection of their value to the true physical behavior in later section. Thus the present model has six adjustable parameters. To obtain these model parameters, we adopted a specific regression technique called global regression[8]. The parameters are regressed at the same time by fitting the model to critical points, supercritical PVT data, saturated vapor pressure, and liquid density simultaneously over a wide temperature range. Objective function for the regression is defined as sum of average absolute relative deviation (AARD) of experimental data as follows,

$$\rho = \frac{\sum_{i=1}^{N} \left| \frac{\rho_{\text{exp}} - \rho_{\text{calc}}}{\rho_{\text{exp}}} \right|}{N} + \frac{\sum_{i=1}^{N} \left| \frac{\rho_{\text{calc}} - \rho_{\text{exp}}}{\rho_{\text{exp}}} \right|}{N} \hspace{1cm} (21)$$

where $NP_1$ and $NP_2$ are the number of experimental data of saturated properties and supercritical PVT data respectively and superscript L, exp, and calc stand for
liquid phase, experimental data and calculated data. Table 1 presents the best fitted parameters for the present models and AARD(%) of vapor pressure and saturated liquid density for each component. Most of components have AARD of less than 2% and 3% for saturated vapor pressures and saturated liquid densities respectively. The average AARD for all components are 1.3% for saturated vapor pressure and 2.2% for saturated liquid density. These large deviations may be further reduced if temperature dependent classical parameter is employed. But such strategy may yield the effect of critical anomaly to be partially included in the temperature dependence. These small deviations indicate that the constraint of correlating critical point does not impair the accuracy of VLE calculation.

It is a fundamental attribute for an EOS to accurately correlate volumetric properties such as saturated liquid density and supercritical PVT data.

4. Conclusion

This paper proposes a new formulation of long-range density fluctuation in terms of molecular cluster. The proposed contribution is developed for the classical EOS which overpredicts both critical temperature and critical pressure. It was incorporated into the Sanchez–Lacombe EOS and showed a good agreement with experimental volumetric and caloric data. The flatness of the top of coexistence curve and critical isotherm could be reproduced. In obtaining fluctuation effect, our approach is similar to the recent proposed version of crossover theory in that fluctuation effect is obtained by solving quadratic equation where the solution is analytically expressed. These quadratic form for fluctuation effect is more effective than other non-analytic fluctuation term.

References