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An Algorithm for Calculation of Phase Equilibria in Polydisperse Polymer Solutions Using the SAFT Equation of State

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ABSTRACT: We propose an algorithm for calculating phase equilibria of polydisperse polymer systems using the SAFT equation of state. The algorithm is formally exact and the computation time is independent of the number of pseudocomponents used to represent the polymer molecular weight distribution. The algorithm is based on the assumptions that the discrete pseudocomponents have the same segment size, the chain length is directly proportional to the molecular weight, and the binary interaction parameter k_{ij} between the discrete pseudocomponents is zero. The basic version of the algorithm assumes that the dispersion energy parameter (u^0/k) is the same for all the pseudocomponents and the binary interaction parameter k_{ij} is the same between all the pseudocomponents and the solvent. The algorithm is then generalized to the case where the dispersion energy parameter (u^0/k) is different for each pseudocomponent and the polymer/solvent binary interaction parameter is different for each pseudocomponent. Distinctive features of the phase diagrams of polydisperse systems are illustrated by calculating the cloud point and shadow point curves of polyethylene solutions in ethylene using the algorithm proposed in this work.

1. Introduction

The phase behavior of polymer solutions plays an important role in polymer synthesis and processing.[1] Many polymers are produced in solution, and in many cases it is important that the polymer solution remains homogeneous during the polymerization process in order to obtain a product with good properties and to control the reaction kinetics. Thus the reactor must be operated between the crystallization temperature of the polymer and the temperature of onset of liquid−liquid immiscibility called the cloud point. Polymer solution phase separation also plays an important role in the recovery and fractionation of the polymer from the product stream.

The point of onset of liquid−liquid immiscibility in a polymer solution is called the cloud point. In the case of a binary mixture of a monodisperse polymer in a solvent, the coexistence point corresponds with the cloud point, on the basis of the Gibbs phase rule. In the case of polydisperse polymers, the mixture has more than two components and the coexistence points do not always coincide with the cloud points. In this work, the polydisperse polymer is modeled as a mixture of polymer chains of different molecular weights. The cloud point for this solution is defined as the point of onset of liquid−liquid-phase separation for a solution having a fixed molecular weight distribution of the polymer on a solvent free basis. The molecular weight distribution in the second liquid phase that is formed at the cloud point is different from that of the starting phase. The locus of total polymer compositions of the second phase (plotted against pressure or temperature) is called the shadow point curve.

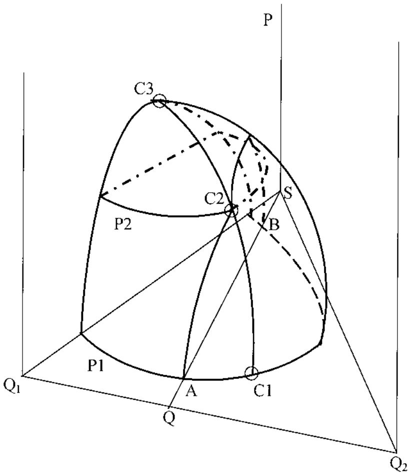

Figure 1. Pressure−composition space for a ternary polymer solution at constant temperature adapted from Koak.[2]

To understand the distinction of phase diagrams of a polydisperse polymer system from those of binary systems, we consider a ternary system of two polymers Q_1 and Q_2 (of the same chemical repeat unit with different chain lengths) in a solvent S.[2] The treatment here follows that of Koningsveld.[3] Figure 1 shows the pressure−composition space for this system at constant temperature. The pressure axis is labeled P. The curves labeled P_1 and P_2 represent the coexistence curves. Points C_1 and C_2 are plait or critical points. SQ is a composition axis for the solutions of Q in S with a constant ratio of Q_1 to Q_2. The total amount of polymer ($Q_1 + Q_2$) increases as one goes from S to Q along the line SQ. Figure 1 contains the binodal surface of this ternary polymer solution. The plane PSQ corresponds to a quasi-binary section for which the ratio of Q_1 to Q_2 is determined by point Q. This quasi-binary section is called the cloud point curve. A polymer solution at a point on this cloud point curve is in equilibrium with a polymer solution that, in general, has a different polymer concentration than Q. It can be seen that on this quasi-binary section, that the $P-x$ curve is highly unsymmetrical with the maximum in the phase boundary (called the precipitation threshold[4]) shifted toward the solvent-rich side. Moreover, the critical point (C_2) is not located at the maximum of the $P-x$ diagram but is shifted to higher polymer concentration.

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To model this complex phase space, we need to account for polydispersity in our flash calculation. Calculation of phase equilibria involves solving the equations representing the conditions of thermodynamic equilibrium namely, equality of temperatures and pressures in all the phases and equality of chemical potential of each component in all the phases. As the number of components in the system increases, the number of equations to be solved increases since there is an equation for each component. In a polydisperse polymer system, there are polymer chains with the same chemical repeat unit but different molecular weights. When a continuous molecular weight distribution is discretized, it results in a large number of pseudocomponents and solving the equations of equilibrium becomes a formidably complex computational problem.[5] In this work we propose an algorithm to calculate phase equilibria of polydisperse polymer solutions using the SAFT equation of state, for which the computation time is independent of the number of pseudocomponents used to represent the polymer molecular weight distribution. The algorithm uses some ideas from previous studies of polydisperse systems with cubic equations of state[6] and the Sanchez–Lacombe equation of state.[7] For a continuous molecular weight distribution, we use the discretization procedure based on the quadrature method.[8−10] Having obtained the pseudocomponents by discretization, our algorithm can be used to perform phase equilibrium calculations with computation time being independent of the number of pseudocomponents. This allows us to use as many pseudocomponents as required to accurately represent the continuous molecular weight distribution without increasing the computational complexity. Our method works under certain assumptions about the nature of pseudocomponents (section 2.1), but the formulation is exact. Further discussion on calculation methods for polydisperse polymer solutions can be found in the work of Hu and others.[11−13]

2. Theory

2.1. Criteria of Thermodynamic Equilibrium.

The molecular weight distribution of the polymer is represented in terms of discrete polymer pseudocomponents. The discrete distribution gives weight fractions corresponding to discrete molecular weights. This discrete distribution can be obtained from chromatographic experiments or discretization of a continuous distribution.[14] If the only information available is the number average and weight average molecular weights of the polymer, a standard continuous molecular weight distribution is fitted to get the same number average and weight average molecular weights and the distribution is then discretized to obtain pseudocomponents. With the discrete components of the polymer, the problem becomes a multicomponent flash problem.

Consider a mixture of p polymer components and s solvents. The polymer components are subject to following assumptions:

1. All the discrete polymer components have the same segment volume parameter (v^{00})
2. They also have the same dispersion energy parameter (u^0/k).
3. The chain-length parameter (m) for the polymer components is directly proportional to the molecular weight of that component.
4. The binary interaction parameter between the pseudocomponents is 0.
5. The binary interaction parameter between all the pseudocomponents and the solvent is the same.

This mixture is treated as a ($p + s$) component system. The problem is formulated as a bubble pressure calculation problem; i.e., given temperature and composition of phase α calculate the equilibrium pressure and composition of the equilibrium phase β.

The conditions of thermodynamic equilibrium for two phases give

$$\mu_1^\alpha = \mu_1^\beta \tag{1}$$

$$\vdots$$

$$\mu_p^\alpha = \mu_p^\beta \tag{p}$$

$$\mu_{p+1}^\alpha = \mu_{p+1}^\beta \tag{$p+1$}$$

$$\vdots$$

$$\mu_{p+s}^\alpha = \mu_{p+s}^\beta \tag{$p+s$}$$

$$P^\alpha = P^\beta \tag{$p+s+1$}$$

The unknowns are x_1^β, ..., x_p^β, x_{p+1}^β, ..., x_{p+s-1}^β, ρ^α, and ρ^β where x stands for composition and ρ for molar density. In the equilibrium equations, μ stands for the chemical potential. Thus we have $p + s + 1$ equations in $p + s + 1$ unknowns. Hence this is a determinate system of nonlinear equations. However, as the number of pseudocomponents (p) increases, the size of the system increases and the computation becomes difficult. Convergence of the flash routine can be a serious problem for a large system of nonlinear equations. In the next section we look at some simplifications that result from assumptions 1−4 listed above which allow us to account for multiple polymer components while keeping the number of equations independent of the number of discrete polymer pseudocomponents.

2.2. Simplification of SAFT for Polydisperse Polymer Solutions.

SAFT[15,16] is an equation of state in the form of a thermodynamic perturbation theory based on Wertheim's theory.[17−20] SAFT was put in the form of an engineering equation of state by Chapman et al.[15,16] Numerous forms of the SAFT equation of state have been proposed. These various forms have modified the segment term of the original SAFT equation of state using a Lennard-Jones[21−26] or square well type potential,[27−31] but the form of the chain and association terms has remained unchanged. We base this work on the form proposed by Huang and Radosz;[31,32] however the results are easily applied to other forms of SAFT. SAFT views a molecule as a chain of tangentially connected spheres with hard-core repulsion and a mean field attractive dispersion interaction between the segments. A pure nonassociating fluid has three SAFT parameters, namely segment volume v^{00} (cm^3/mol), dispersion energy parameter u^0/k (K) and the number of segments in a chain (m). These parameters have been shown to be correlated to the molecular weight in a given homologous series.[31] In this work, we exploit this molecular weight dependence to simplify the flash algorithm.

For a nonassociating fluid the compressibility factor and residual chemical potential can be written as[15,16,31,32]

$$Z = 1 + Z^{\mathrm{hs}} + Z^{\mathrm{chain}} + Z^{\mathrm{dispersion}} \tag{2.2.1}$$

$$\frac{\mu_i}{kT} = \frac{\mu_i^{\mathrm{id}}}{kT} + \frac{\mu_i^{\mathrm{res}}}{kT} = \ln(\rho x_i \Lambda^3) + \frac{\mu_i^{\mathrm{hs}}}{kT} + \frac{\mu_i^{\mathrm{chain}}}{kT} + \frac{\mu_i^{\mathrm{dispersion}}}{kT} \tag{2.2.2}$$

Here the residual chemical potential is residual to an ideal gas at the same temperature, density and composition. Λ^3 includes only temperature-dependent contributions to the chemical potential. As we will show, the phase equilibrium conditions for our polymer/solvent system simplify in part, because the mixture properties depend only on the number average molecular weight of the polymer and not on the detailed polymer molecular weight distribution. The SAFT compressibility factor and chemical potential depend on certain reduced densities. These reduced densities are defined by

$$\begin{aligned}\zeta_k &= \frac{\pi}{6}\rho\sum_{i=1}^{p+s} x_i m_i d_{ii}^k \\ &= \frac{\pi}{6}\rho\Big[\sum_{i=1}^{p} x_i(\alpha M_i) d_p^k + \sum_{i=p+1}^{p+s} x_i m_i d_{ii}^k\Big] \qquad (2.2.3) \\ &= \frac{\pi}{6}\rho\Big[x_p m(\bar{M}_{\mathrm{n}}) d_p^k + \sum_{i=p+1}^{p+s} x_i m_i d_{ii}^k\Big], \quad k = 0, 1, ..., 3\end{aligned}$$

Note that here $m(\bar{M}_{\mathrm{n}}) = \alpha\bar{M}_{\mathrm{n}}$ is the chain length evaluated at the number average molecule weight. ρ is the number density of molecules, α is the proportionality constant between chain length and molecular weight (which is a user specified parameter), d_p is the temperature-dependent hard sphere diameter of the polymer components (all the polymer components have the same segment diameter), x_p is the overall polymer mole fraction defined by

$$x_p = \sum_{j=1}^{p} x_j \tag{2.2.4}$$

and $\bar{M}_{\mathrm{n}}$ is the number average molecular weight of the polymer defined by

$$\bar{M}_{\mathrm{n}} = \sum_{j=1}^{p} x_j M_j \Big/ \sum_{j=1}^{p} x_j = \sum_{j=1}^{p} X_j M_j \tag{2.2.5}$$

where M_j is the molecular weight of component j and

$$X_j = x_j \Big/ \sum_{k=1}^{p} x_k = x_j / x_p \tag{2.2.6}$$

is the mole fraction of polymer component j in the polymer mixture on a solvent free basis. Equation 2.2.3 shows that the polymer can be "lumped" to calculate the reduced density. Thus

$$\zeta_k = f(T, x_p, \bar{M}_{\mathrm{n}}, \{x_s\}) \tag{2.2.7}$$

where $\{x_s\}$ is the vector of solvent compositions. Let us look at the various contributions to pressure and chemical potential. The contact value of the hard sphere pair correlation function is given by[33]

$$g_{ij}(d_{ij})^{\mathrm{hs}} = \frac{1}{1 - \zeta_3} + \left[\frac{3 d_{ii} d_{jj}}{d_{ii} + d_{jj}}\right]\frac{\zeta_2}{(1 - \zeta_3)^2} + 2\left[\frac{d_{ii} d_{jj}}{d_{ii} + d_{jj}}\right]^2 \frac{{\zeta_2}^2}{(1 - \zeta_3)^2} \tag{2.2.8}$$

It is a function of the reduced densities and so from eqs 2.2.7 and 2.2.8

$$g_{ij}(d_{ij})^{\mathrm{hs}} = G(T, x_p, \bar{M}_{\mathrm{n}}, \{x_s\}) \tag{2.2.9}$$

A. Hard Sphere Contribution.

$$Z^{\mathrm{hs,res}} = \frac{2}{3}\pi\rho\sum_{i=1}^{p+s}\sum_{j=1}^{p+s} x_i m_i x_j m_j {d_{ij}}^3\, g_{ij}^{\mathrm{hs}}(d_{ij}) \tag{2.2.10}$$

Note that the compressibility factor is residual to the ideal gas and is based on per mole of molecules [The Mansoori et al.[33] expression gives compressibility factor per mole of segments. It has been scaled to per mole of molecules. One mole of molecules is equivalent to m (average chain length) mole of segments.] With the assumptions we have about the polymer components, this becomes

$$Z^{\mathrm{hs}} = \frac{2}{3}\pi\rho\Big[d_p^3\, x_p^2 m(\bar{M}_{\mathrm{n}})^2 g_{pp}^{\mathrm{hs}}(d_{pp}) + 2 x_p m(\bar{M}_{\mathrm{n}}) \sum_{\mathrm{solvents}} x_k m_k d_{pk}^3\, g_{pk}^{\mathrm{hs}}(d_{pk}) + \sum_{i\to\mathrm{solv}}\ \sum_{j\to\mathrm{solv}} x_i m_i x_j m_j d_{ij}^3\, g_{ij}^{\mathrm{hs}}(d_{ij})\Big] \tag{2.2.11}$$

where d_{pp} is the temperature-dependent hard sphere diameter of polymer component segments (which is the same for all polymer components) and g_{pp} is the contact value of the pair correlation function in the reference fluid between the segments of the polymer components. The function g_{pp} is independent of the index of the polymer component since all the segments are of the same size. The chemical potential contribution is given by

$$\begin{aligned}\frac{\mu_i^{\mathrm{hs}}}{kT} = m_i\Bigg\{&\frac{\pi\rho\big(Z^{\mathrm{hs}} + x_p m(\bar{M}_{\mathrm{n}}) + \sum_{j\to\mathrm{solv}} x_j m_j\big){d_{ii}}^3}{6} - \\ &\ln(1 - \zeta_3) + \frac{3\zeta_2 d_{ii}}{(1 - \zeta_3)} + \frac{3\zeta_1 {d_{ii}}^2}{(1 - \zeta_3)} + \frac{9{\zeta_2}^2\, {d_{ii}}^2}{2(1 - \zeta_3)^2} + \\ &3\left(\frac{\zeta_2 d_{ii}}{\zeta_3}\right)^2\left[\ln(1 - \zeta_3) + \frac{\zeta_3}{(1 - \zeta_3)} - \frac{{\zeta_3}^2}{2(1 - \zeta_3)^2}\right] - \\ &\left(\frac{\zeta_2 d_{ii}}{\zeta_3}\right)^3\left[2\ln(1 - \zeta_3) + \frac{\zeta_3(2 - \zeta_3)}{(1 - \zeta_3)}\right]\Bigg\}\end{aligned} \tag{2.2.12}$$

Note that for all the polymer components the segment diameter is the same. Hence the hard sphere contribution to the compressibility factor depends on the number average molecular weight of the polymer components. From eqs 2.2.7–2.2.10 we see that

$$Z^{\mathrm{hs}} = Z^{\mathrm{hs}}(\rho, T, x_p, \bar{M}_{\mathrm{n}}, \{x_s\}) \tag{2.2.13}$$

Also, since $m_i = \alpha M_i$ for a polymer, M_i being the molecular weight and α a user specified parameter, the hard sphere contribution to the chemical potential of a polymer component is proportional to its molecular weight

$$\frac{\mu_i^{\text{hs}}}{kT} = \begin{cases} M_i f(\rho, T, x_p, \bar{M}_{\text{n}}, \{x_s\}) & \text{for a polymer component} \\ f(\rho, T, x_p, \bar{M}_{\text{n}}, \{x_s\}) & \text{for a solvent} \end{cases} \tag{2.2.14}$$

Equations 2.2.13 and 2.2.14 are the key to the reduction of the system of nonlinear equations (equations of equilibrium). We derive similar equations for the chain and dispersion contributions.

B. Chain Contribution. The chain contribution to the compressibility factor is given by

$$Z^{\text{chain}} = \frac{P^{\text{chain}}}{\rho_{\text{mol}} kT} = \sum_{i=1}^{p+s} x_i (1 - m_i) \rho [\partial \ln(g_{ii}(d_{ii}))/\partial \rho] = x_p (1 - m(\bar{M}_{\text{n}}))\ \rho\ \partial \ln(g_{pp}(d_{pp}))/\partial \rho + \sum_{\text{solvents}} x_k (1 - m_k)\ \rho\ \partial \ln(g_{kk}(d_{kk}))/\partial \rho \tag{2.2.15}$$

where

$$\rho \frac{\partial g_{ii}}{\partial \rho} = \frac{\zeta_3}{(1-\zeta_3)^2} + \frac{3}{2} d_{ii} \left[\frac{\zeta_2}{(1-\zeta_3)^2} + \frac{2\zeta_2\zeta_3}{(1-\zeta_3)^3} \right] + \frac{d_{ii}^{\ 2}}{2} \left[\frac{2\zeta_2^{\ 2}}{(1-\zeta_3)^3} + \frac{3\zeta_2^{\ 2}\zeta_3}{(1-\zeta_3)^4} \right] \tag{2.2.16}$$

For all the polymer components, $d_{ii} = d_p$ and the densities ζ_k depend on the total polymer composition and number average molecular weight (eq 2.2.7). Thus, we see that

$$Z^{\text{chain}} = f(\rho, T, x_p, \bar{M}_{\text{n}}, \{x_s\}) \tag{2.2.17}$$

The chain contribution to the chemical potential is given by

$$\frac{\mu_j^{\text{chain}}}{kT} = (1 - m_j) \ln(g_{jj}(d_{jj})) + \frac{\pi}{6} \rho \sum_{i=1}^{p+s} \frac{x_i (1 - m_i)}{g_{ii}(d_{ii})} m_j \left\{ \frac{d_{jj}^{\ 3}}{(1-\zeta_3)^2} + \frac{3 d_{ii}}{2} \times \left[\frac{d_{jj}^{\ 2}}{(1-\zeta_3)^2} + \frac{2 d_{jj}^{\ 3} \zeta_2}{(1-\zeta_3)^3} \right] + \frac{d_{ii}^{\ 2}}{2} \times \left[\frac{2 d_{jj}^{\ 2} \zeta_2}{(1-\zeta_3)^3} + \frac{3 d_{jj}^{\ 3} \zeta_2^{\ 2}}{(1-\zeta_3)^4} \right] \right\} \tag{2.2.18}$$

which simplifies to

$$\frac{\mu_j^{\text{chain}}}{kT} = (1 - m_j) \ln(g_{jj}(d_{jj})) + \frac{\pi}{6} \rho \sum_{i \to \text{solv}} \frac{x_i (1 - m_i)}{g_{ii}} m_j \left\{ \frac{d_{jj}^{\ 3}}{(1-\zeta_3)^2} + \frac{3 d_{ii}}{2} \times \left[\frac{d_{jj}^{\ 2}}{(1-\zeta_3)^2} + \frac{2 d_{jj}^{\ 3} \zeta_2}{(1-\zeta_3)^3} \right] + \frac{d_{ii}^{\ 2}}{2} \left[\frac{2 d_{jj}^{\ 2} \zeta_2}{(1-\zeta_3)^3} + \frac{3 d_{jj}^{\ 3} \zeta_2^{\ 2}}{(1-\zeta_3)^4} \right] \right\} + \frac{\pi}{6} \rho \frac{x_p (1 - m(\bar{M}_{\text{n}}))}{g_{pp}} m_j \left\{ \frac{d_{jj}^{\ 3}}{(1-\zeta_3)^2} + \frac{3 d_{pp}}{2} \left[\frac{d_{jj}^{\ 2}}{(1-\zeta_3)^2} + \frac{2 d_{jj}^{\ 3} \zeta_2}{(1-\zeta_3)^3} \right] + \frac{d_{pp}^{\ 2}}{2} \left[\frac{2 d_{jj}^{\ 2} \zeta_2}{(1-\zeta_3)^3} + \frac{3 d_{jj}^{\ 3} \zeta_2^{\ 2}}{(1-\zeta_3)^4} \right] \right\} \tag{2.2.19}$$

Thus,

$$\frac{\mu_j^{\text{chain}}}{kT} = f(T, \rho, x_p, \bar{M}_{\text{n}}, \{x_s\}) \tag{2.2.20}$$

For a polymer component since chain length is proportional to molecular weight, we observe that

$$\frac{\mu_l^{\text{chain}}}{kT} = \mu_{\text{A}}^{\text{chain}}(T, \rho, x_p, \bar{M}_{\text{n}}, \{x_s\}) + M_l \mu_{\text{B}}^{\text{chain}}(T, \rho, x_p, \bar{M}_{\text{n}}, \{x_s\}) \tag{2.2.21}$$

where $l = 1, 2, ..., p$ is the index that runs over the polymer components and M_l is the molecular weight of the polymer component l. Thus, for a given solution, the chain contribution to the chemical potential of a polymer component is a linear function of its molecular weight and the coefficients depend only on the number average molecular weight which is the first moment of the molar mass distribution of the polymer. Now we will derive a similar result for the dispersion term.

C. Dispersion Contribution. Van der Waals one fluid theory is used for the dispersion term in mixtures. According to the vdW1 mixing rules

$$m = \sum_{i=1}^{p+s} x_i m_i = x_p m(\bar{M}_{\text{n}}) + \sum_{j \to \text{solv}} x_j m_j \tag{2.2.22}$$

$$\frac{u}{kT} = \frac{\sum_{i=1}^{p+s} \sum_{j=1}^{p+s} x_i x_j m_i m_j (u_{ij}/kT) v_{ij}^0}{\sum_{i=1}^{p+s} \sum_{j=1}^{p+s} x_i x_j m_i m_j v_{ij}^0} \tag{2.2.23}$$

where

$$u_{ij} = (u_{ii} u_{jj})^{1/2} (1 - k_{ij}) \tag{2.2.24}$$

Introducing assumptions 3 and 4 from section 2.1, eq 2.2.23 simplifies to

$$\frac{u}{kT} = [(u_p/kT)v_p^0(x_p m(\bar{M}_n))^2 + 2x_p m(\bar{M}_n)\sum_{j\to\mathrm{solv}} x_j m_j (u_{pj}/kT)v_{pj}^0 + \sum_{i\to\mathrm{solv}}\sum_{j\to\mathrm{solv}} x_i x_j m_i m_j (u_{ij}/kT)v_{ij}^0]/[v_p^0(x_p m_p(\bar{M}_n))^2 + 2x_p m(\bar{M}_n)\sum_{j\to\mathrm{solv}} x_j m_j v_{pj}^0 + \sum_{i\to\mathrm{solv}}\sum_{j\to\mathrm{solv}} x_i x_j m_i m_j v_{ij}^0] \quad (2.2.25)$$

Note that we have used u_{pj} for the cross interaction energy between all the polymer components and the solvent j. This is because all the polymer components have the same u_{ii} ($i = 1, ..., p$) and the k_{ij} between any polymer component and the solvent j is the same for all polymers ($i = 1, .., p$). So eq 2.2.24 shows that for a given solvent j, u_{ij} between any polymer i and solvent j is the same for all the polymers.

Thus,

$$\frac{u}{kT} = U(T,\rho,x_p,\bar{M}_n,\{x_s\}) \quad (2.2.26)$$

The dispersion contribution to the compressibility factor is given by

$$Z^{\mathrm{disp}} = \frac{P^{\mathrm{disp}}}{\rho_{\mathrm{mol}}kT} = m\sum_i\sum_j D_{ij}\left[\frac{u}{kT}\right]^i j\left[\frac{\zeta_3}{\tau}\right]^j \quad (2.2.27)$$

Note that here $\tau = 0.74048$ is a constant, and D_{ij} are the fitted constants for the dispersion term of Chen and Kreglewski.[34] We observe from eq 2.2.27 that

$$Z^{\mathrm{disp}} = Z^{\mathrm{disp}}(T,\rho,x_p,\bar{M}_n,\{x_s\}) \quad (2.2.28)$$

The dispersion contribution to the chemical potential is given by

$$\frac{\mu_k^{\mathrm{disp}}}{kT} = m_k\left\{\sum_i\sum_j D_{ij}\left[\frac{u}{kT}\right]^i\left[\frac{\zeta_3}{\tau}\right]^j + 2mA_k\sum_i\sum_j D_{ij} i\left[\frac{u}{kT}\right]^{i-1}\left[\frac{\zeta_3}{\tau}\right]^j + m\rho(\pi/6)d_{kk}{}^3\sum_i\sum_j j\left[\frac{u}{kT}\right]^i\left[\frac{\zeta_3{}^{j-1}}{\tau^j}\right]\right\} \quad (2.2.29)$$

where A_k is defined as

$$A_k = [(u_{kp}/kT)x_p m(\bar{M}_n)v_{kp}^0 + \sum_{r\to\mathrm{solv}} x_r m_r (u_{kr}/kT)v_{kr}^0 - (u/kT)(v_{kp}{}^0 x_p m(\bar{M}_n) + \sum_{r\to\mathrm{solv}} x_r m_r v_{kr}^0)]/[v_p^0(x_p m(\bar{M}_n))^2 + 2x_p m(\bar{M}_n)\sum_{j\to\mathrm{solv}} x_j m_j v_{pj}^0 + \sum_{i\to\mathrm{solv}}\sum_{j\to\mathrm{solv}} x_i x_j m_i m_j v_{ij}^0] \quad (2.2.30)$$

Equation 2.2.29 shows that for a polymer component

$$\frac{\mu_k^{\mathrm{disp}}}{kT} = M_k\mu_{\mathrm{B}}^{\mathrm{disp}}(T,\rho,x_p,\bar{M}_n,\{x_s\}) \quad (2.2.31)$$

For a solvent

$$\frac{\mu_s^{\mathrm{disp}}}{kT} = \mu_{\mathrm{S}}^{\mathrm{disp}}(T,\rho,x_p,\bar{M}_n,\{x_s\}) \quad (2.2.32)$$

Equations 2.2.1, 2.2.13, 2.2.17, and 2.2.28 for compressibility factor show that

$$Z = Z(T,\rho,x_p,\bar{M}_n,\{x_s\}) \quad (2.2.33)$$

Combining eqs 2.2.2, 2.2.14, 2.2.20, and 2.2.32 for chemical potential, we see that

$$\frac{\mu_s^{\mathrm{res}}}{kT} = \mu_{\mathrm{S}}^{\mathrm{res}}(T,\rho,x_p,\bar{M}_n,\{x_s\}),\ s \to \text{solvent} \quad (2.2.34)$$

Equations 2.2.14, 2.2.21 and 2.2.31 show that for a polymer component

$$\frac{\mu_p^{\mathrm{res}}}{kT} = \mu_{\mathrm{A}}^{\mathrm{res}}(T,\rho,x_p,\bar{M}_n,\{x_s\}) + M_p\mu_{\mathrm{B}}^{\mathrm{res}}(T,\rho,x_p,\bar{M}_n,\{x_s\}),\ p \to \text{polymer} \quad (2.2.35)$$

The important thing to note here is that the functions $\mu_{\mathrm{A}}^{\mathrm{res}}$ and $\mu_{\mathrm{B}}^{\mathrm{res}}$ are the same for all the polymer components. Similar simplification was used by Tork et al.[35] and Behme et al.[36]

3. Simplification of Phase Equilibrium Equations

Conditions of equilibrium involve equating chemical potentials of the components between the coexisting phases and equating pressures (in a bubble pressure calculation problem). Consider the equality of chemical potentials condition between the two coexisting phases α and β

$$\frac{\mu_i^{\mathrm{res},\alpha}}{kT} + \ln(\rho_\alpha x_i^\alpha) = \frac{\mu_i^{\mathrm{res},\beta}}{kT} + \ln(\rho_\beta x_i^\beta) \quad (3.1)$$

where the second term $\ln(\rho x_i)$ is the ideal gas contribution. We will have to write eq 3.1 for all the polymer components (p equations) and the same equation for the solvent. Hence the number of equations increases with the number of polymer components. However, for polydisperse polymer solutions we can simplify eq 3.1.

Rearranging eq 3.1 gives

$$\ln(x_i^\beta/x_i^\alpha) = \ln(\rho_\alpha/\rho_\beta) + \frac{\mu_i^{\mathrm{res},\alpha}}{kT} - \frac{\mu_i^{\mathrm{res},\beta}}{kT} \quad (3.2)$$

We define the partition coefficient of a component i as

$$K_i = x_i^\beta/x_i^\alpha \quad (3.3)$$

For polymer component, using the fact that residual chemical potential is a linear function of molecular weight (eq 2.2.34) and eqs 3.2 and 3.3 we see that ln(K_p) for a polymer is a linear function of molecular weight. Thus, following Phoenix and Heidemann[7] we can assume that $\ln(K_p)$ is of the form

$$\ln(K_p) = K_{\mathrm{A}} + M_pK_{\mathrm{B}} \quad (3.4)$$

If we set

$$K_{\mathrm{A}} = \ln(\rho_\alpha/\rho_\beta) + \mu_{\mathrm{A}}^\alpha(T,\rho_\alpha,x_p^\alpha,\{x_s^\alpha\},\bar{M}_n^\alpha) - \mu_{\mathrm{A}}^\beta(T,\rho_\beta,x_p^\beta,\{x_s^\beta\},\bar{M}_n^\beta) \quad (3.5)$$

and

$$K_{\mathrm{B}} = \mu_{\mathrm{B}}^{\alpha}(T,\rho_{\alpha},x_{p}^{\ \alpha},\{x_{s}^{\alpha}\},\bar{M}_{\mathrm{n}}^{\alpha}) - \mu_{\mathrm{B}}^{\beta}(T,\rho_{\beta},x_{p}^{\beta},\{x_{s}^{\beta}\},\bar{M}_{\mathrm{n}}^{\beta}) \tag{3.6}$$

we satisfy eq 3.2 (i.e. the equality of chemical potential condition) for all polymer components (note that μ_{A} and μ_{B} in eqs 3.5 and 3.6 are defined in eq 2.2.35). Thus, the p equations of the form of eq 3.2 (one for each polymer component) are reduced to two (eqs 3.5 and 3.6). The equations for the solvent chemical potential can be written as

$$\frac{\mu_{s}^{\alpha}}{kT}(T,\rho_{\alpha},x_{p}^{\alpha},\{x_{s}^{\alpha}\},\bar{M}_{\mathrm{n}}^{\alpha}) = \frac{\mu_{s}^{\beta}}{kT}(T,\rho_{\beta},x_{p}^{\beta},\{x_{s}^{\beta}\},\bar{M}_{\mathrm{n}}^{\beta}), s \rightarrow \text{solvent} \tag{3.7}$$

$$P^{\alpha}(T,\rho_{\alpha},x_{p}^{\alpha},\{x_{s}^{\ \alpha}\},\bar{M}_{\mathrm{n}}^{\alpha}) = P^{\beta}(T,\rho_{\beta},x_{p}^{\beta},\{x_{s}^{\beta}\},\bar{M}_{\mathrm{n}}^{\beta}) \tag{3.8}$$

In the cloud point calculations, the molecular weight distribution of the polymer on a solvent free basis is fixed. If X_j denotes the mole fraction of polymer component j on a solvent free basis then

$$x_j = x_p X_j,\ j \rightarrow \text{polymer} \tag{3.9}$$

where x_j denotes the actual mole fraction of the polymer j in the solution. Since X_j's for one phase are fixed in a cloud point calculation, only x_p needs to be specified in order to specify all the polymer compositions x_j. Note that the polymer distribution in the second phase is different from that of the starting phase and is unknown to start with. Thus, for a cloud point calculation, the unknowns are $\{T,\rho_{\alpha},\rho_{\beta},x_{p}^{\alpha},\{x_{k}^{\alpha}\}_{k=1,..,s-1},K_{\mathrm{A}},K_{\mathrm{B}},\{x_{i}^{\beta}\}_{i=1,...,s-1}\}$. Note that the number average molecular weight ($\bar{M}_{\mathrm{n}}$) of the starting phase is known and that of the second phase can be calculated from the k-factors of the polymer components calculated from K_{A} and K_{B} by eq 3.4. The number average molecular weight is required to calculate various thermodynamic properties as shown above. The number of unknowns is $4 + 2s$ (s being the number of solvents). The number of equations (see eqs 3.5−3.8) is $3 + s$. Thus, we need $s + 1$ more equations for it to be a complete nonlinear equation problem. These equations are the constraint equations specifying the kind of flash calculation we want to do.

1. For a cloud point pressure calculation, we fix temperature and the composition of one phase and calculate the equilibrium pressure and composition of the second phase. In that case, the constraint equations are specification of x_p in phase α, specification of $s - 1$ solvent compositions, and the specification of temperature. This gives us the required $s + 1$ equations.

2. For a cloud point temperature calculation, we specify pressure instead of temperature. Hence the constraint equation for specification of temperature is replaced by setting the pressure calculated from the equation of state to the given value.

In both cases, the problem involves solving $4 + 2s$ equations in $4 + 2s$ unknowns. Thus, for the case of a single solvent, we have to solve six equations in six unknowns to get a single state point on the cloud point curve. The problem size is independent of the number of polymer pseudocomponents (p) used to represent the polymer molecular weight distribution. If we compare this with a monodisperse polymer and solvent system, where we would have to solve $3 + 2s$ equations, we have to solve only one additional equation for a polydisperse system. The solution of the system of nonlinear equations can be calculated by an iterative numerical procedure like Newton−Raphson method. The algorithm is demonstrated in a flowchart in Figure 2.

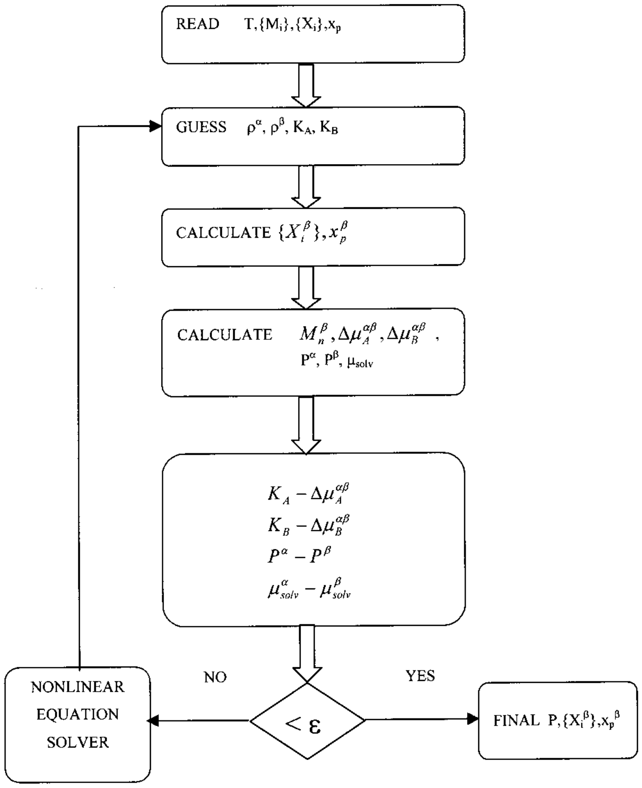


Figure 2. Flowchart of the algorithm to calculate phase equilibrium in polydisperse polymer solutions (with one solvent) using the SAFT equation of state.

Table 1. SAFT Parameters for Polyethylene and Ethylene (solvent)

substance	v^{00} (mL/mol)	u^0/k (K)	m
polyethylene	12.0	228.36	0.0357M
ethylene	18.157	212.06	1.464

Table 2. Molecular Weight Distribution of Polyethylene on a Solvent-Free Basis Expressed in Terms of 36 Pseudocomponents[a]

M_i	3300	4500	6000	8200	8800	10900
w_i	0.000352	0.000837	0.001410	0.003524	0.004405	0.007224
M_i	12300	14400	19300	25900	27900	34200
w_i	0.008810	0.011277	0.018281	0.027884	0.030836	0.040218
M_i	42150	46000	54000	61000	70000	82500
w_i	0.048456	0.052156	0.057266	0.059645	0.060878	0.058412
M_i	86000	90000	109000	110000	118000	132000
w_i	0.057266	0.056385	0.052861	0.051143	0.048456	0.044051
M_i	139000	148000	162000	198000	263000	300000
w_i	0.041848	0.039778	0.035241	0.027796	0.017664	0.014096
M_i	350000	470000	625000	830000	1500000	1700000
w_i	0.010220	0.005859	0.003040	0.001322	0.000661	0.000441

[a] The distribution is expressed as weight fraction of the components.

4. Application to Polyethylene Solutions

We consider the solution of polydisperse polyethylene in ethylene. This is the system studied by Koak et al.[37] The polymer has a number average molecular weight of 56 000 and a weight average molecular weight of 99 000. The polymer molecular weight distribution is represented by 36 components as given in Table 2. The pseudocomponents were reported by de Loos[38] based on experimental data. The solvent is ethylene. Ethylene

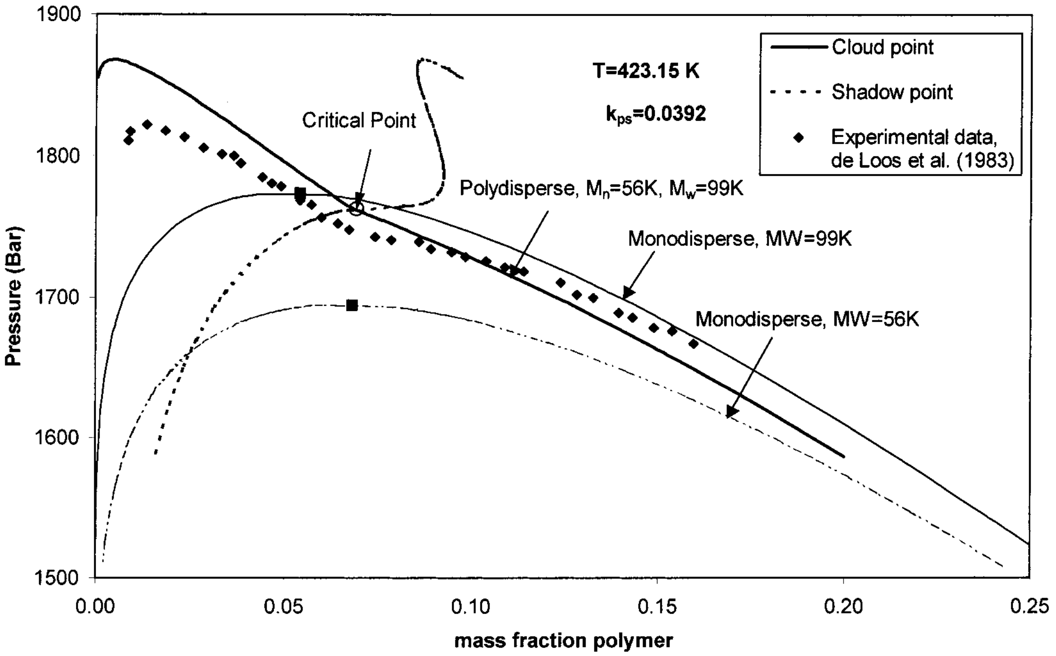
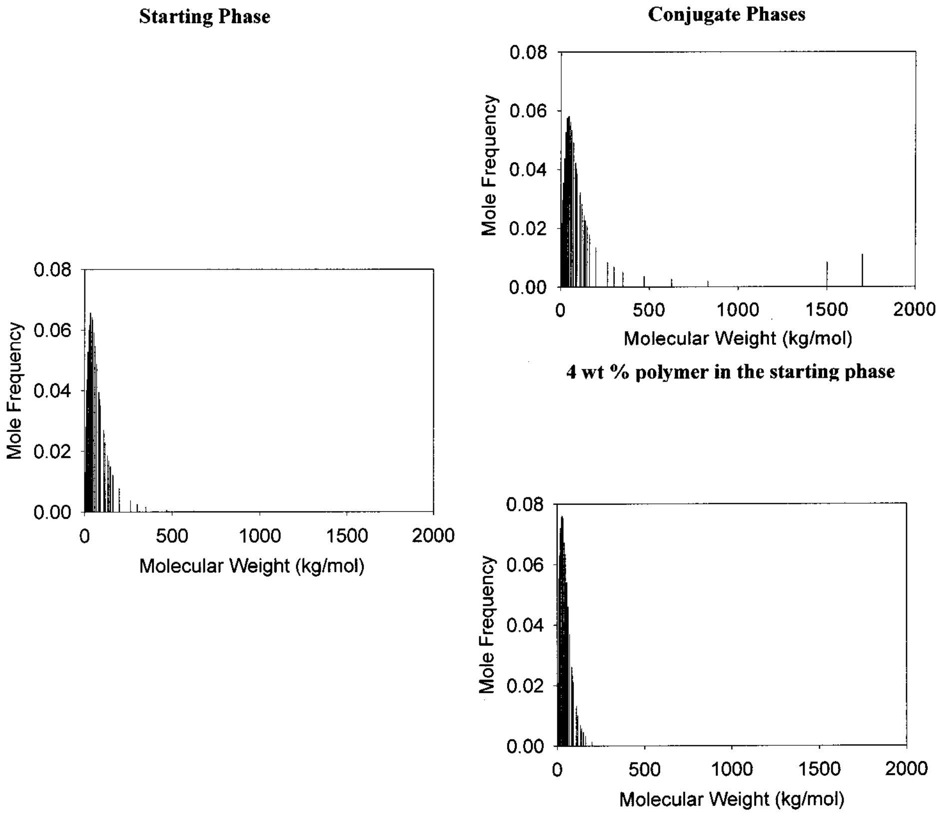


Figure 3. Isothermal pressure–composition section for PE + ethylene system.



4 wt % polymer in the starting phase

10 wt % polymer in the starting phase

Figure 4. Molecular weight distributions of the starting phase and the conjugate phases for two different polymer concentrations in the starting phase.

parameters are from Huang and Radosz[31] (see Table 1). The segment volume parameter for polyethylene is from Huang and Radosz, but the chain length parameter (m) and the dispersion energy parameter (u^0/k) are refitted by Koak et al.[37]

Figure 3 shows the cloud point curve and shadow point curve for the polyethylene + ethylene system at 150 °C. The binary interaction parameter between the polymer components (p) and ethylene (s, stands for solvent) is $k_{ps} = 0.0392$. The binary interaction parameter between the polymer components is $k_{pp} = 0.0$. We observe for this system the following points:

1. The cloud point curve is different from that of the monodisperse polymers with number average and weight average molecular weights. In monodisperse cases the critical point is at the maximum in the pressure. For polydisperse polymer solutions, the critical point is not at the maximum in the cloud point pressure but is

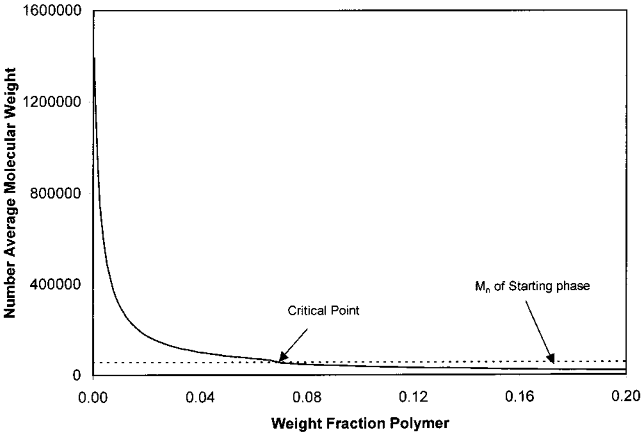


Figure 5. Plot of the number average molecular weight of the conjugate phase versus weight fraction of polymer in the starting phase.

shifted to higher polymer concentration. Hence, unlike the monodisperse case, the cloud point curve continues to higher pressures below the critical concentration. This is explained qualitatively in section 1 and in Figure 1.

2. The cloud point curve has a bend at the critical point. The critical point in Figure 3 is seen to be around 7 wt % polymer.

3. The shadow point curve gives the overall polymer mass fraction in the second phase that is formed at the cloud point (conjugate phase). However, the molecular weight distribution of the conjugate phase is different from that of the starting phase (principal phase).

Figure 4 shows the molecular weight distribution of the conjugate phase at two different polymer concentrations (of the starting phase) for the same molecular weight distribution of the principal phase. At a polymer concentration of 10 wt % in the starting phase, which is higher than the critical polymer concentration, low molecular weight polymer components are preferentially extracted into the conjugate phase which is polymer lean. At a polymer concentration of 4 wt % in the starting phase which is lower than the critical polymer concentration, the high molecular weight components of the polymer are extracted into the conjugate phase which is polymer rich. The number average molecular weight of the conjugate phase decreases with increasing polymer concentration (Figure 5) showing that at lower concentrations high molecular weight fractions are preferentially extracted in the conjugate phase.

It can be seen from Figure 3 that the SAFT predictions for polydisperse polyethylene are in close agreement with the experimental data of de Loos et al.[38] The effect is especially significant at lower polymer concentrations. The continued increase in cloud point pressure up to very low polymer concentrations (lower than the critical points of the two monodisperse curves) are very well predicted by the polydisperse calculations.

5. Generalization of the Algorithm

The algorithm to calculate phase equilibria in polydisperse polymer solutions was based on the assumptions about the segment volume, chain length, and dispersion energy parameters of the polymer pseudocomponents stated in section 2.1. In this section, we present the generalization of the algorithm when assumptions 2 and 5 in section 2.1 are relaxed. So now we have pseudocomponents with the same segment volume (v^{00}), chain length (m) directly proportional to molecular weight, the binary interaction parameter between the pseudocomponents is zero. However, we allow the pseudocomponents to have different dispersion energy parameters (u^0/k) and different binary interaction parameters (k_{ij}) with the solvents. This kind of situation can be important when a polydisperse polymer sample is discretized and some small molecular weight components appear as a result of discretization. Another situation is a polydisperse mixture of relatively low molecular weight components in a homologous series such as alkanes or polynuclear aromatics which can be important in phase equilibrium calculations in the petroleum industry. Since the segment volume (v^{00}) does not vary much with chain length and remains constant for long chains, the assumption of same segment volume is not very restrictive. However at short chain lengths, the dispersion energy parameter and the binary interaction parameter depend on the molecular weight.[31,39]

Since u^0/k and k_{ij} affect only the dispersion term we need to reconsider only the dispersion term. Consider eq 2.2.22 for u/kT. The denominator is unaffected by the assumption about dispersion energy parameter. The numerator becomes

$$\sum_{i=1}^{p+s}\sum_{j=1}^{p+s} x_i x_j m_i m_j (u_{ij}/kT) v_{ij}^0 = v_p^0 \Big(\sum_{i=1}^{p} x_i m_i \sqrt{u_{ii}/kT}\Big)^2 + 2\sum_{j\to \mathrm{solv}} x_j m_j \sqrt{u_{jj}/kT}\, v_{pj}^0 \Big(\sum_{i=1}^{p} x_i m_i \sqrt{u_{ii}/kT}(1-k_{ij})\Big) + \sum_{i\to \mathrm{solv}}\sum_{j\to \mathrm{solv}} x_i m_i x_j m_j (u_{ij}/kT) v_{ij}^0 \tag{5.1}$$

Define an average dispersion energy parameter for the polymer

$$\frac{\bar{u}_p}{kT} = \left[\frac{\sum_{i=1}^{p} x_i m_i \sqrt{u_{ii}/kT}}{\sum_{i=1}^{p} x_i m_i}\right]^2 \tag{5.2}$$

Also, define an average binary interaction parameter between the polymers and a solvent j by

$$\bar{k}_{pj} = \frac{\sum_{i=1}^{p} (x_i m_i \sqrt{u_{ii}/kT}) k_{ij}}{\sum_{i=1}^{p} x_i m_i \sqrt{u_{ii}/kT}} \tag{5.3}$$

$$\bar{u}_{pj}/kT = \sqrt{\bar{u}_p/kT}\,\sqrt{u_{jj}/kT}(1-\bar{k}_{pj}) \tag{5.4}$$

Thus

$$\frac{u}{kT} = [(\bar{u}_p/kT) v_p^0 (x_p m(\bar{M}_\mathrm{n}))^2 + 2x_p m(\bar{M}_\mathrm{n}) \sum_{j\to \mathrm{solv}} x_j m_j (\bar{u}_{pj}/kT) v_{pj}^0 + \sum_{i\to \mathrm{solv}}\sum_{j\to \mathrm{solv}} x_i x_j m_i m_j (u_{ij}/kT) v_{ij}^0]/[v_p^0 (x_p m_p(\bar{M}_\mathrm{n}))^2 + 2x_p m(\bar{M}_\mathrm{n}) \sum_{j\to \mathrm{solv}} x_j m_j v_{pj}^0 + \sum_{i\to \mathrm{solv}}\sum_{j\to \mathrm{solv}} x_i x_j m_i m_j v_{ij}^0] \tag{5.5}$$

Thus, the polymer can be lumped with effective dispersion energy and binary interaction parameters which depend on the molecular weight distribution. Now let us look at the dispersion contribution to chemical potential

$$\frac{\mu_k^{\mathrm{disp}}}{kT} = m_k\left\{\sum_i\sum_j D_{ij}\left[\frac{u}{kT}\right]^i\left[\frac{\zeta_3}{\tau}\right]^j + 2mA_k\sum_i\sum_j D_{ij}i\left[\frac{u}{kT}\right]^{i-1}\left[\frac{\zeta_3}{\tau}\right]^j + m\rho(\pi/6){d_{kk}}^3\sum_i\sum_j j\left[\frac{u}{kT}\right]^i\left[\frac{{\zeta_3}^{j-1}}{\tau^j}\right]\right\} \quad (5.6)$$

where A_k is now given by

$$A_k = [\sqrt{u_{kk}/kT}(x_p m_p(\bar{M}_{\mathrm{n}})v^0_{kp}\sqrt{\bar{u}_p/kT}(1-\bar{k}_{pk}) + \sum_{r\to\mathrm{solv}} x_r m_r\sqrt{u_{rr}/kT}(1-k_{kr})v^0_{kr}) - (u/kT)(v^0_{kp}x_p m(\bar{M}_{\mathrm{n}}) + \sum_{r\to\mathrm{solv}} x_r m_r v^0_{kr})]/[v^0_p(x_p m(\bar{M}_{\mathrm{n}}))^2 + 2x_p m(\bar{M}_{\mathrm{n}})\sum_{j\to\mathrm{solv}} x_j m_j v^0_{pj} + \sum_{i\to\mathrm{solv}}\sum_{j\to\mathrm{solv}} x_i x_j m_i m_j v^0_{ij}] \quad (5.7)$$

From eq 2.2.24 we observe that

$$Z^{\mathrm{disp}} = Z^{\mathrm{disp}}(T, \rho, x_p, \bar{M}_{\mathrm{n}}, \bar{u}_p/kT, \{\bar{k}_{ps}\}, \{x_s\}) \quad (5.8)$$

Equations 2.2.30 and 5.8 show that

$$Z = Z(T, \rho, x_p, \bar{M}_{\mathrm{n}}, \bar{u}_p/kT, \{\bar{k}_{ps}\}, \{x_s\}) \quad (5.9)$$

Equations 5.6 and 5.7 show that for a polymer

$$\frac{\mu_k^{\mathrm{disp}}}{kT} = M_k\mu_{\mathrm{M}}(T,\rho,x_p,\bar{M}_{\mathrm{n}},\bar{u}_p/kT,\{\bar{k}_{ps}\},\{x_s\}) + M_k\sqrt{u_{kk}/kT}\mu_{\mathrm{MU}}(T,\rho,x_p,\bar{M}_{\mathrm{n}},\bar{u}_p/kT,\{\bar{k}_{ps}\},\{x_s\}) + \sum_{r\to\mathrm{solv}} M_k\sqrt{u_{kk}/kT}k_{kr}\mu_r(T,\rho,x_p,\bar{M}_{\mathrm{n}},\bar{u}_p/kT,\{\bar{k}_{ps}\},\{x_s\}) \quad (5.10)$$

Note that the functions $\mu_{\mathrm{M}},\mu_{\mathrm{MU}},\mu_r|_{r\to\mathrm{solv}}$ are the same for all the polymer components.

For the solvent

$$\frac{\mu_s^{\mathrm{disp}}}{kT} = \mu_{\mathrm{S,disp}}(T,\rho,x_p,\bar{M}_{\mathrm{n}},\bar{u}_p/kT,\{\bar{k}_{ps}\},\{x_s\}) \quad (5.11)$$

Note that the hard sphere and chain contributions are the same as before. From eq 5.10, we can generalize eq 3.4 to

$$\ln(K_p) = K_0 + M_pK_{\mathrm{M}} + M_p\sqrt{u_{pp}/kT}K_{\mathrm{MU}} + \sum_{r\to\mathrm{solv}} M_p\sqrt{u_{pp}/kT}k_{pr}K_r \quad (5.12)$$

Note that the upper case K denotes the partition coefficient (k-factor) and the lower case k is the binary interaction parameter. Subsequently, we generalize eqs 3.5 and 3.6 to give

$$K_0 = \ln(\rho_\alpha/\rho_\beta) + \mu^\alpha_{\mathrm{A}}(T,\rho_\alpha,x^\alpha_p,\{x^\alpha_s\},\bar{M}^\alpha_{\mathrm{n}}) - \mu^\beta_{\mathrm{A}}(T,\rho_\beta,x^\beta_p,\{x^\beta_s\},\bar{M}^\beta_{\mathrm{n}}) \quad (5.13)$$

$$K_{\mathrm{M}} = \mu^\alpha_{\mathrm{M}}(T, \rho_\alpha, x^\alpha_p, \{x^\alpha_s\}, \bar{u}^\alpha_p/kT, \{\bar{k}^\alpha_{ps}\}, \bar{M}^\alpha_{\mathrm{n}}) - \mu^\beta_{\mathrm{M}}(T, \rho_\beta, x^\beta_p, \{x^\beta_s\}, \bar{u}^\beta_p/kT, \{\bar{k}^\beta_{ps}\}, \bar{M}^\beta_{\mathrm{n}}) \quad (5.14)$$

$$K_{\mathrm{MU}} = \mu^\alpha_{\mathrm{MU}}(T, \rho_\alpha, x^\alpha_p, \{x^\alpha_s\}, \bar{u}^\alpha_p/kT, \{\bar{k}^\alpha_{ps}\}, \bar{M}^\alpha_{\mathrm{n}}) - \mu^\beta_{\mathrm{MU}}(T, \rho_\beta, x^\beta_p, \{x^\beta_s\}, \bar{u}^\beta_p/kT, \{\bar{k}^\beta_{ps}\}, \bar{M}^\beta_{\mathrm{n}}) \quad (5.15)$$

$$K_r = \mu^\alpha_r(T, \rho_\alpha, x^\alpha_p, \{x^\alpha_s\}, \bar{u}^\alpha_p/kT, \{\bar{k}^\alpha_{ps}\}, \bar{M}^\alpha_{\mathrm{n}}) - \mu^\beta_r(T, \rho_\beta, x^\beta_p, \{x^\beta_s\}, \bar{u}^\beta_p/kT, \{\bar{k}^\beta_{ps}\}, \bar{M}^\beta_{\mathrm{n}})r = 1, 2, ..., S \quad (5.16)$$

Note that $\bar{u}^\alpha_p/kT$, $\{\bar{k}_{ps}\}$, $\bar{M}_{\mathrm{n}}$ for the starting phase are known and those for the second phase can be calculated from the polymer compositions of the second phase (eqs 2.2.5, 5.3, and 5.4) which can be determined from the K values. The key to the reduction is that K_0, K_{M}, K_{MU}, K_r are same for all the polymer components in a given mixture. Thus the equations representing the equality of chemical potentials of polymers are reduced to $3 + s$ equations. The total number of equilibrium equations (including an equation for pressure and equations for solvent chemical potentials) is $4 + 2s$. As explained in section 3, we have to include $s + 1$ constraint equations for a cloud point pressure or a cloud point temperature calculation. Thus, the total number of equations is $5 + 3s$. With these modifications the algorithmic procedure is similar to that demonstrated in Figure 2.

6. Conclusion

In this work, we developed an algorithm to calculate phase equilibria in polydisperse polymer solutions. The algorithm effectively accumulates the pseudocomponents so that the computation time is independent of the number of pseudocomponents. This approach can be very useful in modeling the phase behavior of polymer solutions since polymers are inherently polydisperse. In another work, Jog et al.[40] used this algorithm to calculate the cloud point pressure of polyethylene in hexane. A comparison with the experimental data showed that polydispersity of the polymer accounts for the behavior of the cloud point at low polymer concentrations. At higher polymer concentrations, the results were close to the monodisperse calculations. In this work, the algorithm was used to calculate phase equilibria in solutions of polydisperse polyethylene in ethylene. The critical point is no longer at the maximum in pressure but is rather shifted to higher composition. We also calculated the molecular weight distributions in the conjugate phases. Since the properties of polymers are affected by the molecular weight distribution, the differences in molecular weight distributions in coexisting phases can be important. For example low-density polyethylene (LDPE) produced in a two-phase system exhibits superior film properties because of narrower molecular weight distribution and fewer long chain branches.[41] For polydisperse polymer calculations, the discrete molecular weight distribution of the polymer can be obtained by discretizing the continuous molecular weight distributions. In a process simulator, the type of molecular weight distribution is determined by the kinetics and type of polymerization reaction used to produce the polymer. The algorithm presented here can then be used to calculate phase equilibria. Extension of this algorithm to polar polymers[42,43] and copolymers will be the subject of future work.

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