Equation of State and Group Contribution Method for Polymer Systems

1. Equation of State

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ABSTRACT

We developed an equation of state for systems containing chain-like molecules. The equation consists of three contributions. As a reference, we first adopted the equation for hard-sphere-chain fluids (HSCF) derived through the r-particle cavity-correlation function of sticky hard spheres. The HSCF equation has a simple form similar to the Carnahan-Starling equation and has been satisfactory tested by computer-simulation results for chain fluids with a wide range of chain length. Secondly, for perturbation, we used the square-well equation (SW). Thirdly, for molecules with specific oriented interactions such as hydrogen bonding, we introduced contribution from chemical association (ASS). The corresponding expression for association comes naturally from the sticky model used in deriving the reference equation. The ASS term was well tested with computer-simulation results for associated molecules.. The equation of state was widely tested by fitting experimental vapor-liquid equilibria. For liquid-liquid equilibria, we adopted a lattice model developed previously as a high-pressure limit that virtually serves as a mixing rule.

1. INTRODUCTION

In recent years, much attention has been given toward development of an equation of state for an assembly of chain-like molecules in the free-space (off-lattice) forms. We have made efforts in the same line and developed a HSCF equation [1,2] through the r-particle cavity-correlation function of sticky hard spheres based on the model of Stell, Cumming and Zhou [3,4,5]. The HSCF equation has a simple form similar to the Carnahan-Starling equation and has been satisfactory tested by computer-simulation results for chain fluids with a wide range of chain length. Later, we developed a practical equation of state [6] by combining the HSCF equation with a square-well (SW) perturbation term from Alder et al's work [7].

For ordinary fluids and fluid mixtures, nonideality is usually attributed to physical forces between molecules. However, for carboxylic acids, alcohols, phenols, amides, water and their mixtures, as well as some mixtures of non-associating substances such as acetone and chloroform, self-association or cross-association occur between molecules due to hydrogen bonding. In these cases, chemical theories of association are always adopted in addition to the physical interactions to account for the nonideal behavior. Earlier work based on equations of state was almost exclusively using phenomenological approach (e.g. Heidemann and Prausnitz [8], Hu,

Azevedo, Ludecke and Prausnitz [9], Hong and Hu [10]). Recently, there has been substantial progress in the statistical mechanical theories of association which provide deeper insight into the structure of the fluids containing associated molecules (e.g. SAFT equation by Chapman, Gubbins, Jackson and Radosz [11], shield-sticky theory by Zhou and Stell [5]). The above HSCF equation can also be extended to fluids containing associated molecules.

In this work, we present a practical equation of state for chain-like molecules either associated or non-associated. The equation consists of three contributions, i.e., a HSCF equation as a reference, a SW term as a perturbation, and an association term (ASS) accounting for the specific interactions. The equation of state is widely tested by fitting experimental vapor-liquid equilibrium and liquid-liquid equilibrium data.

2. EQUATION OF STATE FOR PURE FLUIDS

Real fluids containing associated chain-like molecules can be approximated by a square-well-chain fluids with association between molecules. For a pure-component system of molecules with chain length r, the residual Helmholtz function A^r and the compressibility factor Z can be expressed as:

$$A^r = A^{r(\mathrm{HSCF})} + \Delta A^{(\mathrm{SW})} + \Delta A^{(\mathrm{ASS})} \tag{1}$$

$$Z = Z^{(\mathrm{HSCF})} + Z^{(\mathrm{SW})} + Z^{(\mathrm{ASS})} \tag{2}$$

where superscripts denote the contributions of HSCF, SW and ASS, respectively.

Theoretical Basis

We consider a system composed of species S which can form linear r-mer associates S_r by the reaction $r\mathrm{S} \Rightarrow \mathrm{S}_r$. By adopting the sticky-point model of Cummings and Stell [3] for each nearest-neighbor pair, the Mayer function for a group of r segments can be expressed as:

$$\begin{aligned} f^{(r)} &= -1 + \prod_{\substack{i=1 \\ j=i+1}}^{r-1} \left(L \sum_{k=1}^{m} \mathrm{d}\left(\mathbf{r}_{ij} - \mathbf{L}_k\right) / 12\mathrm{t} \right) && r_{ij} < \mathrm{s} \\ &= -1 + \exp\left(-\mathrm{b}\mathrm{e}^{(r)}\right) && r_{ij} > \mathrm{s} \end{aligned} \tag{3}$$

where variables $\mathbf{r}_{ij}$ and r_{ij} are the inter-segment distance vector and the corresponding mode, respectively for segments S_i and S_j , m is the number of different interaction configurations for each nearest-neighbor pair S_i-S_j, each configuration is characterized by an inter-segment distance vector $\mathbf{L}_k$, k=1-m , originated from a definite number of interaction sites on each segment. The corresponding mode is L irrespective of k. Symbol δ is a Kronecker delta, s is the collision diameter, t^{-1} is an association parameter called stickiness parameter, $\mathrm{e}^{(r)}$ is the attractive energy. The corresponding r-particle total correlation function when $r_{ij} < \mathrm{s}$ can be written as

$$h^{(r)} = -1 + \prod_{\substack{i=1 \\ j=i+1}}^{r-1} \left(\lambda \quad L \sum_{k=1}^{m} \delta\left(\mathbf{r}_{ij} - \mathbf{L}_k\right) / 12 \right) \quad , \qquad r_{ij} < \sigma \tag{4}$$

where λ is a distribution parameter theoretically determined by τ^{-1}.

For a pure-component fluid with a total number of monomers N_0, including both unassociated and associated, the corresponding number density $\rho_0 = N_0/V$, the degree of association α could be defined as:

$$\alpha \equiv r\rho_r / \rho_0 = r\omega_0^{r-1} \int_{\mathbf{L}_-}^{\mathbf{L}_+} g^{(r)}(\mathbf{r}_{12}, \mathbf{r}_{23}, \ldots, \mathbf{r}_{r-1,r}) d\mathbf{r}_{12} d\mathbf{r}_{23} \ldots d\mathbf{r}_{r-1,r} / r! \tag{5}$$

where ρ_r is the number density of the r-mer, $g^{(r)}$ is the r-particle radial distribution function, $h^{(r)} = g^{(r)} - 1$. Substitution of eq.(4) into eq.(5) yields

$$\alpha = \omega\rho_0^{r-1}\left(\lambda \quad \pi L^3 / 3\right)^{r-1} (r-1)! \tag{6}$$

where ω is a fraction of possible configurations for an r-mer in the phase space determined by m, it is virtually a surface fraction of a segment responsible for stickiness. Now we define the r-particle cavity correlation function (CCF).

$$y^{(r)} = \exp(\beta\varepsilon^{(r)}) g^{(r)} \tag{7}$$

When $\mathbf{r}_{ij} = \mathbf{L}_k, k = 1 - m$, the r-particle group becomes a r-mer associate. By substituting eqs.(3)(4) and (6) into eq.(7), we have an useful expression of the r-particle CCF for a r-mer associate.

$$y^{(r)}(\mathbf{L}) = \left(\tau \quad \lambda \quad \right)^{r-1} = \frac{\alpha (r-1)!}{\omega\rho_0^{r-1}\left(\lambda \quad \pi L^3 / 3\right)^{r-1}} \tag{8}$$

where $\mathbf{L}$ represents all $\mathbf{L}_k$.

To obtain the Helmholtz function, we use its functional derivative with respect to the Mayer function of a r-particle group, which is related to the r-particle CCF by the following equation.

$$\frac{\delta(\beta A / V)}{\delta f^{(r)}} = -\omega\rho_0^{r} \times y^{(r)}(\mathbf{r}_{12}, \mathbf{r}_{23}, \ldots, \mathbf{r}_{r-1,r}) / r! \tag{9}$$

From eq.(3) we have

$$\mathrm{d}f^{(r)} = \prod_{\substack{i=1\\ j=i+1}}^{r-1}\left(L \sum_{k=1}^{m} \mathrm{d}(\mathbf{r}_{ij} - \mathbf{L}_k)/12 \right) \mathrm{d}t^{-(r-1)} \tag{10}$$

Substituting into eq.(9), integrating from $\mathbf{L}_k$- to $\mathbf{L}_k$+ and 0 to t^{-1}, and using eq.(8), we have

$$\begin{aligned} \frac{\beta[A(\alpha) - A(\alpha=0)]}{N_0} &= -\frac{1}{r}\int y^{(r)}(\mathbf{L})d[\alpha / y^{(r)}(\mathbf{L})] \\ &= -\frac{1}{r}\left[\int_0^{\alpha} d\alpha - \int_{\alpha=0}^{\alpha=\alpha} \alpha d\ln y^{(r)}(\mathbf{L})\right] = -\frac{1}{r}\left[\alpha - \int_{\alpha=0}^{\alpha=\alpha} \alpha d\ln y^{(r)}(\mathbf{L})\right] \end{aligned} \tag{11}$$

.

From eq.(11), we can use thermodynamics to obtain an equation of state.

$$p = \rho_0^2 \left(\frac{\partial(A/N_0)}{\partial\rho_0} \right)_{T,t^{-1}} \tag{12}$$

As shown in eq.(11), to obtain the Helmholtz function and then the equation of state, we must have the information of the r-particle CCF for an r-mer chain with a special configuration. Unfortunately, it is almost impossible to obtain it theoretically for polymers at present. We then approximate it by a product of two contributions: a chemical contribution $(1-\alpha)^r$ dependent on the degree of association, and a physical contribution expressed by the product of nearest-neighbour effective two-particle CCFs $y^{(2e)}_{S_iS_{i+1}}$ and the product of next-to-nearest-neighbour effective two-particle CCFs $y^{(2e)}_{S_iS_{i+2}}$. The correlations between two particles apart from more than one particle are reasonably neglected.

$$y^{(r)}(\mathbf{L}) = (1-\alpha)^r \prod_{i=1}^{r-1} y^{(2e)}_{S_iS_{i+1}} \prod_{i=1}^{r-2} y^{(2e)}_{S_iS_{i+2}} \tag{13}$$

Substitution into eqs.(11) and (12) yields:

$$\beta\left[A(\alpha) - A(\alpha=0)\right]/N_0 = \ln(1-\alpha) + \alpha(r-1)/r \tag{14}$$

$$\frac{\beta[p(\alpha) - p(\alpha=0)]}{\rho_0} = -\frac{\alpha}{r}\left[r - 1 + \rho_0 \sum_{i=1}^{r-1} \frac{\partial \ln y^{(2e)}_{S_iS_{i+1}}}{\partial\rho_0} + \rho_0 \sum_{i=1}^{r-2} \frac{\partial \ln y^{(2e)}_{S_iS_{i+2}}}{\partial\rho_0} \right] \tag{15}$$

If we have density dependence of those nearest-neighbour and next-to-nearest-neighbour effective two-particle CCFs, and the equation of state for corresponding monomers (α=0), we can obtain an equation of state for a chain fluid (α=1). Also we can study the contribution of chemical association by these equations.

Hard-Sphere-Chain Reference Term

The density dependence of the effective two-particle CCF $y^{(2e)}_{S_iS_{i+1}}$ for the nearest-neighbour pair can be accurately derived from the rigorous Tildesley-Streett equation [12]. The density dependence of the effective two-particle CCF $y^{(2e)}_{S_iS_{i+2}}$ for the next-to-nearest-neighbour pair is obtained by fitting computer simulation data of compressibility factors for linear homonuclear hard-sphere trimers. Carnahan-Starling equation is used for the corresponding monomer system to express $A(\alpha=0)$ and $Z(\alpha=0)$. The final residual Helmholtz function and the equation of state for homonuclear HSCFs [1] are then obtained by substituting $\alpha=1$ into eqs.(11) and (15).

$$\frac{\beta A^{r(\mathrm{HSCF})}}{N^0} = \frac{(3+a-b+3c)\eta-(1+a+b-c)}{2(1-\eta)} + \frac{1+a+b-c}{2(1-\eta)^2} + (c-1)\ln(1-\eta) \quad (16)$$

$$Z^{(\mathrm{HSCF})} = \frac{1+a\eta+b\eta^2-c\eta^3}{(1-\eta)^3} \quad (17)$$

where $\eta = \pi\rho_0\sigma^3/6$ is the reduced density, a, b and c are functions of chain length.

Square-Well Perturbation Term

For practical reason, we do not try to find correlation functions for square-well fluids. Instead, we use a perturbation term from Alder et al's work [7].

$$\frac{\beta\Delta A^{SW}}{N_0} = \pi\sum_m^9\sum_n^4 A_{mn}(3\sqrt{2}/\eta)^m\eta^m\tilde{T}^{-n} \quad (18)$$

$$Z^{(SW)} = \pi\sum_m^9\sum_n^4 mA_{mn}\left(3\sqrt{2}/\eta\right)^m\eta^m\tilde{T}^{-n} \quad (19)$$

where $\tilde{T} = kT/\varepsilon$ is the reduced temperature, ε is the depth of the square well, A_{mn} are numerical coefficients.

Contribution by Chemical Association

We consider a pure-component system composed of N_0 spherical molecules with number density $\rho_0 = N_0/V$. Associated dimers with bond length L can be formed by these molecules. With r=2, eqs.(14) become

$$\frac{\beta\Delta A^{ass}}{N_0} = \ln(1-\alpha) + \frac{1}{2}\alpha \quad (20)$$

From thermodynamics, we have the corresponding contribution to the compressibility factor due to association,

$$Z^{ass} = \beta[p(\alpha) - p(\alpha = 0)]/\rho_0 = \rho_0\left[\partial\left(\beta\Delta A^{ass}/N_0\right)/\partial\rho_0\right]_{T,\tau^{-1}}$$

$$= -\frac{\rho_0}{2}\left(\frac{1+\alpha}{1-\alpha}\right)\left(\frac{\partial\alpha}{\partial\rho_0}\right)_{T,\tau^{-1}} \tag{21}$$

From eqs.(8) and (13), we have

$$\alpha = \frac{\left[2\rho_0\Delta + 1\right] - \sqrt{1 + 4\rho_0\Delta}}{2\rho_0\Delta} \tag{22}$$

$$\Delta = \rho\omega L^3\tau^{-1} y^{(2e)}_{S_iS_{i+1}}/3 \tag{23}$$

where the sticky parameter $\tau^{-1} = e^{\beta\varepsilon} - 1$, ε is the sticky or association energy, $y^{(2e)}_{S_iS_{i+1}}$ is the effective two-particle CCF for the nearest-neighbour pair calculated in previous work [1]. Equation (21) has been satisfactory tested by computer-simulation data [13] for an associated hard-sphere-dumbbell fluid (a mixture of hard-sphere dimers and linear hard-sphere quadrimers) at different associating strength.

3. EQUATION OF STATE AND VLE FOR FLUID MIXTURES

For fluid mixtures, eqs.(1) and (2) can still be used for residual Helmholtz function A^r and the compressibility factor Z. The difference from that for pure substance lies in the following. For the HSCF contribution, instead of Carnahan-Starling equation, Mansoori-Carnahan-Starling-Leland equation is used for the corresponding monomer system to express $A(\alpha=0)$ and $Z(\alpha=0)$, details refer to [1,2]. For the SW contribution, a mixing rule is used for calculate the reduced temperature,

$$\tilde{T}^{-1} = \sum_{i=1}^{K}\sum_{j=1}^{K}\phi_i\phi_j\left(\varepsilon_{ij}/kT\right)\sigma_{ij}^3 \Big/ \sum_{i=1}^{K}\sum_{j=1}^{K}\phi_i\phi_j\sigma_{ij}^3 \tag{24}$$

$$\sigma_{ij} = \left(\sigma_i + \sigma_j\right)/2, \quad \varepsilon_{ij} = \left(1 - k_{ij}\right)\left(\varepsilon_i\varepsilon_j\right)^{1/2} \tag{25}$$

where ϕ_i is volume fraction of segment i. For ASS contribution, another mixing rule is used for the cross association between molecules of different kind.

$$\omega_{ij} = (\omega_{ii} + \omega_{jj})/2 \quad , \quad \varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2} \tag{26}$$

Figs. 1-4 show examples of vapor-liquid equilibrium calculations for systems PS+ toluene, PS+cyclohexane, PEO+water and PVAc+methanol, respectively. The later two systems involve hydrogen-bonding molecules. With one adjustable parameter k_{12}, vapor pressures for solutions in different temperature can be fit quite satisfactory.

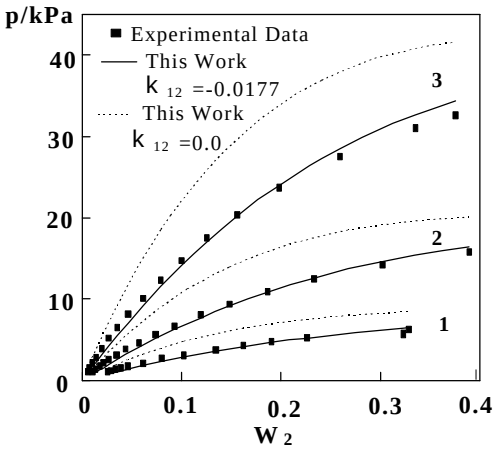

Fig.1 VLE of PS+toluene at 1-353.15K, 2-333.15K, 3-313.15K. $Mw_1 = 218000$.

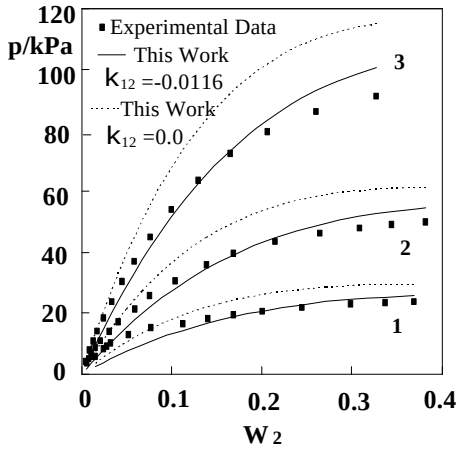

Fig.2 VLE of PS+cyclohexane at 1-353.15K. 2-333.15K, 3-313.15K. $Mw_1 = 218000$.

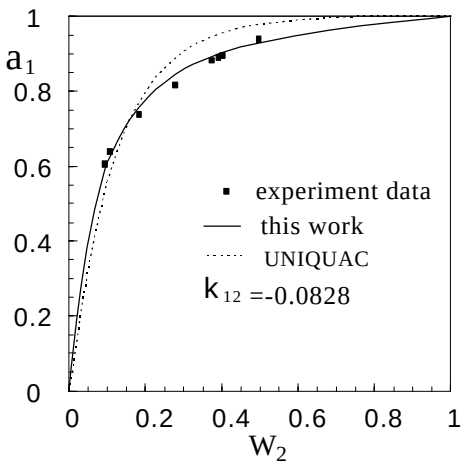

Fig.3 VLE of PEO+water water at 313.15K. $Mw_1 = 1500$.

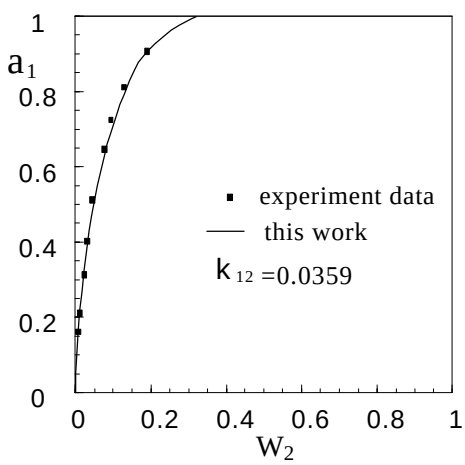

Fig.4 VLE of PVAc+Methanol. at 293.15K. $Mw_1 = 74000$

4. LIQUID-LIQUID EQUILIBRIA

For the calculation of liquid-liquid equilibria, we need a special mixing rule on the basis of a lattice approach. The Helmholtz function can be expressed as

$$A = A(\text{off-lattice}) + A^{(\text{CORR})} \tag{27}$$

$$A^{(\text{CORR})} = f[\Delta_{mix} A(\text{lattice}) - \Delta_{\text{mix}} A(\text{off-lattice}, p = \infty)] \tag{28}$$

$$f = g\eta / (1 + g\eta) \tag{29}$$

where A(off-lattice) can be expressed by eq.(1) with no adjustable parameter, k_{ij}=0. The correction term $A^{(\text{CORR})}$ accounts for the difference between lattice approach and off-lattice approach. It is introduced because the chain-like molecules are better represented by a lattice in the high-density liquid state. The $\Delta_{\text{mix}}A$(lattice) can be expressed by any lattice model. f expressed by eq.(29) is introduced to accout for the density dependence, where g is an empirical coefficient, g=18. Two adjustable

parameters is used for the revised Freed lattice model developed previously [14]: a size parameter c_r determining the effective volume fraction by

$$r_i^{eff} = r_i(1+\sum_j c_{rij} f_j) \quad , \quad c_{rij} = -c_{rji} \tag{30}$$

and an exchange energy parameter ¸ , they are obtained by fitting LLE data.

Figures 5 and 6 show examples of liquid-liquid-equilibrium calculations for systems PS+PBD and PS+PVE, respectively. The former shows UCST while the later exhibits LCST. For good fit, a temperature dependence for the exchange energy parameter ¸ is better to be used as shown in Fig. 6.

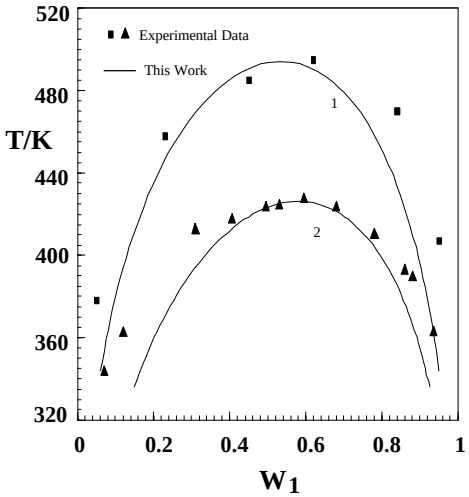

Fig.5 LLE of PS+PBD. 1- $Mn_1 = 3302$, $Mn_2 = 2350$, $c_r = 0.0812$, $\in = -40.789$; 2- $Mn_1 = 2220$,- $Mn_1 = 3302$, $Mn_2 = 2350$, $c_r = 0.0758$, $\in = -29.983$. ®®

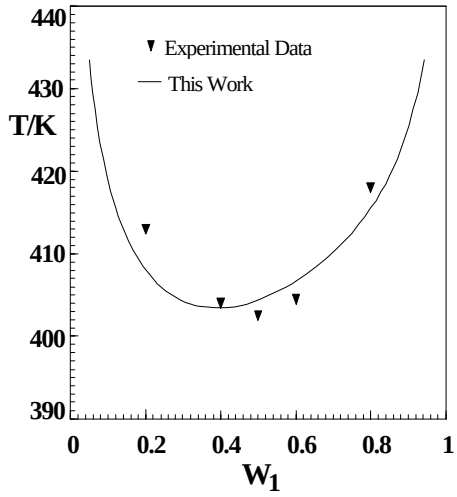

Fig 6 LLE of PS+PVE. $Mw_1 = 67000$, $Mw_2 = 95000$, $c_r = 0.1208$, $\in = -65.468 + 1873/T - 20340/T^2$,

5. DISCUSSION AND CONCLUSION

Although the equation developed is semiempirical because of the approximations inherently introduced during the derivation, it can stand the test of computer simulation to ensure its sound theoretical backgroud. On the other hand, the equation has simple form that usually can not be obtained by rigorous theoretical method. The model developed can be used both for ordinary fluids and for polymers. Limited by the length, only a few of examples are presented. Further results for a group contribution method will be reported in the second part of this paper.

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