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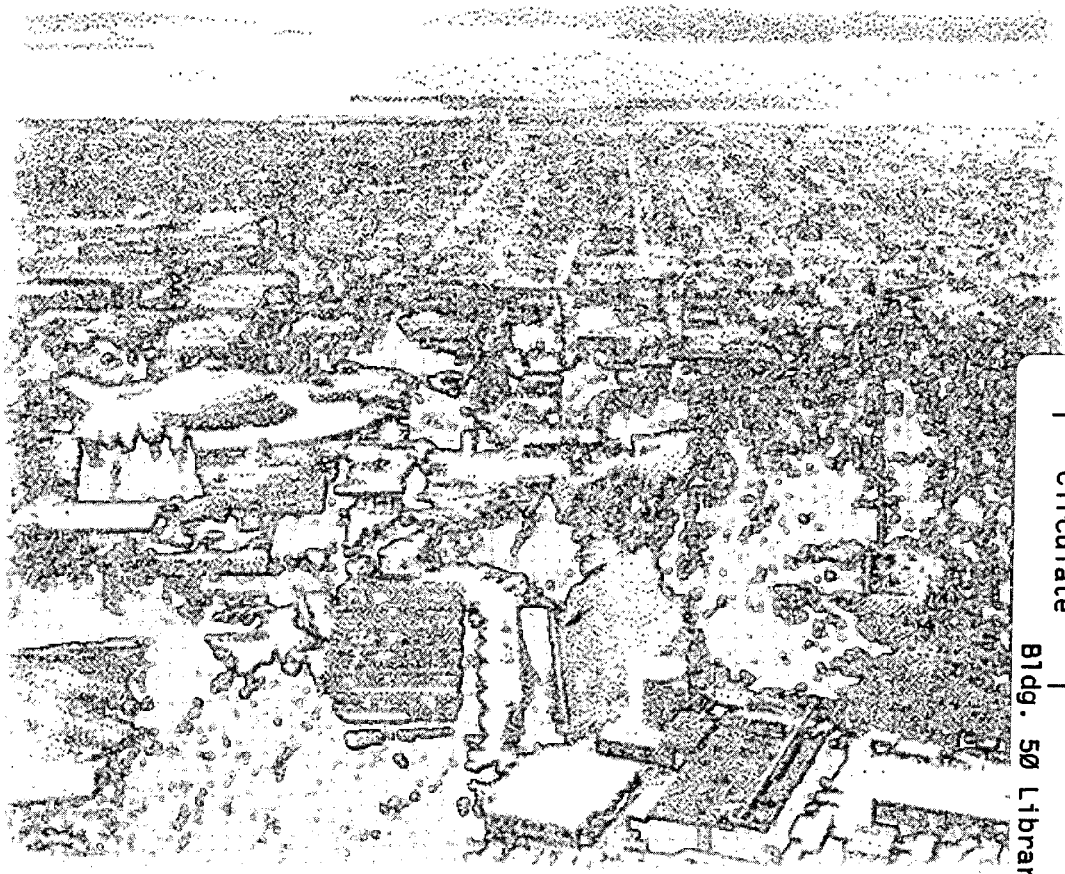

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A PERTURBED HARD-SPHERE-CHAIN EQUATION OF STATE FOR NORMAL FLUIDS AND POLYMERS USING THE SQUARE-WELL POTENTIAL OF VARIABLE WIDTH

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Abstract

A perturbed hard-sphere-chain (PHSC) equation of state is developed for normal fluids and polymers, including mixtures. The new PHSC equation of state for pure fluids uses a perturbation term based on the analytic solution by Chang and Sandler to the second-order perturbation theory of Barker and Henderson for the square-well fluid of variable width. The reference equation of state is the modified Chiew equation of state for athermal mixtures of hard-sphere chains as used in the original PHSC equation of state. The analytic solution by Chang and Sandler is simplified such that theory is readily extended to mixtures by conventional mixing rules. Using an optimum system-independent reduced well width, the new PHSC equation of state correlates the vapor pressures and liquid densities of saturated liquids with good accuracy. Combined with one-fluid type mixing rules for the perturbation term, theory is applied to liquid-liquid and vapor-liquid equilibria for binary mixtures where all components have the same reduced well width. Calculations were also made for a polymer solution where each component has a different reduced well width. In solvent/polymer systems, calculated liquid-liquid equilibria are sensitive to the reduced well width. The perturbation term, however, neglects chain connectivity.

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1. Introduction

Because of recent advances in the theory of athermal, chain-like molecules in continuous space, much attention has been given to the development of off-lattice equations of state for real chain fluids based on perturbation theories. Equations of state for chain fluids are capable of correlating the thermodynamic properties of normal fluids as well as those of polymers. Using appropriate mixing rules for the perturbation term, these equations of state are also applicable to fluid mixtures, including polymer solutions and blends. Recent off-lattice equations of state that have been applied to real systems include the statistical association fluid theory (SAFT) equation of state by Huang and Radosz (1990 and 1991), the simplified SAFT equation of state by Fu and Sandler (1995), the generalized Flory dimer equation of state by Bokis et al. (1994), and the perturbed hard-sphere-chain (PHSC) equation of state by Song et al. (1996) The present work concerns an improvement of the PHSC equation of state.

The PHSC equation of state uses the modified Chiew equation of state (Song et al., 1994a) for athermal hard-sphere-chain mixtures as the reference equation of state and a van der Waals type perturbation term (Song et al., 1994b). The PHSC equation of state requires three parameters to describe pure fluids: the depth of the pair potential, the segmental diameter, and the number of effective hard spheres per molecule. The PHSC equation of state has been used to correlate and in part to predict vapor-liquid equilibria (VLE) for polymer solutions (Gupta and Prausnitz, 1995) and liquid-liquid equilibria (LLE) for polymer solutions and blends (Lambert et al., 1995b; Song et al., 1996; Hino et al., 1996), including those for copolymer blends (Hino et al., 1995). Extensive application of the PHSC equation of state to real systems, however, revealed some shortcomings of the model.

For some normal alkanes (Koak and Heidemann, 1996), the PHSC equation of state does not correlate the thermodynamic properties of saturated liquids as well as lattice-based models such as the lattice-fluid theory of Sanchez and Lacombe (1976;

1978). When applied to LLE for dilute and semidilute polymer solutions, the PHSC equation of state overestimates the equation-of-state effect that causes lower critical solution temperatures (LCSTs) at elevated temperatures (Hino et al., 1996). In polymer solutions, the PHSC equation of state predicts LCSTs at temperatures lower than those measured. To correct the overestimated equation-of-state effect, the perturbation term requires a semiempirical parameter that decreases the contribution from polymer molecules in the perturbation term for polymer solutions (Hino et al., 1996). In addition, to fit mixture data, the additivity equation of effective hard-sphere diameters was often relaxed between a pair of unlike segments in the reference equation of state (Song et al., 1996).

The occasional poor performance of the PHSC equation of state is partly due to the use of a simple van der Waals type perturbation term whose density dependence is proportional to the number density. As a first step to improve the PHSC equation of state, for pure fluids, we replace the van der Waals perturbation term with a theoretical perturbation term; we use the analytic solution by Chang and Sandler (1994a, b) to the second-order perturbation theory of Barker and Henderson (1967) for the square-well fluid of variable width. The solution by Chang and Sandler is completely analytic because it uses the real expression for the radial distribution function of hard spheres obtained by the same authors (1994a). We simplify the analytic solution by Chang and Sandler (1994b) such that the perturbation term is readily extended to mixtures through conventional mixing rules. Unfortunately, however, the perturbation term neglects chain connectivity.

No mixing rules are required for the reference term. To extend the perturbation term for pure fluids to mixtures, we use a one-fluid type mixing rule. We examine the effect of well width on phase equilibria for mixtures; particular attention is given to LLE and VLE for binary solvent/polymer systems. In one set of calculations, all reduced well

widths are equal; in another set, we allow the reduced well width of one component to be different from that of the other.

2. The PHSC equation of state

The PHSC equation of state consists of a reference term and a perturbation term that represent repulsive and attractive interactions, respectively:

$$\left(\frac{p}{\rho k_B T}\right) = \left(\frac{p}{\rho k_B T}\right)_{\text{ref}} + \left(\frac{p}{\rho k_B T}\right)_{\text{pert}} \tag{1}$$

where p is the pressure, $\rho \equiv N/V$ is the number density (N is the total number of molecules and V is the volume), k_B is the Boltzmann constant, T is the absolute temperature, and subscripts ref and pert denote the reference equation of state and the perturbation term, respectively.

2.1. Reference equation of state

The PHSC equation of state (Lambert et al., 1995b; Song et al., 1994b and 1996) uses the modified Chiew equation of state (Song et al., 1994a) for athermal hard-sphere-chain mixtures as the reference equation of state. For mixtures of homonuclear hard-sphere chains, the reference equation of state is

$$\left(\frac{p}{\rho k_B T}\right)_{\text{ref}} = 1 + \rho \sum_{i=1}^{m} \sum_{j=1}^{m} x_i x_j r_i r_j b_{ij} g_{ij}\left(d_{ij}^{+}\right) - \sum_{i=1}^{m} x_i (r_i - 1)\left[g_{ii}\left(d_{ii}^{+}\right) - 1\right] \tag{2}$$

where m is the number of components, x_i is the mole fraction, r_i is the number of hard spheres per molecule, d_{ij}^{+} is the hard-sphere diameter, and $g_{ij}\left(d_{ij}^{+}\right)$ is the radial distribution function at contact prior to bonding; $b_{ij}=2\pi d_{ij}^{+}/3$ is the parameter that represents repulsive interaction on a segmental basis. In the above and following equations, subscript i

denotes component i and subscript ij denotes a pair of hard spheres comprising components i and j.

In the new PHSC equation of state, we do not introduce a temperature dependence into the hard-sphere diameter; parameter b_{ij} is therefore given by

$$b_{ij} = \frac{1}{8}\left(b_{ii}^{1/3} + b_{jj}^{1/3}\right)^3 \tag{3}$$

where

$$b_{ii} = \frac{2}{3}\pi\sigma_{ii}^3 \tag{4}$$

where σ_{ii} is the hard-sphere diameter of component i.

The radial distribution function at contact is given by (Song et al., 1994a)

$$g_{ij}\left(d_{ij}^{+}\right) = \frac{1}{1-\eta} + \frac{3}{2}\frac{\xi_{ij}}{(1-\eta)^2} + \frac{1}{2}\frac{\xi_{ij}^2}{(1-\eta)^3} \tag{5}$$

where η is the packing fraction of the mixture given by

$$\eta = \frac{\rho}{4}\sum_{i=1}^{m} x_i r_i b_{ii} \tag{6}$$

and ξ_{ij} is a particular form of the reduced density defined by

$$\xi_{ij} = \frac{\rho}{4}\left(\frac{b_{ii}b_{jj}}{b_{ij}}\right)^{1/3} \sum_{i=1}^{m} x_i r_i b_{ii}^{2/3} \quad . \tag{7}$$

2.2. Perturbation term

To improve the PHSC equation of state for pure fluids, we replace the oversimplified van der Waals perturbation term in the original theory by a theoretical perturbation term for the square-well fluid. Our perturbation term differs from those used in the original and simplified SAFT equations of state which also use perturbation theories for the square-well fluid. For perturbation terms, the original SAFT equation of state (Huang and Radosz, 1990 and 1991) uses the equation of Chen and Kreglewski (1977) based on computer simulations and the simplified SAFT equation of state (Fu and Sandler, 1995) uses the theoretical equation of Lee et al. (1985)

In this work, we use the analytic solution by Chang and Sandler (1994a, b) to the second-order perturbation theory of Barker and Henderson (1967) for the square-well fluid of variable width. Chang and Sandler derived a completely analytic solution by using the real expression for the radial distribution function of hard spheres obtained by the same authors (1994a). We simplify the analytic solution by Chang and Sandler (1994b) such that the perturbation term is readily extended to mixtures using a conventional one-fluid mixing rule. A useful advantage of the theory by Chang and Sandler is that the well width can be varied systematically.

2.2.1. Pure fluids

Consider a molecular fluid consisting of r segments per molecule at packing fraction η. We assume that the perturbation term for the Helmholtz energy is given by

$$\left(\frac{A}{Nk_{\mathrm{B}}T}\right)_{\mathrm{pert}} = r\left(\frac{A^{r=1}}{Nk_{\mathrm{B}}T}\right)_{\mathrm{pert}} \tag{8}$$

where $A^{r=1}$ is the Helmholtz energy of N molecules of the simple fluid at packing fraction η. For $\left(A^{r=1}/Nk_{\mathrm{B}}T\right)_{\mathrm{pert}}$, we use the Helmholtz energy for the square-well fluid.

The square-well potential is defined by

$$u(R)=\begin{cases}\infty & R<\sigma \\ -\varepsilon & \sigma\le R<\lambda\sigma \\ 0 & R\ge\lambda\sigma\end{cases} \tag{9}$$

where $u(R)$ is the pair potential, R is the intermolecular distance, σ is the hard-sphere diameter, ε is the depth of the well, and λ is the reduced well width.

By combining Eq. (8) with the second-order perturbation theory of Barker and Henderson for the square-well fluid (1967; Chang and Sandler, 1994b), the perturbation term for the Helmholtz energy is given by

$$\left(\frac{A}{Nk_BT}\right)_{\text{pert}}=\left(\frac{A_1}{Nk_BT}\right)_{\text{pert}}+\left(\frac{A_2}{Nk_BT}\right)_{\text{pert}} \tag{10}$$

where A_1 and A_2 are the first- and second-order perturbation terms, respectively, for the Helmholtz energy; they are given by

$$\left(\frac{A_1}{Nk_BT}\right)_{\text{pert}}=-4r\left(\frac{\varepsilon}{k_BT}\right)\eta\Psi \tag{11}$$

$$\left(\frac{A_2}{Nk_BT}\right)_{\text{pert}}=-2r\left(\frac{\varepsilon}{k_BT}\right)^2\frac{\eta(1-\eta)^4}{\left(1+4\eta+4\eta^2\right)}\left(\Psi+\eta\frac{\partial\Psi}{\partial\eta}\right) \tag{12}$$

where Ψ is a function of η and λ resulting from the integration of the radial distribution function for hard spheres in the range $\sigma\le R\le\lambda\sigma$. To assure that Eq. (11) reduces to the perturbation term in the original PHSC equation of state, the numerical coefficients in Eqs. (11) and (12) were chosen to be 4 and 2, respectively, instead of 12 and 6 as used by Chang and Sandler (1994b).

For Ψ=1, the right-hand side of Eq. (11) is $-r^2a\rho/k_BT$ where $a=2\pi\sigma^3\varepsilon/3$, namely, the original perturbation term without the universal function which provides an additional

temperature dependence (Song et al., 1996). Therefore, the perturbation term in the original PHSC equation of state is identified as the limiting expression of the present model. The original PHSC equation of state sets A_2=0; it uses only Eq. (11) with a density-independent Ψ and an additional temperature dependence. Essentially, the van der Waals perturbation term employs the mean-field approximation where the radial distribution function is assumed to be independent of density.

Similar to Eq. (10), the perturbation term for the equation of state is given by

$$\left(\frac{p}{\rho k_B T}\right)_{\text{pert}} = \left(\frac{p_1}{\rho k_B T}\right)_{\text{pert}} + \left(\frac{p_2}{\rho k_B T}\right)_{\text{pert}} \tag{13}$$

where p_1 and p_2 are the first- and second-order perturbation terms for the equation of state given by

$$\left(\frac{p_1}{\rho k_B T}\right)_{\text{pert}} = -4r\left(\frac{\varepsilon}{k_B T}\right)\eta\left(\Psi + \eta\frac{\partial\Psi}{\partial\eta}\right) \tag{14}$$

$$\left(\frac{p_2}{\rho k_B T}\right)_{\text{pert}} = -2r\left(\frac{\varepsilon}{k_B T}\right)^2\eta\left[\frac{(1-\eta)^3\left(1-5\eta-20\eta^2-12\eta^3\right)}{\left(1+4\eta+4\eta^2\right)^2}\left(\Psi+\eta\frac{\partial\Psi}{\partial\eta}\right)\right.$$

$$\left.+\frac{\eta(1-\eta)^4}{\left(1+4\eta+4\eta^2\right)}\left(2\frac{\partial\Psi}{\partial\eta}+\eta\frac{\partial^2\Psi}{\partial\eta^2}\right)\right]. \tag{15}$$

By substituting $\eta = r\rho\pi\sigma^3/6$ into the packing fraction in Eqs. (11) to (15), the perturbation terms can also be written as

$$\left(\frac{A_1}{Nk_B T}\right)_{\text{pert}} = -\frac{2}{3}\pi r^2\sigma^3\left(\frac{\varepsilon}{k_B T}\right)\rho\Psi \tag{16}$$

$$\left(\frac{A_2}{Nk_BT}\right)_{\text{pert}} = -\frac{1}{3}\pi r^2\sigma^3\left(\frac{\varepsilon}{k_BT}\right)^2\rho\,\frac{(1-\eta)^4}{\left(1+4\eta+4\eta^2\right)}\left(\Psi+\eta\frac{\partial\Psi}{\partial\eta}\right) \tag{17}$$

$$\left(\frac{p_1}{\rho k_BT}\right)_{\text{pert}} = -\frac{2}{3}\pi r^2\sigma^3\left(\frac{\varepsilon}{k_BT}\right)\rho\left(\Psi+\eta\frac{\partial\Psi}{\partial\eta}\right) \tag{18}$$

$$\left(\frac{p_2}{\rho k_BT}\right)_{\text{pert}} = -\frac{1}{3}\pi r^2\sigma^3\left(\frac{\varepsilon}{k_BT}\right)^2\rho\left[\frac{(1-\eta)^3\left(1-5\eta-20\eta^2-12\eta^3\right)}{\left(1+4\eta+4\eta^2\right)^2}\left(\Psi+\eta\frac{\partial\Psi}{\partial\eta}\right)\right.$$

$$\left.+\frac{\eta(1-\eta)^4}{\left(1+4\eta+4\eta^2\right)}\left(2\frac{\partial\Psi}{\partial\eta}+\eta\frac{\partial^2\Psi}{\partial\eta^2}\right)\right]. \tag{19}$$

Chang and Sandler (1994b) gave an analytic expression for $\Psi(\eta,\lambda)$ in the range $1<\lambda\leq 2$ using the real expression for the radial distribution function of hard spheres obtained by the same authors (1994a). In this work, we obtain a simplified expression for Ψ by fitting the analytic equations by Chang and Sandler to a polynomial function of η for a given value of λ; Ψ is given by

$$\Psi(\eta,\lambda) = \sum_{k=1}^{10} c_k(\lambda)\eta^{k-1} \tag{20}$$

where c_k is a coefficient that depends only on λ. Table 1 gives c_k for several values of λ used in this work.

2.2.2. Mixtures

To extend rigorously the perturbation theory of Barker and Henderson to mixtures, we require real expressions for the radial distribution functions for hard-sphere mixtures. Such expressions, however, are not available at present. Therefore, we use

conventional one-fluid mixing rule to extend the perturbation term for pure fluids to mixtures.

We consider first the case where all components of the mixture have the same reduced well width, i.e., where $\lambda_{ij} = \lambda$. We then introduce one-fluid type mixing rules by defining the average quantities of equation-of-state parameters appearing in Eqs. (16) to (19) by

$$\langle r^2\sigma^3\varepsilon\rangle = \sum_{i=1}^{m}\sum_{j=1}^{m} x_i x_j r_i r_j \sigma_{ij}^3 \varepsilon_{ij} \tag{21}$$

$$\langle r^2\sigma^3\varepsilon^2\rangle = \sum_{i=1}^{m}\sum_{j=1}^{m} x_i x_j r_i r_j \sigma_{ij}^3 \varepsilon_{ij}^2 \tag{22}$$

where the angular bracket denotes an average property of the mixture. Equations (21) and (22) assume a random mixing of segments and neglect chain connectivity. For function Ψ in Eqs. (16) to (19), Eq. (20) still holds for mixtures by using the packing fraction of the mixture.

We also consider a mixture where each component has a different reduced well width. In that event, possible mixing rules for the first- and second-order perturbation terms for the Helmholtz energy are

$$\left(\frac{A_1}{Nk_BT}\right)_{\text{pert}} = -\frac{2}{3}\pi\rho \sum_{i=1}^{m}\sum_{j=1}^{m} x_i x_j r_i r_j \sigma_{ij}^3 \left(\frac{\varepsilon_{ij}}{k_BT}\right)\Psi_{ij} \tag{23}$$

$$\left(\frac{A_2}{Nk_BT}\right)_{\text{pert}} = -\frac{1}{3}\pi\rho \frac{(1-\eta)^4}{\left(1+4\eta+4\eta^2\right)} \sum_{i=1}^{m}\sum_{j=1}^{m} x_i x_j r_i r_j \sigma_{ij}^3 \left(\frac{\varepsilon_{ij}}{k_BT}\right)^2 \left(\Psi_{ij} + \eta\frac{\partial\Psi_{ij}}{\partial\eta}\right). \tag{24}$$

Mixing rules similar to Eqs. (23) and (24) also define the first- and second-order perturbation terms for the equation of state. For a given reduced well width λ_{ij}, function

$\Psi_{ij}(\eta,\lambda_{ij})$ is assumed to be Ψ given by Eq. (20) with $\lambda=\lambda_{ij}$; $\Psi_{ij}(\eta,\lambda_{ij})$ is therefore defined by

$$\Psi_{ij}(\eta,\lambda_{ij}) = \sum_{k=1}^{10} c_{ij,k}(\lambda_{ij})\eta^{k-1} \tag{25}$$

We use conventional combining rules to define parameters for interactions between a pair of unlike segments

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \tag{26}$$

$$\varepsilon_{ij} = (1 - \kappa_{ij})\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \qquad (i \neq j) \tag{27}$$

where κ_{ij} is an adjustable intersegmental parameter.

3. Phase-equilibrium calculations

The Helmholtz energy of the mixture is calculated by (Prausnitz et al., 1986)

$$\frac{A}{Nk_{\mathrm{B}}T} = \sum_{i=1}^{m} x_i \frac{A_i^{\mathrm{o}}}{Nk_{\mathrm{B}}T} + \int_0^{\rho} \left(\frac{p}{\rho k_{\mathrm{B}}T} - 1\right)\frac{\mathrm{d}\rho}{\rho} + \sum_{i=1}^{m} x_i \ln(x_i \rho k_{\mathrm{B}}T) \tag{28}$$

where A_i^{o} is the Helmholtz energy of N molecules of component i in the reference state. The reference state is pure ideal gas at unit pressure and at the temperature of the mixture. The Helmholtz energy of the mixture is given by Song et al. (1994c) and by Lambert et al. (1995 a and b).

We compute temperature-composition diagrams for binary mixtures containing two solvents, a polymer and a solvent or two polymers. For a fixed temperature, the

coexistence curve is calculated by equating the pressure and, for each component, chemical potential μ_i of coexisting phases. The chemical potential of component i is defined by

$$\mu_i \equiv \left(\frac{\partial A}{\partial N_i}\right)_{T,\,V,\,N_{j\neq i}} \tag{29}$$

where N_i is the number of molecules of component i. For polymer solutions, theoretical coexistence curves are calculated at the vapor pressure of the solution. In that event, the vapor phase is assumed to be a pure solvent. Calculations are made at zero pressure for polymer blends and for mixtures of normal fluids at low or ambient temperatures.

We also compute the liquid-liquid critical point of the mixture where the coexisting phases become identical. For binary mixtures, the conditions for the critical point are

$$\frac{\partial^2}{\partial x^2}\left(\frac{G}{Nk_{\mathrm{B}}T}\right)\bigg|_{T,\,p} = 0 \tag{30}$$

$$\frac{\partial^3}{\partial x^3}\left(\frac{G}{Nk_{\mathrm{B}}T}\right)\bigg|_{T,\,p} = 0 \ . \tag{31}$$

where x is the mole fraction of component 1 or 2 and $G \equiv A + pV$ is the Gibbs energy of the mixture. Equation (30) alone is the condition for the spinodal curve which defines the boundary between metastable and unstable regions in a temperature-composition diagram. Equations (30) and (31) are expressed in terms of the partial derivatives of the pressure and those of the Helmholtz energy per molecule (Prigogine, 1957); these derivatives can be obtain analytically. The coexistence curve and the spinodal curve merge at the critical point.

The new PHSC equation of state is also applied to VLE for binary polymer solutions by computing pressure-composition diagrams at constant temperature. VLE for binary polymer solutions are calculated by assuming that the vapor phase is pure solvent. For a fixed temperature, the pressure of the system and the composition of the liquid phase are computed by equating the pressure and the chemical potential of solvent in the vapor phase to those in the liquid phase. This computational procedure, however, does not provide information on the stability of the liquid phase; it does not tell us if the vapor is in equilibrium with one or two liquid phases The condition for the spinodal curve is particularly useful to examine if the model predicts a single homogeneous liquid phase using the binary parameter obtained from VLE data.

4. Results

4.1. Pure components

4.1.1 Normal fluids

In the present model, we are free to specify the reduced well width represented by parameter λ in Eq. (9). Essentially, λ affects the density dependence of the perturbation term through function Ψ given by Eq. (20). In our first set of calculations, we first obtain the optimum λ for methane and use it for all fluids, including polymers.

We regress equation-of-state parameters for normal fluids by fitting simultaneously the saturated vapor pressure (P^{sat}) and liquid density (ρ_{liq}^{sat}) of the saturated liquid at several equally spaced temperatures. The nonlinear least-squares regression defines the objective function as the sum of squares of the relative deviations between calculated and experimental values with respect to the experimental values. In the objective function, we equally weight the contribution from saturated vapor pressure and that from saturated liquid density.

Using r=1, the optimum reduced well width for methane is λ=1.455. Table 2 gives equation-of-state parameters for the new PHSC equation of states for normal fluids

with λ=1.455. For each fluid, Table 2 also gives the range of temperature and the number of data points used in the regressions. Although data close to the critical point are included, the root-mean-square relative deviations for the new PHSC equation of state are smaller than those for the original PHSC equation of state (Lambert, 1995a). Lambert used data between $0.5<T/T_c<0.9$ where T_c is the vapor-liquid critical temperature of a pure fluid.

Figures 1a and 1b show the percentage relative deviation between calculated and experimental vapor pressure and saturated liquid density, respectively, for *n*-hexane (T_c=507.7 K). To compare the new with the original model, we redetermine the equation-of-state parameters for the original PHSC equation of state (Lambert, 1995a; Song et al., 1996) from the same data used to regress the equation-of-state parameters for the new PHSC equation of state. The new PHSC equation of state with λ=1.455 correlates the saturated properties of *n*-hexane much better than the original PHSC equation of state. However, similar to all equations of state of the van der Waals form, the new PHSC equation of state performs poorly near the critical point.

Table 2 also shows, for selected fluids, the equation-of-state parameters for the new PHSC equation of state with λ=1.38, 1.32, and 1.3. The quality of correlations of saturated properties declines as λ decreases. Therefore, only the data up to about 0.9 times the critical temperature were used to regress the equation-of-state parameters for λ=1.32 and 1.3. In Table 2, we present equation-of-state parameters for $\lambda \leq 1.455$ because, when theory uses the same λ for all components, theory with $\lambda \geq 1.455$ does not give good predictions of LLE for solvent/polymer systems. As shown later, predictions of LLE for polymer solutions improve as λ decreases.

The present model is not applicable to associating fluids such as water and acetic acid. As shown in Table 2, the correlation of saturated properties of acetic acid is not as good as those for non-associating fluids.

4.1.2. Polymers

We use the pure-component pressure-volume-temperature (PVT) data of polymers to regress equation-of-state parameters for polymers. The pure-component PVT data of poly(vinyl methyl ether) (PVME), however, are not tabulated in the literature. The PVT data of PVME were therefore simulated in the range 100 to 200 °C and 1 to 500 bar by the Simha and Somcynsky equation of state (Rodgers, 1993) using parameters given by Rodgers (1993).

Similar to the regression procedure for polymers used with the original PHSC equation of state, we use the equation of state in the limit $r \rightarrow \infty$ (Lambert, 1995a; Song et al., 1994b). Table 3 gives the equation-of-state parameters for the new PHSC equation of state for common polymers with λ=1.455. For polymers, one of the equation-of-state parameters is r/M where M is the molecular weight of polymer. Table 3 also gives, for selected polymers, equation-of-state parameters for different values of λ. Using only PVT data, it is not possible to determine an optimum λ for polymers.

4.2. Mixtures of fluids having the same λ

4.2.1. Mixtures with λ=1.455

We first compare calculated phase diagrams with experiment for mixtures where all components are characterized by λ=1.455. In that event, mixing rules for the first- and second-order perturbation terms for the Helmholtz energy are given by Eqs. (21) and (22), respectively. Figures 2a and 2b compare theoretical coexistence curves with experiment for the systems methane / tetrafluoromethane (Croll and Scott, 1958) and *n*-octane/acetic acid (Sorensen and Arlt, 1979), respectively. In the latter system, specific interactions between acetic acid molecules are not considered in mixtures as well as in pure fluids. As shown in Table 2, reasonable correlations are obtained for the saturated vapor pressure and liquid density of acetic acid without introducing specific interactions. In both systems shown in Figure 2, calculated coexistence curves are narrow compared to

experiment, probably because the present model assumes random mixing of segments in Eqs. (21) and (22).

Using equation-of-state theories, it is difficult to correlate LLE for polymer solutions. Typical miscible polymer solutions exhibit LCSTs at elevated temperatures due to the equation-of-state effect. The equation-of-state effect in polymer solutions results from the compressibility disparity between expanded solvents and relatively dense polymers. When the equation-of-state parameters for polymers are obtained from polymer PVT data, equation-of-state theories often overestimate the equation-of-state effect in polymer solutions, predicting LCSTs which are lower than those measured. As discussed in detail by Hino et al. (1996), the original PHSC equation of state overestimates the equation-of-state effect in polymer solutions.

Figure 3 compares theoretical coexistence curves for λ=1.455 with experiment for the system benzene/polystyrene (Saeki et al., 1973b). In polymer solutions, the new PHSC equation of state also predicts LCSTs at temperatures lower than those measured. The new model, however, does not overestimate the equation-of-state effect as severely as the original model. In the system benzene/polystyrene, the new PHSC equation-of-state at least predicts miscibilities at low temperatures without using a binary parameter. The calculated LCST, however, cannot be matched with experiment by adjusting binary parameter κ_{12}, because that parameter primarily affects the enthalpic effect, not the entropic equation-of-state effect.

As discussed by Hino et al. (1996), it is necessary to introduce a semiempirical parameter to correlate LLE for polymer solutions. The overestimation of the equation-of-state effect in polymer solutions is most likely caused by the overestimated contribution from the polymer in the perturbation term. Because segmental interactions (e.g., excluded-volume effect) are not sufficiently screened out in dilute and semidilute polymer solutions, a pair of polymer molecules in these concentration ranges may not interpenetrate as extensively as they do in pure polymer melts where equation-of-state

parameters for polymers are obtained. The number of contacts between polymer segments may be overestimated in Eqs. (21) and (22) because these equations assume uniform distribution of polymer segments at all mixture compositions.

Consider a binary polymer solution where components 1 and 2 represent the solvent and polymer, respectively. Similar to previous studies (Hino et al., 1996; Song et al., 1996), we replace r_2, the number of segments per polymer molecule, in Eqs. (21) and (22) by r_2^* defined by

$$r_2^* = \zeta r_2 \tag{32}$$

where parameter ζ is a constant smaller than unity. Equation (32) replaces r_2 in Eqs. (21) and (22) only. All other equations remain unchanged. Strictly, parameter ζ is a function of the mixture composition and, possibly, of the molecular weight of polymer. To simplify the problem, however, we assume that parameter ζ is independent of these variables. As shown in Figure 3, the calculated LCST is readily raised toward the experimental result by using parameter ζ alone. However, for the system shown in Figure 3, the calculated critical composition is small compared to experiment.

Figure 4a compares the theoretical coexistence curve for λ=1.455 with experiment for the system *n*-pentane/polyisobutylene (Liddell and Swinton, 1970). Theory and experiment show good agreement using only one adjustable parameter ζ. The parameter obtained from the LLE data in Figure 4a, however, cannot correlate the VLE data for the same system. Figure 4b compares theoretical pressure-composition curves for λ=1.455 with experiment for the system *n*-pentane / polyisobutylene at 35 °C (Prager et al., 1953). The solid curve is for λ=1.455 with κ_{12}=0 and ζ=0.8347; they are obtained from the LLE data shown in Figure 4a. The solid curve overestimates the amount of solvent in the liquid phase.

To correlate the VLE data shown in Figure 4b, it is necessary to make the interaction between solvent and polymer segments more unfavorable by increasing κ_{12}. The broken curve in Figure 4b was calculated for λ=1.455 with κ_{12}=0.03 and ζ=0.8347. Using these parameters at 35 °C, however, theory predicts phase separation as the weight fraction of polymer declines.

An analysis based on the Flory-Huggins theory (Flory, 1953) also shows that for the system *n*-pentane/polyisobutylene, a composition-independent χ parameter correlates the VLE data shown in Figure 4b but incorrectly predicts phase separation at high dilution (Prager et al., 1953). We note some similarities between the Flory-Huggins theory and the PHSC equation of state. The athermal entropy of mixing calculated from Eq. (28) reduces to that of the incompressible Flory-Huggins lattice model (Flory, 1953) when mixing is at constant temperature and constant volume, assuming that the segment diameter is the same for all components and that the packing fractions of pure components before mixing are the same as those in the mixture (Song et al., 1994 a and c). In addition, Eqs. (21) and (22) assume random mixing of segments as used by the Flory-Huggins theory. To represent simultaneously the LLE and VLE of the system *n*-pentane/polyisobutylene, it would be necessary to introduce a composition dependence into parameter κ_{12} and/or parameter ζ. The need for such empiricism indicates serious shortcomings in our present ability to establish a satisfactory theory for polymer solutions applicable to the entire composition range using a unique set of binary parameters.

The new PHSC equation of state is also applicable to polymer blends. Figures 5a and 5b compare theoretical coexistence curves with experiment for the systems poly(α-methylstyrene)/polystyrene and poly(vinyl methyl ether)/polystyrene, respectively. Because experimental PVT data are not available for poly(α-methylstyrene), the equation-of-state parameters for poly(*o*-methylstyrene) are used as those for poly(α-methylstyrene). For each system, only parameter κ_{12} is adjusted to match calculated and observed critical solution temperatures. The new PHSC equation of state is able to

represent upper-critical-solution-temperature (UCST) behavior as well as LCST behavior. In the system poly(vinyl methyl ether)/polystyrene, theoretical coexistence curves are narrow compared to experiment. As discussed by Sanchez and Balazs (1989), one possible explanation for this discrepancy is the presence of weak specific interactions between poly(vinyl methyl ether) and polystyrene.

For the systems shown in Figure 5, the new PHSC equation of state shows an improvement over the original model because the new model requires only κ_{12} to correlate the dependence of critical solution temperature on the polymer molecular weight. To achieve such correlations, the original PHSC equation of state (Song et al., 1996) required two adjustable parameters; namely, κ_{12} and an additional adjustable parameter that relaxes the additivity equation for effective hard-sphere diameters $b_{ij}(i \neq j)$ given by Eq. (3).

4.2.2. Polyethylene solutions with λ=1.32

Because the van der Waals perturbation term corresponds to the square-well potential in the limit $\lambda \rightarrow \infty$, we expect that the overestimated equation-of-state effect decreases as λ declines. Compared to the original PHSC equation of state, with a van der Waals-type perturbation term, the magnitude of overestimation of the equation-of-state effect decreases slightly in the new PHSC equation of state with λ=1.455.

Indeed, for binary polyethylene solutions in *n*-alkanes, the calculated LCSTs for λ=1.32 agree with those measured without using the semiempirical parameter ζ defined by Eq. (32). Figures 6a and 6b compare theoretical coexistence curves with experiment for the systems *n*-hexane/polyethylene (high density) and *n*-octane / polyethylene (high density), respectively (Hamada et al., 1973). For each system, intersegmental parameter κ_{12} was adjusted slightly to match the calculated LCST with the measured LCST for the highest molecular weight of polyethylene. Equation-of-state parameters for λ=1.32 are given in Tables 2 and 3 for solvents and polyethylene, respectively. While good

correlations of polymer PVT data are obtained, calculations with λ=1.32 do not correlate the saturated properties of solvents as well as those with λ=1.455.

In polymer solutions, the overestimated equation-of-state effect decreases as parameter λ declines probably because the density dependence of the perturbation term becomes strong as parameter λ decreases. Equation-of-state parameters for polymers are regressed from PVT data of pure polymer melts whose densities are larger than those of dilute and semidilute polymer solutions. Therefore, in the perturbation term for a binary polymer solution, the contribution from the polymer, relative to that from the solvent, may decrease as parameter λ declines. The overestimation of the equation-of-state effect can be reduced by decreasing the contribution from the polymer to the perturbation term.

4.2.3. Polystyrene solutions with λ=1.3

As shown in Figure 7a, calculations with λ=1.3 give good correlations of LCSTs for the system benzene/polystyrene (Saeki et al., 1973b). Intersegmental parameter κ_{12} was adjusted slightly to match the calculated LCST with that measured for the highest molecular weight of polystyrene. In polystyrene solutions in various solvents, calculated coexistence curves are always narrow compared to experiment.

Figure 7b compares theoretical pressure-composition curves for λ=1.3 with experiment for the system benzene/polystyrene (Noda et al., 1984) Intersegmental parameter κ_{12}(= – 0.006) is the same as that used to correlate the LLE data shown in Figure 7a. At 60 and 45 °C, theoretical curves are slightly underpredicted. Although not shown in Figure 7b, good correlations of the VLE data can be achieved by slightly adjusting intersegmental parameter κ_{12}.

However, calculations with λ=1.3 overestimate the equation-of-state effect in the system cyclohexane/polystyrene. Using λ=1.3, Figure 8 compares theoretical and experimental coexistence curves for the system cyclohexane/polystyrene which exhibits both UCST and LCST as shown in Figures 8a and 8b, respectively (Saeki et al., 1973a).

In this system, theory overestimates the dependence of UCST on the molecular weight of polymer.

Figure 9 compares theoretical pressure-composition curves for the system cyclohexane/polystyrene at 34 °C (Krigbaum and Geymer, 1959). Contrary to the system *n*-pentane/polyisobutylene shown in Figure 4b, there is no single set of parameters κ_{12} and ζ that correlates the experimental VLE data over the entire composition range. To fit the VLE data shown in Figure 9, intersegmental parameter κ_{12} needs to become progressively unfavorable as the weight fraction of polystyrene rises. This observation for the system cyclohexane/polystyrene is consistent with the analysis based on the Flory-Huggins theory (Krigbaum and Geymer, 1959).

4.3. Mixtures of fluids having different λ

Finally, we consider the mixture where each component has a different reduced well width. In that event, mixing rules for the first- and second-order perturbation terms for the Helmholtz energy are given by Eqs. (23) and (24), respectively. In Eqs. (23) to (25), the reduced well width is adjustable for every *ij* pair of segments.

We consider binary solvent/polymer systems where components 1 and 2 represent solvent and polymer, respectively. The mixing rules given by Eqs. (23) and (24) also eliminate the overestimated equation-of-state effect in polymer solutions when smaller reduced well widths are assigned for polymers. Figure 10 compares theoretical coexistence curves with experiment for the system cyclohexane/polystyrene. Theoretical curves are calculated with Eqs. (23) to (25) for the mixture where each component has a different reduced well width. In Figure 10, λ_{11}=1.455, λ_{22}=1.24, and λ_{12}=1.33.

For calculations of LLE in polymer solutions, the new PHSC equation of state no longer overestimates the equation-of-state effect when small reduced well widths are assigned for the polymer. The reduced well width of the solvent does not affect significantly the degree of overestimation of the equation-of-state effect in polymer

solutions. When LLE calculations are performed for a binary polymer solution with component-dependent reduced well width, the reduced well width for solvent can be set to 1.455 for all solvents. However, the reduced well width for polymer and that between solvent and polymer are adjustable parameters which may depend on solvent.

4.4. Use of a more accurate reference equation of state

The modified Chiew equation of state for non-attracting chains does not represent accurately all of the available computer-simulation data for athermal hard-sphere chains and their mixtures. For example, the modified Chiew equation of state fails to predict the second virial coefficient of athermal hard-sphere chains in the limit $r \rightarrow \infty$. This failure probably follows because in the chain-connectivity term, i.e., the last term of Eq. (2), the modified Chiew equation of state uses the radial distribution function at contact for hard-sphere systems prior to forming hard-sphere chains.

Recently, Hu et al. (1996) presented an equation of state for athermal hard-sphere-chain systems which accurately represents available computer-simulation data for hard-sphere-chain systems, including those for the second virial coefficient for hard-sphere chains. Hu's equation considers the nearest-neighbor and next-to-nearest-neighbor correlations in the chain-connectivity term; these correlations are neglected in the modified Chiew equation.

We have also combined the perturbation term presented in this work with Hu's reference equation of state. The resulting equation of state differs from the new PHSC equation of state developed in this work only in the chain-connectivity term of the reference equation of state. Although Hu's equation for athermal systems is slightly better than Chiew's equation, when applied to real systems, the behavior of the perturbed Hu equation of state is very similar to that of the new PHSC equation of state. The perturbed Hu equation of state with component-independent λ=1.455 also overestimates the equation-of-state effect in polymer solutions. Therefore, overestimation of the

equation-of-state effect is most likely caused by neglect of chain connectivity in the perturbation term.

5. Conclusions

The new PHSC equation of state uses the perturbation term for the square-well fluid of variable reduced well width represented by parameter λ. Parameter λ systematically varies the density dependence of the perturbation term. Chain connectivity, however, is neglected in the perturbation term. The reference equation of state is the modified Chiew equation of state for athermal mixtures of hard-sphere chains as used in the original PHSC equation of state.

Without introducing temperature dependences into equation-of-state parameters, the new PHSC equation of state with λ=1.455 correlates the saturated thermodynamic properties of normal fluids much better than the original PHSC equation of state that uses a van-der-Waals-type perturbation term. For polymers, the new PHSC equation of state gives good correlations of pure-component PVT data for several values of λ.

In the perturbation term for mixtures, the present model assumes one-fluid mixing rules. Mixture calculations were made first for the mixture where all components have the same well width. The new PHSC equation of state is applicable to mixtures of normal fluids, polymer solutions, and polymer blends. Theory is able to represent UCST and LCST behaviors in polymer solutions and blends. For polymer solutions where all components have the same λ, the new PHSC equation of state with λ=1.455 overestimates the equation-of-state effect and predicts LCSTs at temperatures lower than those measured. Similar to the original PHSC equation of state, the new model with λ=1.455 requires a semiempirical adjustable parameter to correlate LCSTs in polymer solutions.

For mixtures where all components have the same λ, the magnitude of overestimation of the equation-of-state effect decreases as parameter λ declines. When

parameter λ is adjusted for a given mixture, the new PHSC equation of state is able to correlate LCSTs in polymer solutions without using the semiempirical parameter required for the theory with λ=1.455. In that event, however, theory does not correlate the saturated properties of normal fluids as well as that with λ=1.455.

Calculations were also made for the mixture where each component has a different reduced well width. In that event, the overestimated equation-of-state effect is also eliminated when the equation-of-state parameters for λ=1.455 and those for an appropriate smaller λ are used for solvent and polymer, respectively.

Probably because of the neglect of chain connectivity in the perturbation term, it is necessary to adjust the reduced well width for polymers to eliminate the overestimated equation-of-state effect in polymer solutions. The present model for polymer solutions may be improved further by explicitly taking account of chain connectivity in the perturbation term using the radial distribution function for hard-sphere chains.

6. List of symbols

A	Helmholtz energy
A_1	first-order perturbation term for the Helmholtz energy
A_2	second-order perturbation term for the Helmholtz energy
b	equation of state parameter
c_k	coefficient in Eq. (20)
d	hard sphere diameter
G	Gibbs energy
$g(d^+)$	radial distribution function of hard spheres at contact
k_B	Boltzmann constant (1.3806×10^{-23} J K^{-1})
M	molecular weight of polymer (g mol^{-1})
m	number of component
N	total number of molecules

p	pressure
p_1	first-order perturbation term for the equation of state
p_2	second-order perturbation term for the equation of state
R	intermolecular distance
r	number of hard spheres per molecule
r_2^*	reduced number of hard spheres per polymer defined by Eq. (32)
T	absolute temperature (K)
T_c	vapor-liquid critical temperature of pure fluid (K)
$u(R)$	pair potential
V	volume
x	mole fraction

Greek symbols

ε	depth of the square well
ζ	adjustable parameter in Eq. (32)
η	packing fraction
κ	intersegmental parameter
λ	reduced well width of the square well
μ	chemical potential
ξ	reduced density defined by Eq. (7)
ρ	number density
σ	hard sphere diameter
Ψ	function defined by Eq. (20)

Subscripts

i	component i
ij	a pair of components i and j

liq refers to the saturated liquid

pert perturbation

ref reference

Superscripts

o refers to the reference state of pure component

r=1 refers to the simple fluid

sat refers to the saturated liquid and vapor

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TABLE 1. Coefficient $c_k(\lambda)$ for Function Ψ

	λ		
	1.24	1.3	1.32
c_1	0.3022084253E+00	0.3990016466E+00	0.4333244221E+00
c_2	0.5909127869E+00	0.7267314500E+00	0.7701829549E+00
c_3	0.5901659702E+00	0.5910623606E+00	0.5756557353E+00
c_4	0.3931775147E+00	0.2867504940E+00	0.2387357806E+00
c_5	0.3330695650E-01	– 0.8372612452E+00	– 0.1178836507E+01
c_6	– 0.3240785675E+00	– 0.3090138820E+00	– 0.2977590070E+00
c_7	– 0.5646700630E+00	0.5461269194E+00	0.1016870911E+01
c_8	– 0.7915445254E+00	– 0.3069345676E+01	– 0.3789310942E+01
c_9	– 0.1422055965E+01	– 0.1070150195E+02	– 0.1398985372E+02
c_{10}	– 0.3119946463E+01	0.1098142848E+02	0.1646871843E+02

	λ		
	1.33	1.38	1.455
c_1	0.4508819050E+00	0.5426960550E+00	0.6934288007E+00
c_2	0.7912919849E+00	0.8931396311E+00	0.1031329977E+01
c_3	0.5702738359E+00	0.5051042499E+00	0.3231430915E+00
c_4	0.1726714408E+00	– 0.1296608562E+00	– 0.7601028313E+00
c_5	– 0.1247787445E+01	– 0.1719837958E+01	– 0.1898718617E+01
c_6	– 0.3024234271E+00	– 0.4306453819E+00	– 0.1129836508E+01
c_7	0.9375405280E+00	0.9137249599E+00	– 0.5829453430E+00
c_8	– 0.4168557590E+01	– 0.5310857462E+01	– 0.4161049123E+01
c_9	– 0.1434968334E+02	– 0.1633017689E+02	– 0.8040279885E+01
c_{10}	0.1816031097E+02	0.2642645661E+02	0.2470320458E+02

TABLE 2. Equation-of-State Parameters for Normal Fluids

Substance	T range T/T_C	r	σ (Å)	ε/k_B (K)	% rms [a] deviation p^{sat}	% rms [a] deviation ρ_{liq}^{sat}	ref [b]
			λ=1.455				
methane	0.48 – 0.95	1.0	3.672	164.9	1.0	2.4	1 (21)[c]
ethane	0.49 – 0.97	1.690	3.449	188.1	1.0	2.6	1 (16)
propane	0.50 – 0.96	2.133	3.505	199.6	1.5	2.1	1 (15)
n-butane	0.53 – 0.98	2.422	3.619	215.1	0.85	2.5	2 (20)
n-pentane	0.49 – 0.97	2.825	3.640	220.4	1.1	1.8	1 (16)
n-hexane	0.48 – 0.97	3.220	3.661	224.2	1.5	1.7	1 (18)
n-heptane	0.49 – 0.97	3.599	3.681	227.4	1.7	1.6	1 (17)
n-octane	0.49 – 0.97	4.044	3.674	227.6	1.6	1.5	1 (18)
cyclopentane	0.49 – 0.97	2.461	3.618	256.0	1.3	1.7	1 (18)
cyclohexane	0.50 – 0.98	2.619	3.749	268.1	1.5	2.3	1 (23)
benzene	0.50 – 0.98	2.559	3.541	276.9	1.4	2.4	3 (28)
acetone	0.50 – 0.97	2.961	3.147	238.5	1.0	3.6	1 (17)
ethyl acetate	0.52 – 0.98	3.731	3.176	217.2	1.1	2.9	3 (13)
tetrafluoromethane	0.48 – 0.94	2.325	3.030	116.9	0.84	0.96	4 (12)
carbon dioxide	0.71 – 0.97	2.705	2.484	145.1	0.81	2.3	5 (17)
acetic acid	0.49 – 0.96	3.497	2.767	265.0	3.4	3.2	3 (16)
			λ=1.38				
n-pentane	0.49 – 0.97	2.068	4.217	301.9	1.8	3.6	1 (16)
n-hexane	0.48 – 0.97	2.385	4.226	303.6	2.3	3.6	1 (18)
n-octane	0.49 – 0.97	3.036	4.224	304.0	2.4	3.1	1 (18)

			λ=1.32				
n-pentane	0.49 – 0.90	1.430	4.935	424.0	2.4	3.3	1 (14)
n-hexane	0.48 – 0.90	1.685	4.904	418.4	2.9	2.9	1 (15)
n-octane	0.49 – 0.91	2.201	4.875	408.7	3.1	3.0	1 (15)
			λ=1.3				
n-pentane	0.49 – 0.90	1.227	5.268	486.0	2.6	3.9	1 (14)
n-hexane	0.48 – 0.90	1.462	5.216	474.8	3.2	3.5	1 (15)
n-octane	0.49 – 0.91	1.930	5.169	458.7	3.4	3.6	1 (16)
cyclohexane	0.50 – 0.91	1.098	5.489	610.1	2.9	4.2	1 (19)
benzene	0.50 – 0.91	1.068	5.187	633.1	2.8	4.5	3 (24)
acetone	0.50 – 0.88	1.288	4.527	524.0	2.0	4.2	1 (14)

[a] root-mean-square relative deviations. [b] Reference: 1, Smith and Srivastava (1986); 2, Younglove and Ely (1987); 3, Vargaftik (1975); 4, Rubio et al. (1991); 5, Duschek et al. (1990). [c] Numbers in parentheses indicate numbers of data points used in the correlations.

TABLE 3. Equation-of-State Parameters for Polymers

Polymer	r/M (mol/g)	σ (Å)	ε/k_B (K)	% rms [a] deviation ρ_{liq}	% rms [a] deviation ref [b]
		λ=1.445			
polyethylene 1 (high density)	0.03841	3.485	271.1	0.10	1 (67)[c]
polyethylene 2 (low density)	0.04771	3.223	249.6	0.10	1 (60)
polyethylene 3	0.02303	4.217	330.7	0.13	2 (42)
polyisobutylene	0.02505	4.025	390.4	0.07	2 (55)
polystyrene	0.02123	4.059	409.9	0.09	3 (69)
poly(*o*-methylstyrene)	0.02312	3.958	400.9	0.08	3 (50)
poly(methyl methacrylate)	0.02659	3.583	366.9	0.04	1 (41)
poly(vinyl methyl ether)	0.03053	3.571	299.9	0.05	4 (66)
		λ=1.38			
polyethylene 1 (high density)	0.03119	3.809	305.5	0.06	1 (67)
polyisobutylene	0.02076	4.350	412.8	0.05	2 (55)
polystyrene	0.01735	4.413	442.1	0.07	3 (69)
		λ=1.32			
polyethylene 1 (high density)	0.02455	4.213	342.9	0.03	1 (67)
polyisobutylene	0.01663	4.766	441.3	0.04	2 (55)
polystyrene	0.01365	4.869	480.6	0.06	3 (69)
		λ=1.3			
polyethylene 1 (high density)	0.02231	4.384	357.6	0.03	1 (67)
polyisobutylene	0.01517	4.948	453.0	0.04	2 (55)
polystyrene	0.01238	5.065	495.8	0.05	3 (69)

		λ=1.24			
polyethylene 1 (high density)	0.01577	5.055	410.2	0.08	1 (67)
polyisobutylene	0.01088	5.657	493.7	0.03	2 (55)
polystyrene	0.008678	5.842	549.1	0.07	3 (69)

[a] root-mean-square relative deviations. [b] Reference: 1, Olabisi and Simha (1975); 2, Beret and Prausnitz (1975); 3, Quach and Simha (1971); 4, Rodgers (1993). [c] Numbers in parentheses indicate numbers of data points used in the correlations.

Figure Captions

Figure 1. The percentage relative deviations between calculated and experimental values for n-hexane (T_c=507.7 K): (a) saturated vapor pressure (P^{sat}), (b) saturated liquid density (ρ_{liq}^{sat}). Equation-of-state parameters for the new PHSC equation of state are given in Table 2. For the original PHSC equation of state, the equation-of-state parameters for n-hexane are r=3.628, σ=3.981 Å, and ε/k_B=228.6 K. The new PHSC equation of state is for λ=1.455.

Figure 2. Comparison of theoretical coexistence curves with experiment for the systems (a) methane/tetrafluoromethane (κ_{12}=0.09044) and (b) n-octane/acetic acid (κ_{12}=0.00747). Theoretical curves are for λ=1.455.

Figure 3. Comparison of theoretical coexistence curves with experiment for the system benzene/polystyrene (M_w=200,000). Theoretical curves are for λ=1.455. M_w≡weight-average molecular weight.

Figure 4Comparison of theory with experiment for the system n-pentane/polyisobutylene: (a) LLE (M_η=72,000), (b) VLE at 35 °C (M_η=1000,000). Theoretical curves are for λ=1.455. M_η≡viscosity-average molecular weight.

Figure 5. Comparison of theoretical coexistence curves with experiment for the systems (a) poly(α-methylstyrene)/polystyrene (PMS/PS, κ_{12}=0.00032) and (b) poly(vinyl methyl ether) / polystyrene (PVME/PS, κ_{12}=0.00785). Theoretical curves are for λ=1.455.

Figure 6. Comparison of theoretical coexistence curves with experiment for polyethylene (high-density) solutions: (a) *n*-hexane / polyethylene (κ_{12}=0.0031), (b) *n*-octane / polyethylene (κ_{12}=0.00363). Theoretical curves are for λ=1.32.

Figure 7. Comparison of theory with experiment for the system benzene/polystyrene: (a) LLE, (b) VLE (M_w=900,000). Theoretical curves are for λ=1.3 with κ_{12}= – 0.006 for both LLE and VLE calculations.

Figure 8. Comparison of theoretical coexistence curves with experiment for the system cyclohexane/polystyrene: (a) LCST branch, (b) UCST branch. Theoretical curves are for λ=1.3.

Figure 9. Comparison of theoretical pressure-composition curves with experiment for the system cyclohexane/polystyrene (M_η=25,900) at 34 °C. Theoretical curves are for λ=1.3.

Figure 10. Comparison of theoretical coexistence curves with experiment for the system cyclohexane/polystyrene: (a) LCST branch, (b) UCST branch. Theoretical curves are calculated with Eqs. (23) and (24) for the mixture where each component has a different reduced well width: λ_{11}=1.455; λ_{22}=1.24, and λ_{12}=1.33.

Figure 1

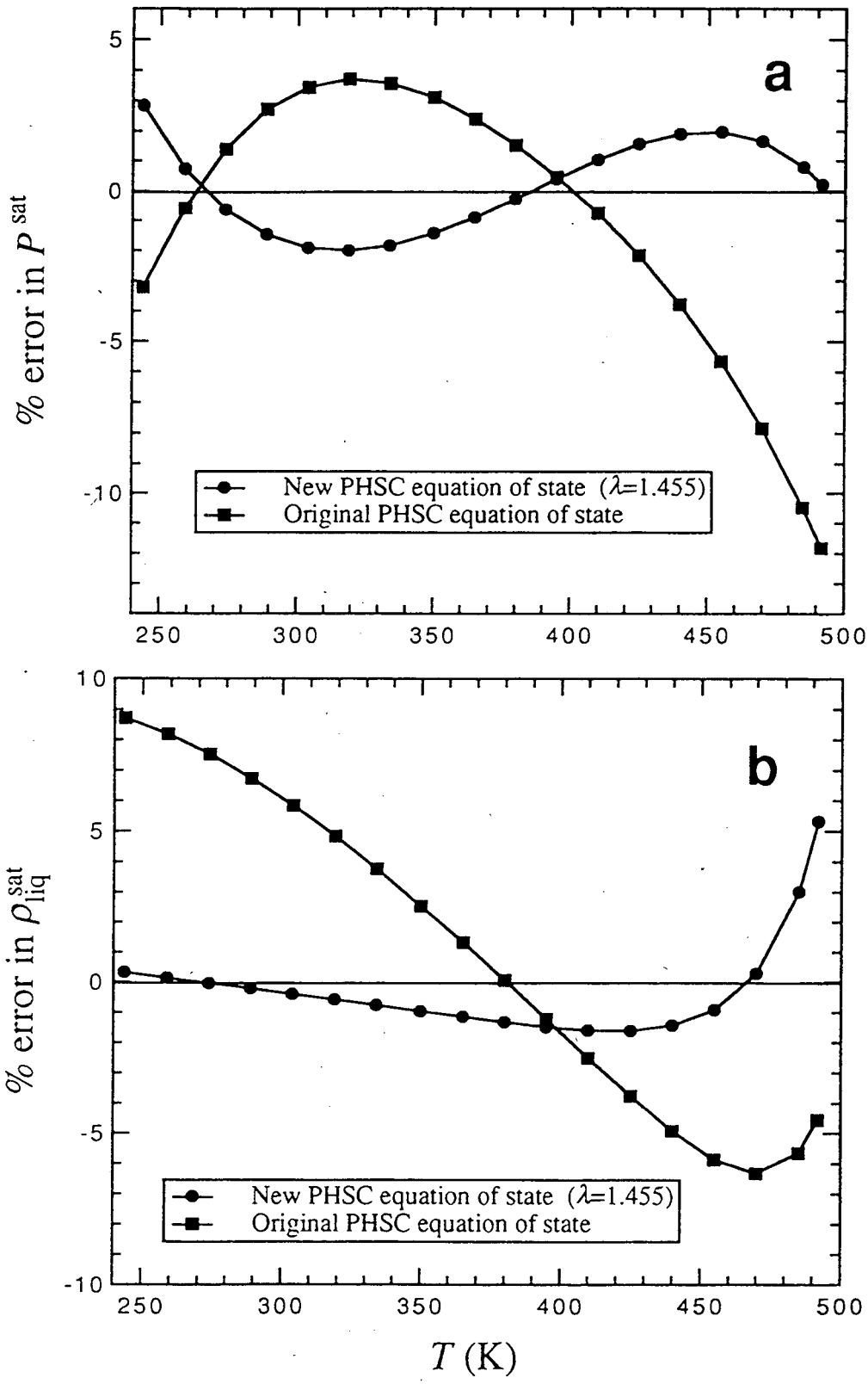

a
% error in P^{sat}
New PHSC equation of state (λ=1.455)
Original PHSC equation of state
5
0
-5
-10
250
300
350
400
450
500
b
% error in ρ_{liq}^{sat}
New PHSC equation of state (λ=1.455)
Original PHSC equation of state
10
5
0
-5
-10
250
300
350
400
450
500
T (K)

Figure 2

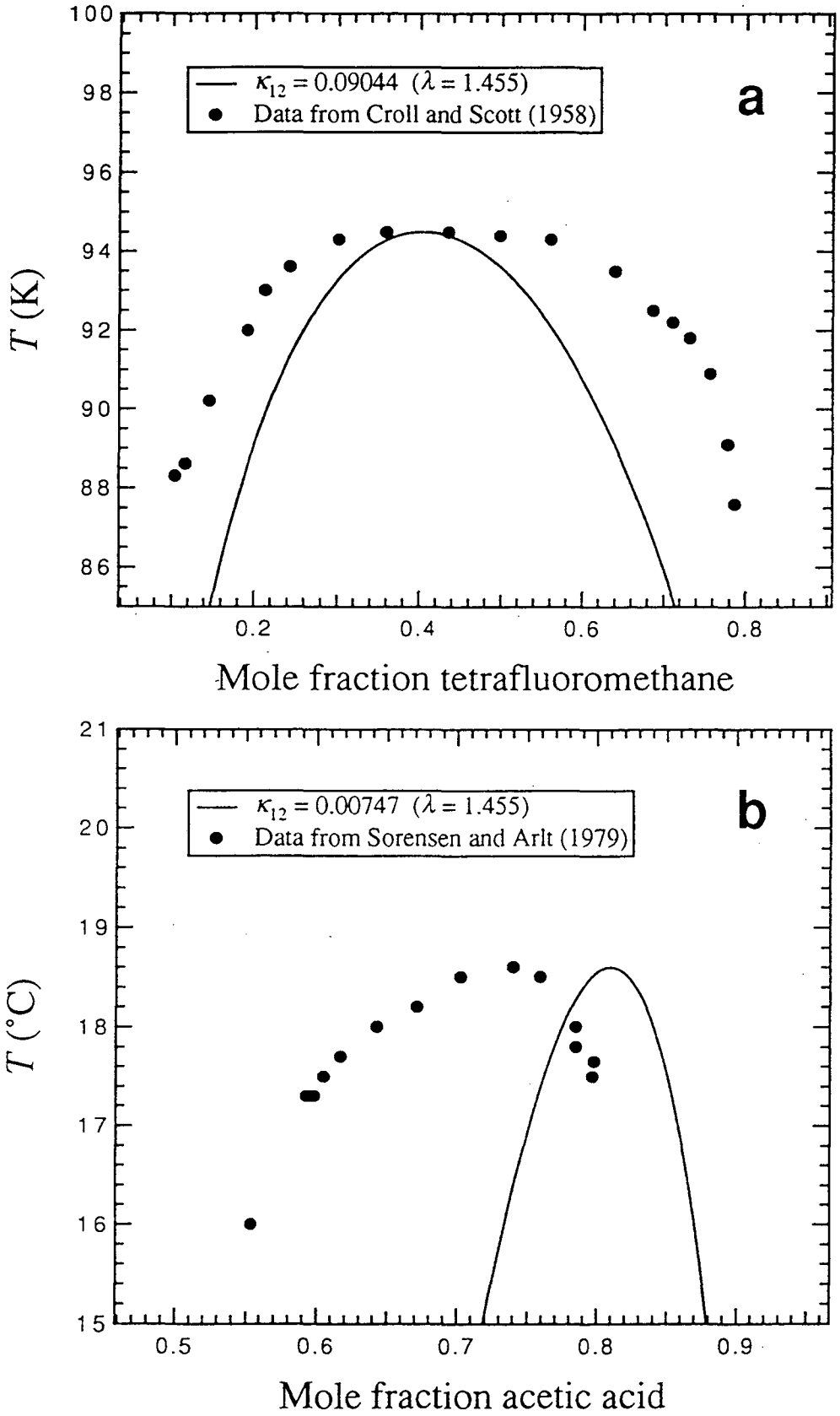

a
$\kappa_{12} = 0.09044$ ($\lambda = 1.455$)
Data from Croll and Scott (1958)
T (K)
100
98
96
94
92
90
88
86
0.2
0.4
0.6
0.8
Mole fraction tetrafluoromethane
b
$\kappa_{12} = 0.00747$ ($\lambda = 1.455$)
Data from Sorensen and Arlt (1979)
T (°C)
21
20
19
18
17
16
15
0.5
0.6
0.7
0.8
0.9
Mole fraction acetic acid

Figure 3

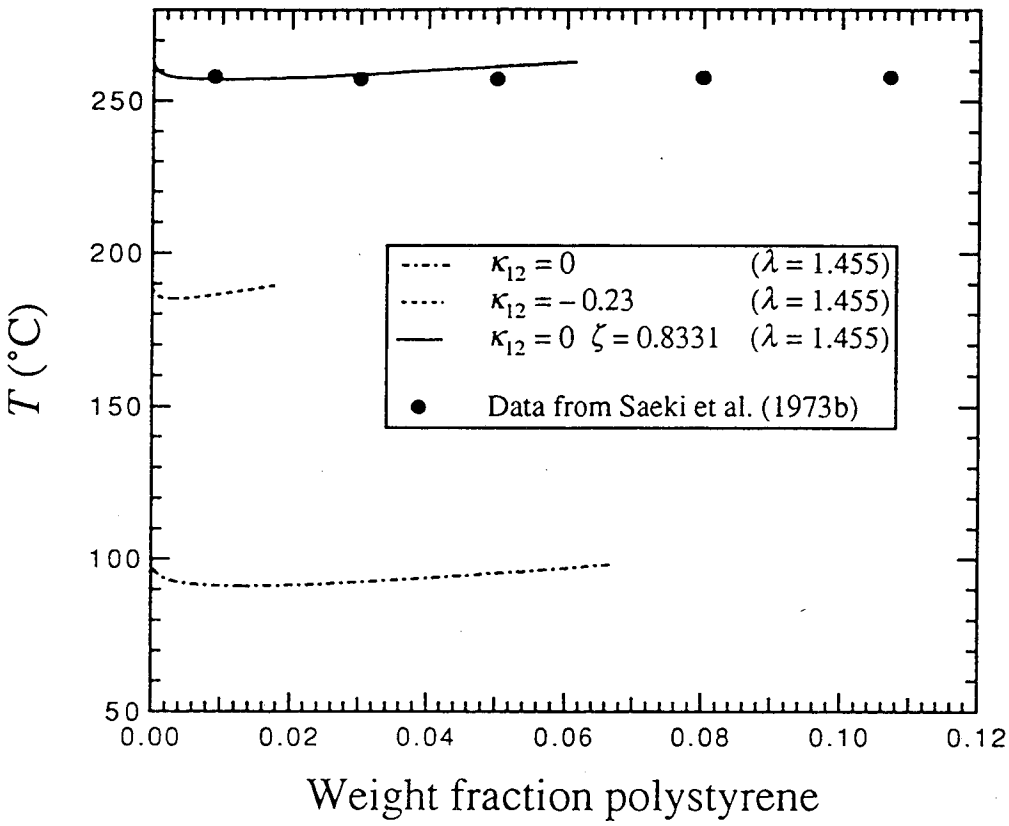

250
200
150
100
50
0.00
0.02
0.04
0.06
0.08
0.10
0.12
T (°C)
Weight fraction polystyrene
$\kappa_{12} = 0$ ($\lambda = 1.455$)
$\kappa_{12} = -0.23$ ($\lambda = 1.455$)
$\kappa_{12} = 0$ $\zeta = 0.8331$ ($\lambda = 1.455$)
Data from Saeki et al. (1973b)

Figure 4

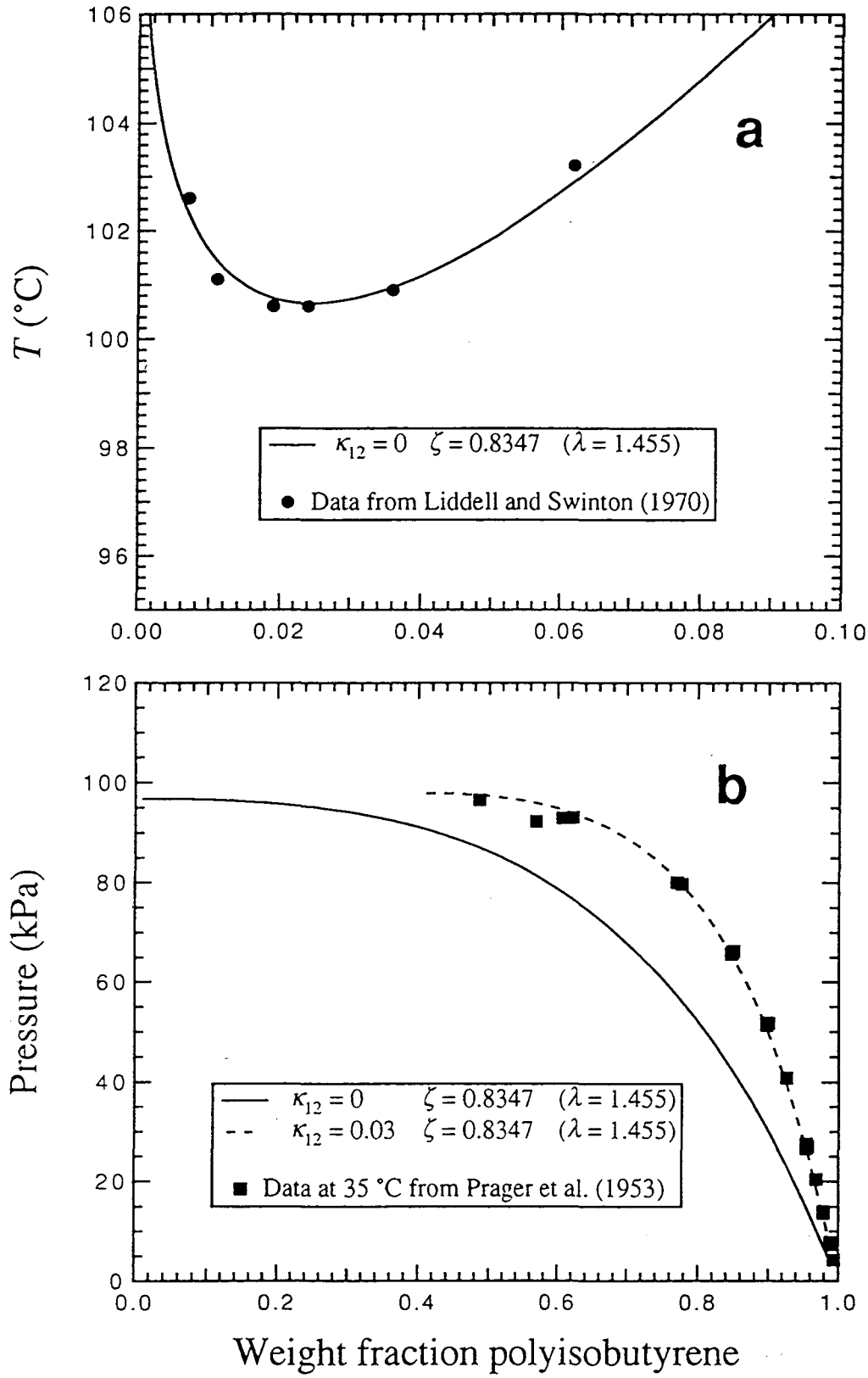

a
T (°C)
106
104
102
100
98
96
0.00
0.02
0.04
0.06
0.08
0.10
κ12 = 0 ζ = 0.8347 (λ = 1.455)
Data from Liddell and Swinton (1970)
b
Pressure (kPa)
120
100
80
60
40
20
0
0.0
0.2
0.4
0.6
0.8
1.0
κ12 = 0 ζ = 0.8347 (λ = 1.455)
κ12 = 0.03 ζ = 0.8347 (λ = 1.455)
Data at 35 °C from Prager et al. (1953)
Weight fraction polyisobutyrene

Figure 5

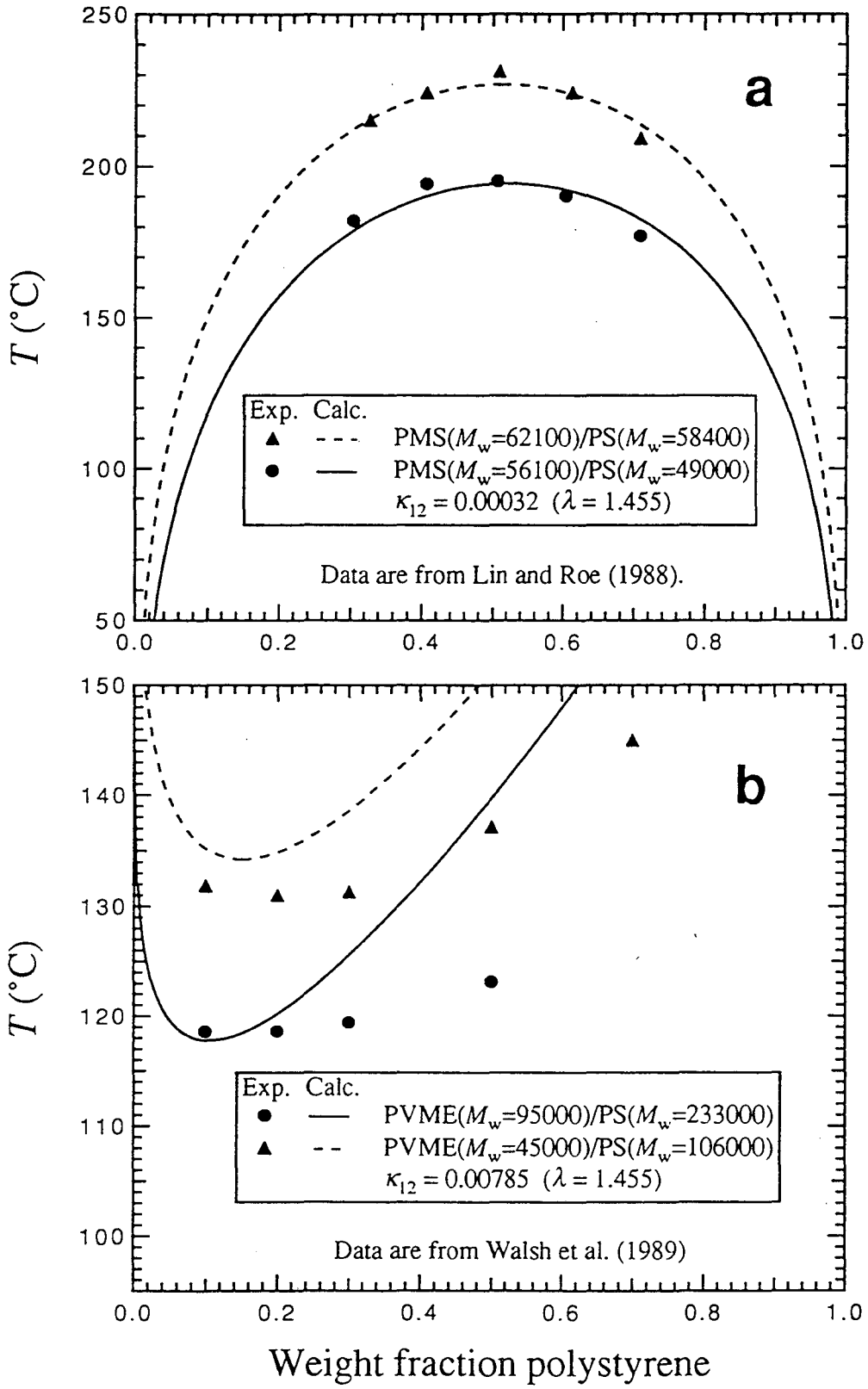

a
Exp. Calc.
PMS(M_w=62100)/PS(M_w=58400)
PMS(M_w=56100)/PS(M_w=49000)
κ_{12} = 0.00032 (λ = 1.455)
Data are from Lin and Roe (1988).
b
Exp. Calc.
PVME(M_w=95000)/PS(M_w=233000)
PVME(M_w=45000)/PS(M_w=106000)
κ_{12} = 0.00785 (λ = 1.455)
Data are from Walsh et al. (1989)
T (°C)
Weight fraction polystyrene

Figure 6

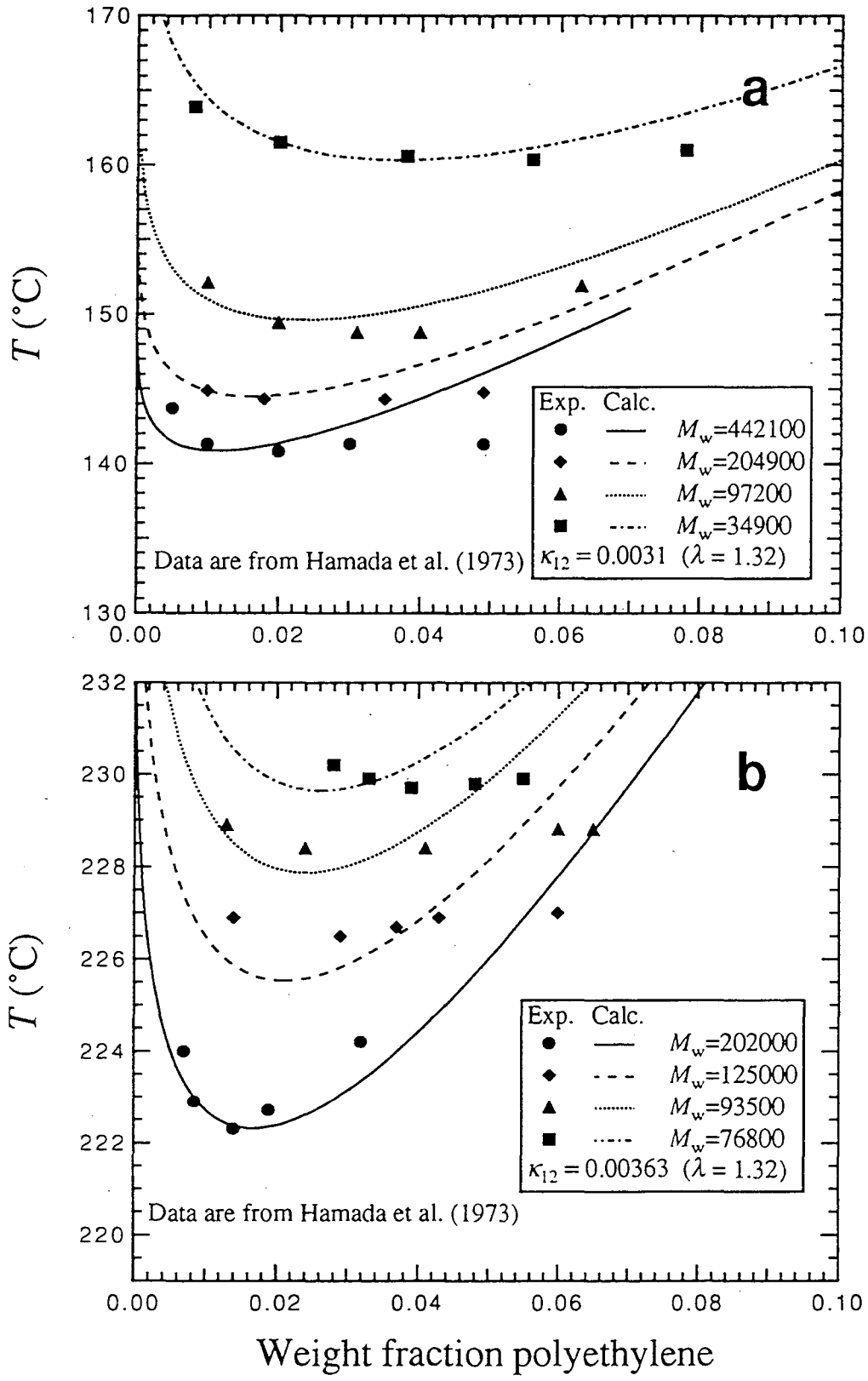

a
b
T (°C)
Exp. Calc.
M_w=442100
M_w=204900
M_w=97200
M_w=34900
κ_{12} = 0.0031 (λ = 1.32)
Data are from Hamada et al. (1973)
M_w=202000
M_w=125000
M_w=93500
M_w=76800
κ_{12} = 0.00363 (λ = 1.32)
Weight fraction polyethylene

Figure 7

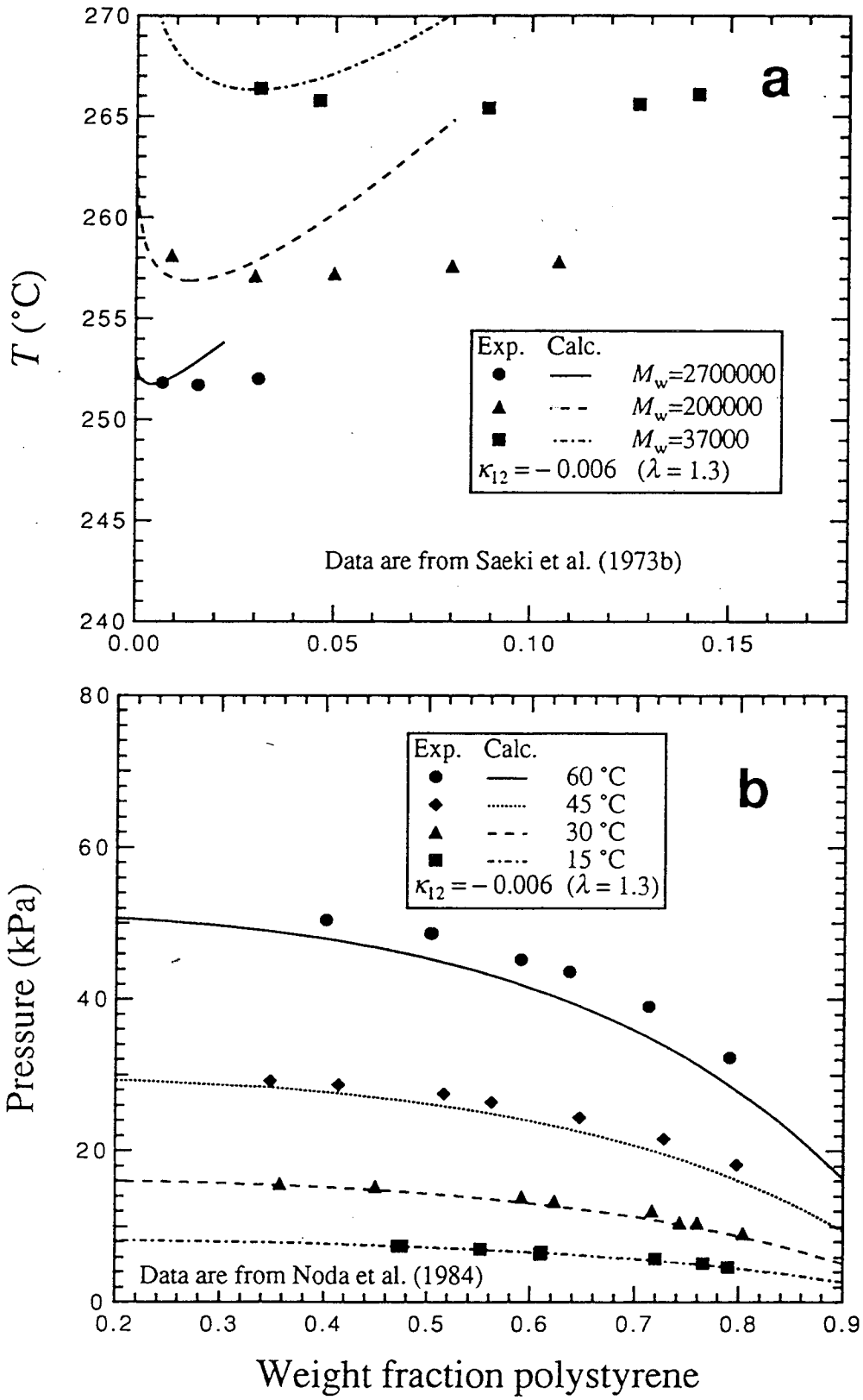

a
T (°C)
270
265
260
255
250
245
240
0.00
0.05
0.10
0.15
Exp. Calc.
M_w=2700000
M_w=200000
M_w=37000
$\kappa_{12} = -0.006$ ($\lambda = 1.3$)
Data are from Saeki et al. (1973b)
b
Pressure (kPa)
80
60
40
20
0
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Exp. Calc.
60 °C
45 °C
30 °C
15 °C
$\kappa_{12} = -0.006$ ($\lambda = 1.3$)
Data are from Noda et al. (1984)
Weight fraction polystyrene

Figure 8

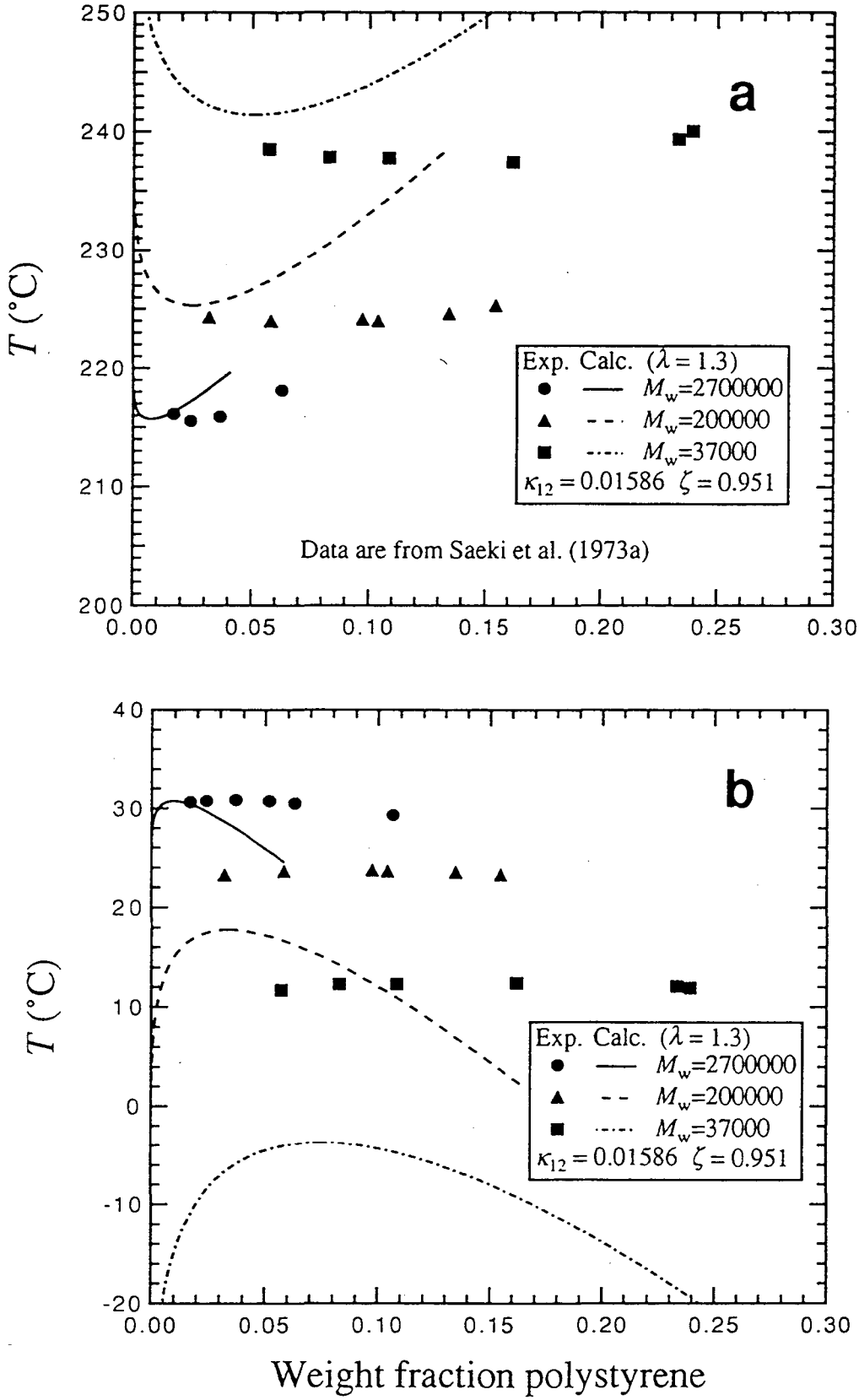

a
b
T (°C)
Exp. Calc. (λ = 1.3)
M_w=2700000
M_w=200000
M_w=37000
κ_{12} = 0.01586 ζ = 0.951
Data are from Saeki et al. (1973a)
Weight fraction polystyrene

Figure 9

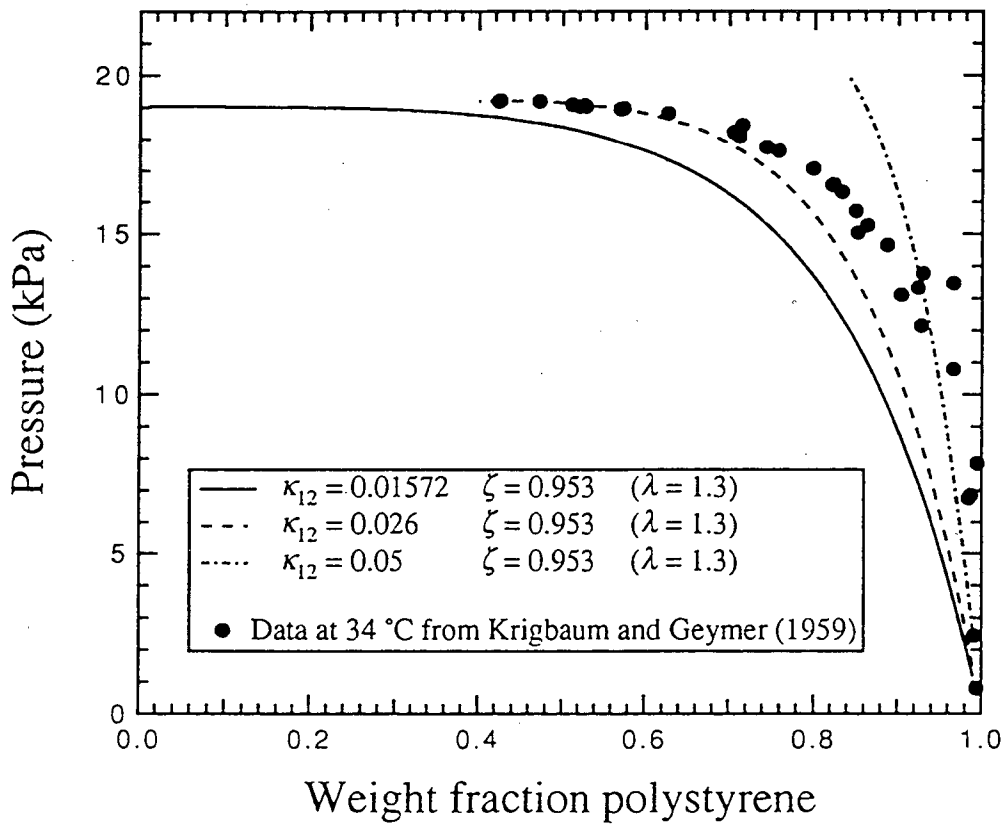
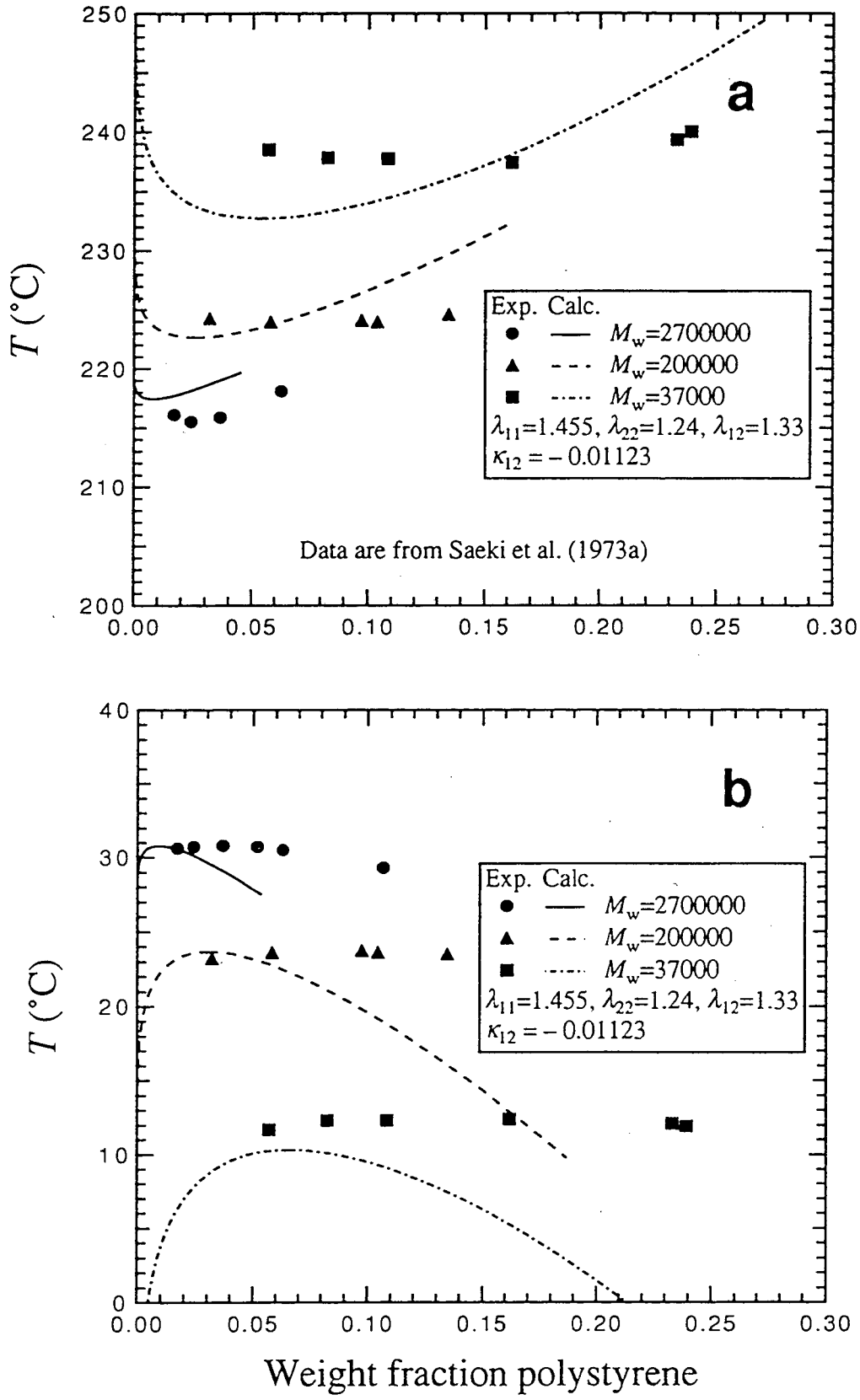

Pressure (kPa)
Weight fraction polystyrene
0
5
10
15
20
0.0
0.2
0.4
0.6
0.8
1.0
$\kappa_{12} = 0.01572$ $\zeta = 0.953$ $(\lambda = 1.3)$
$\kappa_{12} = 0.026$ $\zeta = 0.953$ $(\lambda = 1.3)$
$\kappa_{12} = 0.05$ $\zeta = 0.953$ $(\lambda = 1.3)$
Data at 34 °C from Krigbaum and Geymer (1959)

Figure 10


a
b
T (°C)
Exp. Calc.
M_w=2700000
M_w=200000
M_w=37000
λ_{11}=1.455, λ_{22}=1.24, λ_{12}=1.33
κ_{12} = – 0.01123
Data are from Saeki et al. (1973a)
Weight fraction polystyrene

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