On the information and methods for calculation of Sanchez-Lacombe and group-contribution lattice-fluid equations of state

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Abstract−The algorithms for calculation of densities from Sanchez-Lacombe (S-L) and group-contribution lattice-fluid (GCLF) equations of state have been put forward, respectively. From the S-L equation of state the relationship between the equation characteristic parameters and critical properties was deduced, and the influence of molecular weight of the polymers on critical properties was investigated. However, for the GCLF equation of state, it was surprising to find that there as many as four roots were found at a saturation temperature and pressure for gases, while still two roots above the critical temperature. For polymers, only two roots could be found. So the formerly accepted consistency between the magnitude of the density and vapor or liquid phase is not applicable yet. A way about how to identify the root and corresponding phase was suggested.

Key words: Sanchez-Lacombe (S-L) Equation of State, Group-contribution Lattice-fluid (GCLF) Equations of State, Calculation, Polymers, Algorithm

INTRODUCTION

The gas solubility and the effects of dissolved gases on the physical properties of a polymer at rubbery or molten state, such as swelling volume, are important in optimal design and process control of polymer production because the permeation rate is a function of the gas diffusion coefficient and solubility [Garg et al., 1994]. Even when measuring the solubility by means of magnetic suspension balance (MSB) method, and correlating the solubility data of polymer-gas systems, the densities of the individual component and the mixture must be estimated. Especially, in recent years the use of polymers as the solvents of distillation processes has received increasing attention [Lei et al., 2003, 2005; Li et al., 2005]. But no thermodynamic model has been used to describe the phase equilibrium of polymer-gas systems. However, the familiar cubic equations of state such as van der Waals, Redlich-Kwong, Peng-Robinson equations of state, etc. are not suitable for polymer-gas systems [Lee and Kang, 2005; Serbanovic et al., 2004]. The most commonly used equations of state (EOS) describing the P-V-T behavior of polymer-gas systems are the Sanchez-Lacombe (S-L) [Sanchez and Lacombe, 1976, 1978] and group-contribution lattice-fluid (GCLF) [Byun and Choi, 2004; High and Danner, 1990; Peng et al., 2001] both of which are based on lattice-fluid models in which a mean field approximation is used to determine the number of configurations available to a system of N molecules each of which occupies r sites and N_0 vacant sites (holes). In this approximation, firstly, random mixing of the r sites with each other and with the vacant sites is assumed. Then, local nonrandomness is considered by adding extra parameters to account for molecular interaction.

Since the S-L and GCLF equations of state are of the form of transcendental equations, the calculation of densities (or molar vol-

umes) is more complicated than that of common cubic equations of state which, however, are only suitable for low molecular weight compounds. It is known that cubic equations of state can be transformed into cubic polynomials with respect to molar volume. Unfortunately, even for these simple forms we often get into trouble in solving them using the traditional Newton-Raphson method because unreasonable densities (or molar volumes) are obtained, let alone S-L and GCLF equations of state. As we know, most of the equations of state are of the property of multiple peaks, and the Newton-Raphson method is only valid for solving local extremum. Thus, the converged results strongly depend on the initial values. The appropriate initial values are sometimes in a very narrow range at high pressure. In order to find all of the meaningful roots, various initial values should be set by trial and error by hand. For a one-stage equilibrium calculation, it may be possible to discard unmeaningful roots immediately. But for multi-stage equilibrium calculation, this would not be feasible. However, to date no computation methods for solving the S-L and GCLF equations of state are readily available in the references. Therefore, one has to look for a new algorithm for solving equations of state.

CALCULATION FOR THE S-L EQUATION OF STATE

The S-L equation of state is given by

$$\tilde{P} = -\tilde{\rho}^2 - \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1-\frac{1}{r}\right)\tilde{\rho}\right] \qquad (1)$$

$$\tilde{P} = \frac{P}{P^*}, \quad \tilde{\rho} = \frac{\rho}{\rho^*}, \quad \tilde{T} = \frac{T}{T^*}, \quad r = \frac{MP^*}{RT^*\rho^*} \qquad (2)$$

where $\tilde{P}$, $\tilde{\rho}$ and $\tilde{T}$ are the reduced pressure, density and temperature, respectively; P^*, ρ^* and T^* are characteristic parameters of the S-L equation of state either for pure components or for mixtures (only the mixing and combing rules need to be incorporated).

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In the case of the reduced density $\tilde{\rho}$ as variable, Eq. (1) becomes

$$f(\tilde{\rho}) = \tilde{P} + \tilde{\rho}^2 + \tilde{T}\left[\ln(1-\tilde{\rho}) + \left(1-\frac{1}{r}\right)\tilde{\rho}\right] \qquad (3)$$

Deriving Eq. (3) with respect to $\tilde{\rho}$,

$$f'(\tilde{\rho}) = 2\tilde{\rho} + \tilde{T}\left[\frac{-1}{1-\tilde{\rho}} + \left(1-\frac{1}{r}\right)\right] \qquad (4)$$

For the Newton-Raphson method,

$$\tilde{\rho}^{n+1} = \tilde{\rho}^n - \frac{f(\rho)}{f'(\rho)} \qquad (5)$$

which might lead to undesirable solutions if directly used. But in another way we can investigate the solution configuration by locating the extremum points satisfying that

$$f'(\tilde{\rho}) = 0 \qquad (6)$$

The roots of Eq. (6) are

$$\tilde{\rho}_1 = \frac{-[\tilde{T}(1-1/r) - 2] - \sqrt{[\tilde{T}(1-1/r) - 2]^2 - 8\tilde{T}/r}}{4} \qquad (7)$$

and

$$\tilde{\rho}_2 = \frac{-[\tilde{T}(1-1/r) - 2] + \sqrt{[\tilde{T}(1-1/r) - 2]^2 - 8\tilde{T}/r}}{4} \qquad (8)$$

Fig. 1. Algorithm for solving S-L equation of state to obtain the vapor and liquid densities.

Evidently,

$$|\tilde{T}(1-1/r) - 2| > \sqrt{[\tilde{T}(1-1/r) - 2]^2 - 8\tilde{T}/r} \qquad (9)$$

from which one can conclude that $\tilde{\rho}_1$ and $\tilde{\rho}_2$ have the same sign, provided that $\Delta = [\tilde{T}(1-1/r) - 2]^2 - 8\tilde{T}/r \geq 0$.

Thus, an algorithm for solving S-L equation of state to obtain the vapor and liquid densities is proposed (see the block diagram Fig. 1).

In addition, we can go a further step to explore some interesting phenomena on the basis of the above analysis:

1. For polymers, due to enormous molecular weights, $r \to \infty$. In other words, $\Delta \geq 0$ and $\tilde{\rho}_1 \to 0$ ($\tilde{P}_1 \to 0$ corresponding to the vapor phase). This means that the vapor pressure of polymers can be neglected.

2. According to the S-L equation of state, the P-V-T behavior of long polymers does not depend on their molecular weight.

3. If $\Delta = [\tilde{T}(1-1/r) - 2]^2 - 8\tilde{T}/r = 0$ (which is equivalent to $(\partial \tilde{P}/\partial \tilde{\rho})_{Tc} = 0$ and $(\partial^2 \tilde{P}/\partial \tilde{\rho}^2)_{Tc} = 0$), then $T = T_c$. Therefore, the critical temperature, density and pressure are obtained as follows:

$$T_c = \frac{2T^*r}{(1+\sqrt{r})^2} \qquad (10)$$

$$\rho_c = \frac{\rho^*}{1+\sqrt{r}} \qquad (11)$$

$$P_c = \frac{2P^*[r\ln(1+1/\sqrt{r}) + 1/2 - \sqrt{r}]}{(1+\sqrt{r})^2} \qquad (12)$$

Eqs. (10)-(12) construct a bridge between the characteristic parameters of S-L equation of state (P^*, ρ^* and T^*) and critical properties (T_c, ρ_c and P_c). In particular, this can be used to determine the critical properties of polymers, which, otherwise, cannot be done by well-known prediction methods, e.g., the Joback method [Poling et al., 2001].

Figs. 2 through 4 illustrate the influence of molecular weight of polypropylene (PP) and polystyrene (PS) on critical properties (T_c, ρ_c and P_c). The critical pressure, P_c, is so minute that it is approximately equal to zero as the molecular weight increases to some extent; with increasing the molecular weight, the critical density ρ_c de-
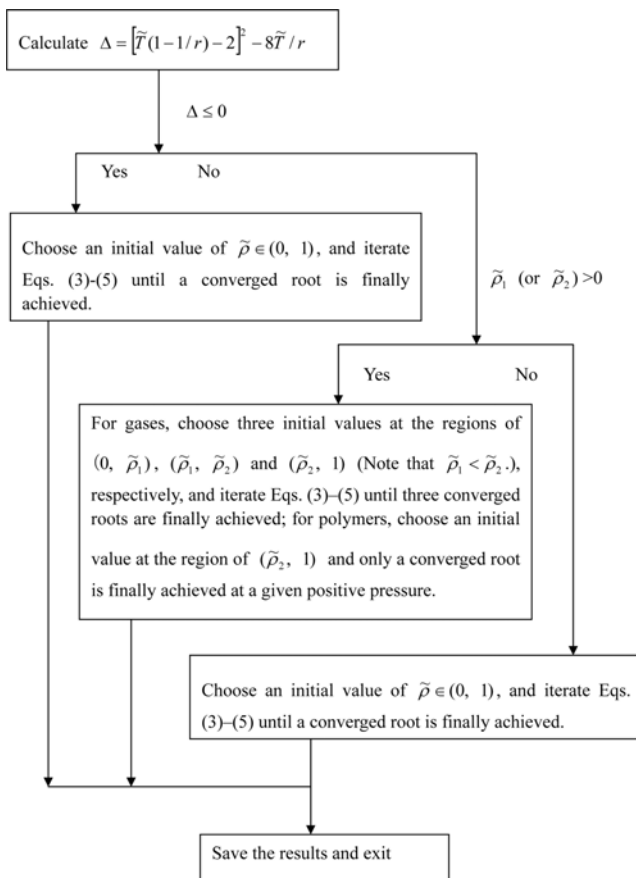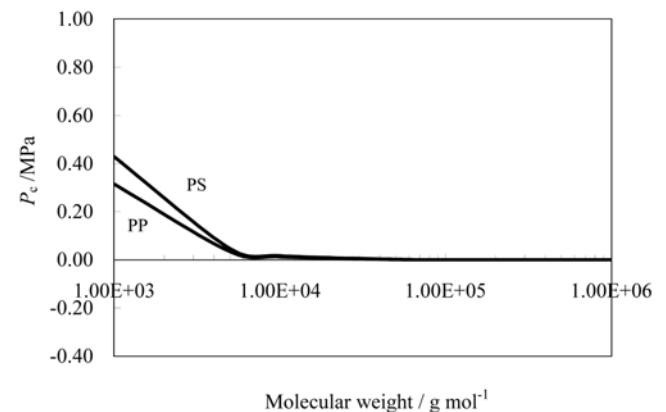

Fig. 2. Influence of the molecular weight of PP and PS on the critical pressure P_c.

creases but the critical temperature T_c increases; however, the higher the molecular weight, the slower the change of ρ_c and T_c. In contrast to the low value of P_c, T_c is very high, above 1,000 K for PP and PS.

CALCULATION FOR THE GCLF EQUATION OF STATE

The GCLF equation of state is established based on the Panayiotou-Vera EOS, and is of the form:

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\right) + \frac{z}{2}\ln\left(\frac{\tilde{v}+q/r-1}{\tilde{v}}\right) - \frac{\theta^2}{\tilde{T}} \tag{13}$$

where $\tilde{P}$, $\tilde{T}$ and $\tilde{v}$ are the reduced pressure, temperature and molar volume, respectively, defined by

$$\tilde{P} = \frac{P}{P^*}, \quad \tilde{T} = \frac{T}{T^*}, \quad \tilde{v} = \frac{v}{v^*} = \frac{1}{\tilde{\rho}}, \quad \theta = \frac{q/r}{\tilde{v}+q/r-1} \tag{14}$$

and

$$P^* = \frac{z\varepsilon^*}{2v_h}, \quad T^* = \frac{z\varepsilon^*}{2R}, \quad v^* = v_h r \tag{15}$$

$$zq = (z-2)r+2 \tag{16}$$
$z=10$, $R=8.314\,J\,mol^{-1}\,K^{-1}$, $v_h=9.75\times10^{-3}\,m^3\,kmol^{-1}$.

where q is the interaction surface area parameter, r the number of lattice sites occupied by a molecule, z the coordination number, R the universal gas constant, v_h the volume of a lattice site, and P^*, T^* and v^* referred to as scaling parameters.

This equation of state contains two adjustable parameters, molecular interaction energy ε^* and molecular reference volume v^*, that are suitable for either pure components or mixtures (only the mixing and combing rules need to be incorporated). Once these two parameters are known, all of the remaining parameters in Eq. (13) can then be determined from Eqs. (14)-(16) with respect to reduced volume at a given temperature and pressure. In contrast to the S-L equation of state, here it is more convenient to search for the roots using reduced volume instead of reduced density since Eq. (13) is formulated with respect to reduced volume.

Ethane and polypropylene (PP) are selected as the representatives of gases and polymers, respectively. The equation parameters come
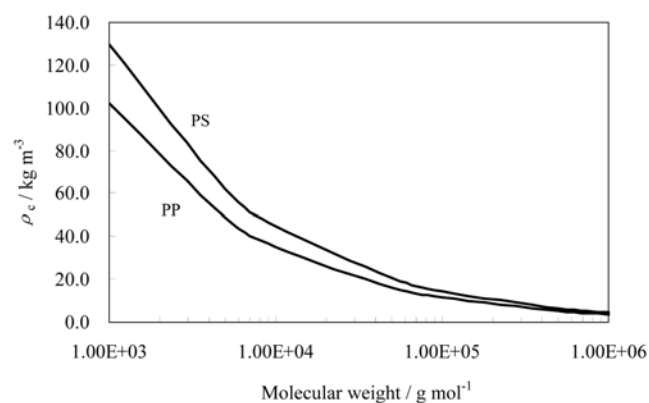

Fig. 3. Influence of the molecular weight of PP and PS on the critical density ρ_c.
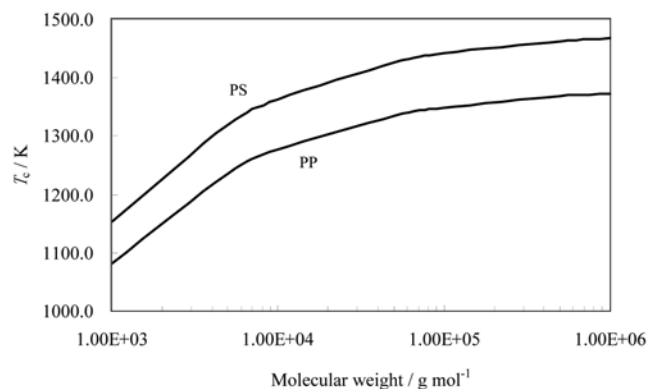
Fig. 4. Influence of the molecular weight of PP and PS on the critical temperature T_c.
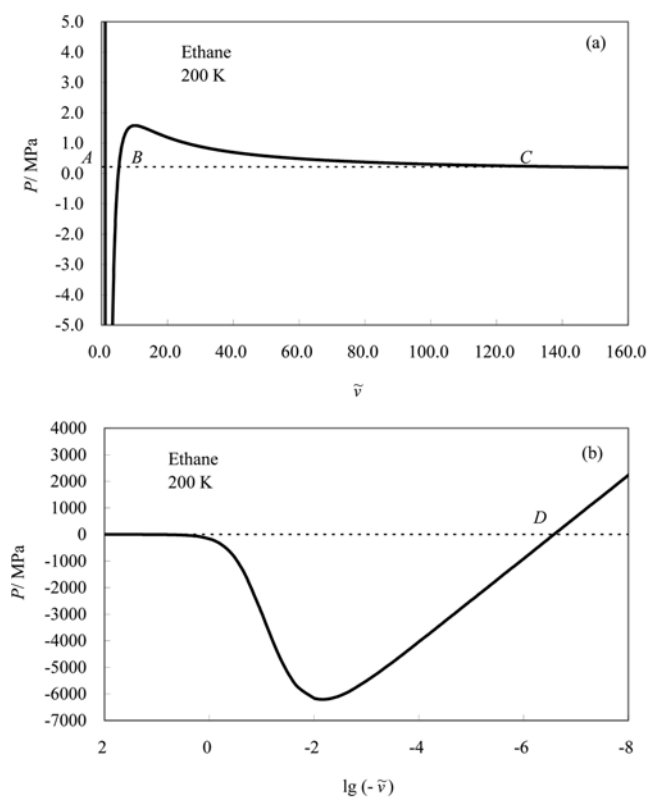

Fig. 5. 200 K isotherm of ethane, calculated with the GCLF equation of state: (a) in the positive direction of $\tilde{v}$; (b) in the negative direction of $\tilde{v}$; the dashed line represents P=saturated vapor pressure (0.2176 MPa) at 200 K; $\tilde{v}=1/\tilde{\rho}$.

from Lee and Danner [1996]. Figs. 3-5 illustrate the isotherms of ethane and polypropylene (PP). It can be seen that:

1. From the isotherm of ethane at 200 K shown in Fig. 5, four roots corresponding to the saturated vapor pressure are found: points A ($\tilde{v}=1.10$), B ($\tilde{v}=5.25$), C ($\tilde{v}=141.05$) and D ($\tilde{v}=-2.0\times10^{-7}$). Thus, the question arises, which root corresponds to which phase? Comparison with the results coming from the website (NIST data bank): http://webbook.nist.gov/chemistry/form-ser.html shows that the root with the highest density (point A) corresponds to the liquid phase,
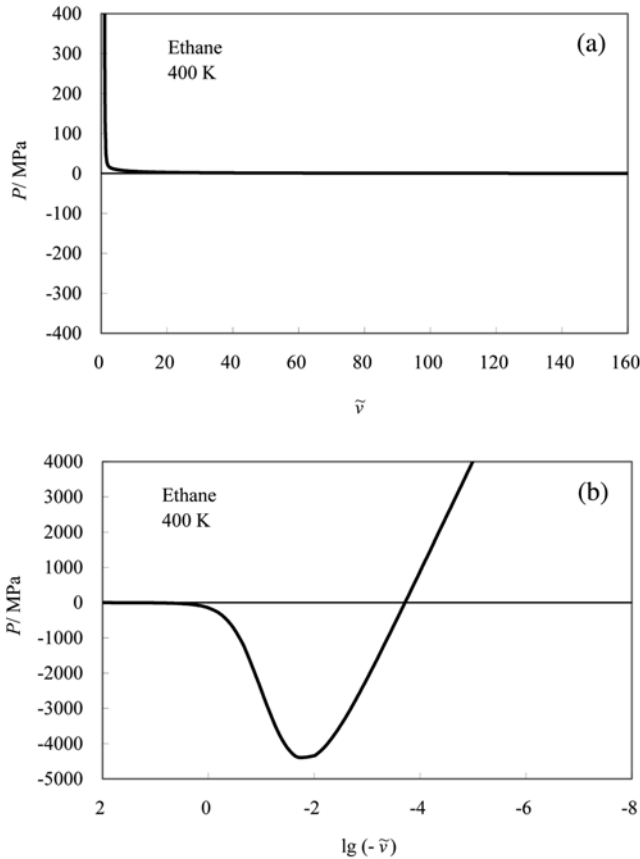
Fig. 6. 400 K isotherm of ethane, calculated with the GCLF equation of state: (a) in the positive direction of $\tilde{v}$; (b) in the negative direction of $\tilde{v}$; $\tilde{v}=1/\tilde{\rho}$.
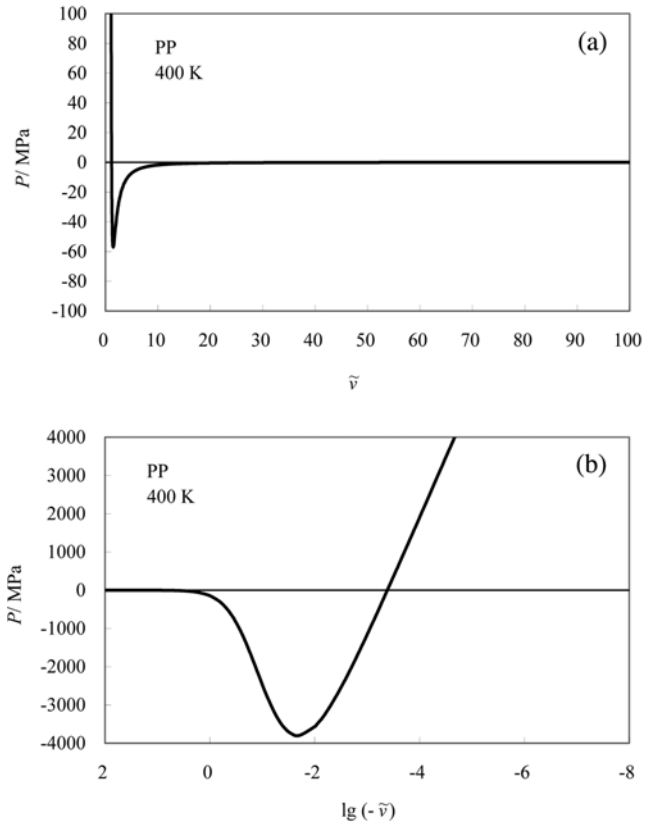

Fig. 7. 400 K isotherm of polypropylene (PP), calculated with the GCLF equation of state: (a) in the positive $\tilde{v}$ direction; (b) in the negative $\tilde{v}$ direction; $\tilde{v}=1/\tilde{\rho}$.

and the third one (point C) to the gas phase, while the other two solutions (points B and D) with no physical meaning. Therefore, in this case the formerly accepted opinion that the lowest root belongs to the vapor phase and the highest to the liquid phase is no longer tenable.

2. From the isotherm of ethane at 400 K (above critical point) shown in Fig. 6, two roots are found at a given positive pressure. Evidently, the solution with the highest density (in the positive direction of $\tilde{v}$) is associated with the supercritical fluid phase, while the remaining root is negative and has no physical meaning.

3. From the isotherm of polypropylene (PP) at 400 K shown in Fig. 7, two roots are also found at a given positive pressure. It should also be mentioned that the P-V-T behaviour of polymers is independent of molecular weight in terms of the GCLF equation of state.

Thus, an algorithm for solving the GCLF equation of state to obtain the vapor and liquid densities is proposed:

1. Rearrange Eq. (13), and it becomes

$$f(\tilde{v}) = \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\right) + \frac{z}{2}\ln\left(\frac{\tilde{v}+q/r-1}{\tilde{v}}\right) - \frac{\theta^2}{\tilde{T}} - \frac{\tilde{P}}{\tilde{T}} \qquad (17)$$

Deriving Eq. (17) with respect to $\tilde{v}$,

$$f'(\tilde{v}) = 0 \qquad (18)$$

That is,

$$\tilde{v}^3 + b_2\tilde{v}^2 + b_1\tilde{v} + b_0 = 0 \qquad (19)$$

where $b_2 = \dfrac{10a^2 - 2a - b}{5a+1}$; $b_1 = \dfrac{5a^3 - 7a^2 + b}{5a+1}$; $b_0 = \dfrac{-4a^3}{5a+1}$;

$a = \dfrac{q}{r} - 1$; $b = 2\dfrac{(q/r)^2}{\tilde{T}}$.

Eq. (19) is a cubic equation and thus Deiters' method [Deiters, 2002] can be adopted. It is thought that the CPU velocity of Deiters' method is almost twice faster than that of Cardano's method without loss of accuracy. Herein, Deiters' method is attached in the appendix and interested readers can refer to it.

2. Evaluate the Discriminant

$$d = \left(\frac{p}{3}\right)^3 + \left(\frac{q}{2}\right)^2 \qquad (20)$$

where $p = b_1 - \dfrac{b_2^2}{3}$, $q = b_0 - \dfrac{b_1 b_2}{3} + \dfrac{2b_2^3}{27}$.

If $d \geq 0$, go to step 3; otherwise, there are three different real roots that can be found from Eq. (19), $\tilde{v}_1$, $\tilde{v}_2$ and $\tilde{v}_3$. Taking account of the discontinuous points in Eq. (17), $\tilde{v}_4 = 0 - \delta$ and $\tilde{v}_5 = 1 + \delta$ (δ is a very small positive number arbitrarily given beforehand), the whole solution space is divided into six regions: $(-\infty, \tilde{v}_1)$, $(\tilde{v}_1, \tilde{v}_2)$, $(\tilde{v}_2, \tilde{v}_3)$, $(\tilde{v}_3, \tilde{v}_4)$, $(\tilde{v}_4, \tilde{v}_5)$ and $(\tilde{v}_5, +\infty)$ after sorting the sequence of $\tilde{v}_1$, $\tilde{v}_2$, $\tilde{v}_3$, $\tilde{v}_4$ and $\tilde{v}_5$ from the low to high values. For the convenience of numerical calculation, $-\infty$ and $+\infty$ may be replaced by big neg-

ative and positive numbers. In each region, for instance, $(\tilde{v}_1, \tilde{v}_2)$, judge whether $f(\tilde{v}_1)f(\tilde{v}_2)<0$ or not. If no, stop searching in this region; if yes, search the root by the Newton-Raphson method. In this way all of the roots in Eq. (13) will be found.

Since our purpose is to obtain the vapor and liquid densities from the physical insight, only two regions, $(\tilde{v}_3, \tilde{v}_4)$ and $(\tilde{v}_5, +\infty)$, need to be emphasized so as to shorten the run time and exclude unreasonable solutions. The liquid density lies in the region of $(\tilde{v}_3, \tilde{v}_4)$, the vapor density in the region of $(\tilde{v}_5, +\infty)$.

3. If $d\geq0$, for polymers there are two different real roots that can be found from Eq. (19), while for gases two different real roots at $T=T_c$ and one root at $T>T_c$. Under this condition, only the densities of liquid phase for polymers and of supercritical phase for gases are of concern. However, initial values for the Newton-Raphson method should be selected with caution. For polymers the initial value of $\tilde{v}$ should be very close to unity because the extremum in the positive direction of $\tilde{v}$ approaches unity as shown in Fig. 7. Divergence will occur if the initial value is on the right side of the extremum in the positive direction of $\tilde{v}$. For gases the only requirement for the initial value is that $\tilde{v}>1$.

CONCLUSION

Although the S-L and GCLF equations of state are commonly used for describing the P-V-T behaviour of polymer-gas systems, the problem about how to solve them was not discussed before. Since the S-L and GCLF equations of state are of the form of transcendental equations, the calculation of densities is more complicated than that of common cubic equations of state which are of the form of simple cubic polynomial equation. Moreover, some unusual phenomenon can arise from these equations of state.

From the S-L equation of state the relationship between the equation characteristic parameters and critical properties was deduced, and the influence of molecular weight of the polymers on critical properties was investigated. As we know, critical properties are very important in estimating many thermodynamic properties such as molar volumes, thermal conductivity, diffusion coefficient, etc. Therefore, it is possible that the critical properties of polymers may be applied in this estimation, which leads to the range of thermodynamic equations to be extended to the systems containing polymers.

However, for GCLF equation of state, physically unreasonable solutions may appear. It is surprising to find that there are as many as four roots found at a saturation temperature and pressure for gases, while still two roots above critical temperature. For polymers, only two roots can be found. So the formerly accepted consistency between the magnitude of the density and vapor or liquid phase is not applicable yet.

ACKNOWLEDGMENT

APPENDIX: DEITERS' ALGORITHMS FOR SOLVING CUBIC EQUATIONS

Given is a polynomial equation with real coefficients a_i:

$$a_3x^3+a_2x^2+a_1x+a_0=0 \qquad \text{with } a_3\neq0$$

1. Divide by a_3 to obtain the normalized form

$$g(x)=x^3+b_2x^2+b_1x+b_0=0 \qquad \text{with } b_i=\frac{a_i}{a_3}$$

$$g'(x)=3x^2+2b_2x+b_1, \quad g''(x)=6x+2b_2.$$

2. Determine an interval containing all real roots:

$$-r\leq x_k\leq+r \qquad \text{with } r=1+\max(|b_i|)$$

3. Select an initial value from the interval boundaries:

$$x^{(0)} = \begin{cases} -r & \text{if } g(x_{infl})>0 \\ +r & \text{if } g(x_{infl})\leq0 \end{cases}$$

where $x_{infl}=-1/3b_2$ is the location of the inflection point. This choice ensures that no extremum lies between the initial value and the nearest root.

4. Iterate of the first root by Kepler's method:

$$x^{(k+1)}=x^{(k)}-\frac{g(x^{(k)})g'(x^{(k)})}{[g'(x^{(k)})]^2-\frac{1}{2}g(x^{(k)})g''(x^{(k)})}$$

As no inflection points or extrema are lying between the initial value and the nearest root, as ensured by the previous step, convergence is guaranteed.

5. Perform a deflation (division of the normalized cubic polynomial by a linear factor containing the first root, x_1):

$$h(x)=\sum_{i=0}^{2}c_ix^i \qquad \text{with } c_2=1, c_1=c_2x_1+b_2, c_0=c_1x_1+b_1$$

6. Find the roots (if any) of the quadratic polynomial $h(x)$ analytically.

NOMENCLATURE

M   : molecular weight [kg/kmol]
P   : pressure [Pa]
P^* : characteristic pressure [Pa]
$\tilde{P}$: reduced pressure [dimensionless]
P_c : critical pressure [Pa]
q   : effective chain length or surface area parameter [dimensionless]
r   : number of lattice sites [dimensionless]
R   : gas constant [kJ/(kmol K)]
T   : temperature [K]
T^* : characteristic temperature [K]
$\tilde{T}$: reduced temperature [dimensionless]
T_c : critical temperature [K]
v : molar volume [m³/kmol]
v^* : reference volume [m³/kmol]
$\tilde{v}$: reduced volume [dimensionless]
v_h : volume of a lattice site [m³/kmol]
z   : coordination number [dimensionless]

Greek Letters

ε^* : molecular interaction energy [kJ/kmol]
θ : molecular surface fraction [dimensionless]

ρ : density [kg/m^3]
ρ^* : characteristic density [kg/m^3]
$\tilde{\rho}$: reduced density [dimensionless]
ρ_c : critical density [kg/m^3]

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