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Continuous Thermodynamics of Polymer Solutions: The Effect of Polydispersity on the Liquid-Liquid Equilibrium

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ABSTRACT

Owing to their very large number, the composition of polymers is usually described by continuous distribution functions. A version of thermodynamics–called continuous thermodynamics–is established which is based directly on a continuous distribution function instead of the mole fractions, weight fractions, etc. of individual components or pseudocomponents. This continuous thermodynamics is applicable to all complex multicomponent systems such as petroleum, coal-derived liquids, tars, and polymers. Continuous thermodynamics is used in this paper for treating the influence of polymer polydispersity on the liquid-liquid equilibrium of polymer solutions. From a practical point of view, the main advantages of continuous thermodynamics in comparison with the pseudocomponent method are fewer convergence problems and a drastic reduction of computer time.

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INTRODUCTION

The composition of synthetic polymers is usually characterized by a continuous distribution function of the molar mass M. Thermodynamics is used to consider phase separation. However, thermodynamics is based on individual components. If we split the continuous distribution into the true polymer species, a number of components much too large for the numerical management of the thermodynamic equations is obtained. Thus, for thermodynamic treatment, the continuous distribution is usually split into an arbitrarily chosen number of pseudocomponents.

This method is shown in Fig. 1. The real polymer species are represented by many small bars. The area of each bar indicates the amount of the corresponding polymer species. The upper ends of the bars form the real discontinuous distribution function $W_{dis}(M)$. The smoothed approximation of $W_{dis}(M)$ shown in the left-hand side of

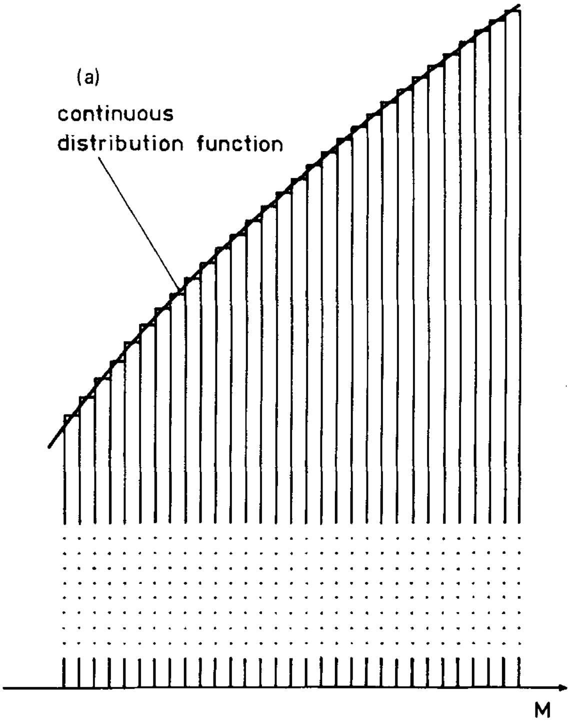

FIG. 1. True polymer species: Continuous distribution function (a) and pseudocomponent approach (b).

the figure is the continuous distribution function $W_{cont}(M)$ which may be determined experimentally by fractionation or gel permeation chromatography. The pseudocomponent approach shown in the right-hand side of the figure consists of uniting a number of neighboring polymer species to a pseudocomponent. The corresponding distribution is represented by a small number of broad bars and, thus, the function $W_{pseud}(M)$ exhibits relatively large deviations from the real discontinuous distribution function $W_{dis}(M)$. Therefore, the pseudocomponent approach is a relatively crude method.

Thus, it is desirable to use the continuous distribution function directly—without splitting into pseudocomponents—as the basis for thermodynamic treatment. Suggestions for applying a continuous description within the framework of thermodynamics were published by three groups of authors. The first group used continuous distribu-

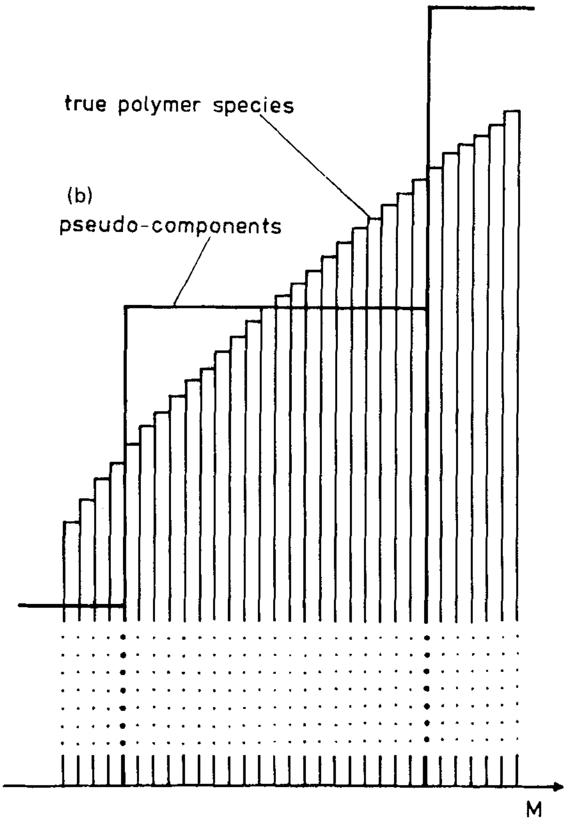

FIG. 1 (continued)

tion functions mainly for treating problems of statistical mechanics and nonequilibrium thermodynamics. Thus, Onsager [1] described the orientational distribution of liquid crystals by a continuous function. Prigogine and Mazur [2] applied a continuous description for treating internal degrees of freedom. Vrij [3] and Blum and Stell [4] discussed scattering phenomena on this basis. Gal-Or et al. [5] suggested the use of the moments of a distribution as independent thermodynamic variables. Dickinson [6] applied a continuous description within conformal solution theory. The second group of authors (e.g., Katz and Brown [7], Bowman [8], Edmister [9], Hoffman [10, 11], Aris and Gavalas [12], Roth [13], Koningsveld and Staverman [14], and Solc [15]) introduced a continuous description in considering phase equilibria for multicomponent systems. The authors of this group restricted themselves to specific cases (e.g., Raoult's law) and did not consider the general fundamentals of the problems. However, by applying a continuous distribution function instead of mole fractions, etc. of individual components, it is possible to establish a consistent version of the total building of thermodynamics as presented by the third group of authors (Kehlen and Rätzsch [16], Salacuse and Stell [17], Gualtieri et al. [18], Briano and Glandt [19]). This building is called "continuous thermodynamics." It permits a concise treatment of all complex multicomponent systems.

In this paper, continuous thermodynamics is applied to the liquid-liquid equilibrium of polydisperse polymer solutions. To illustrate, the phase separation in an ethylene + polyethylene mixture is calculated.

THERMODYNAMIC BACKGROUND

We consider a solution of solvent A and polymer B. The composition of the polymer is described by the distribution function W(M). This function is defined in such a way that W(M) dM gives the segment fraction of all polymer species with molar masses between M and M + dM divided by the total segment fraction ψ of all polymer species.

In traditional thermodynamics, the condition for equilibrium between two phases ' and " may be expressed by the chemical potentials

$$\begin{aligned} \mu_A' &= \mu_A'' \\ \mu_{B_i}' &= \mu_{B_i}''; \qquad i = 1, \ldots, \omega \end{aligned} \tag{1}$$

where 1, . . . , ω indicates the different discrete polymer species. In continuous thermodynamics, instead of Eq. (1) we obtain

$$\mu_A' = \mu_A'' \qquad (2)$$
$$\mu_B'(M) = \mu_B''(M); \qquad M_O \le M \le M^O$$

Here the phase equilibrium condition for the polymer holds for all continuous polymer species within the molar mass interval occurring from M_O up to M^O. Instead of the discrete index i, the continuous characterization variable M occurs.

In traditional thermodynamics, the chemical potentials may be written as follows:

$$\mu_A = \mu_A{}^*(T,P) + RT\left[\ln(1-\psi) + 1 - \frac{r_A}{\bar{r}}\right] + r_A\,RT\ln\bar{\bar{\gamma}}_A \qquad (3)$$

$$\mu_{B_i} = \mu_{B_i}{}^*(T,P) + RT\left[\ln\psi_{B_i} + 1 - \frac{r_{B_i}}{\bar{r}}\right] + r_{R_i}\,RT\ln\bar{\bar{\gamma}}_{B_i} \qquad (4)$$

The first term is the chemical potential of the pure species, the second term is the well-known Flory-Huggins contribution, and the last term describes the deviation from a Flory-Huggins mixture. The quantities $\bar{\bar{\gamma}}_A$ and $\bar{\bar{\gamma}}_{B_i}$, named segment molar activity coefficients, are introduced for this reason. The symbols r_A and r_{B_i} are the segment numbers of the species indicated, $\bar{r}$ is the corresponding mean value for the phase considered, and ψ_{B_i} is the segment fraction for the polymer species B_i. In the continuous case, instead of Eq. (4) we write

$$\mu_B(M) = \mu_{B,O}{}^*(M,\ T,\ P) + RT\left[\ln\psi W(M) + 1 - \frac{r_B(M)}{\bar{r}}\right]$$
$$+\ r_B(M)RT\ln\bar{\bar{\gamma}}_B(M) \qquad (5)$$

The mean $\bar{r}$ may be calculated by

$$\frac{1}{\bar{r}} = \frac{(1-\psi)}{r_A} + \frac{\psi}{\bar{r}_B}; \qquad \frac{1}{\bar{r}_B} = \int_{M_O}^{M^O} \frac{W(M)}{r_B(M)}\,dM \qquad (6)$$

Introducing Eqs. (3) and (5) into Eq. (2), we obtain, after rearranging,

$$1 - \psi'' = (1 - \psi') \exp (\rho_A' - \rho_A'') \tag{7}$$

$$W''(M) = \frac{\psi'}{\psi''} W'(M) \exp \left[\frac{M}{M_S} (\rho_B' - \rho_B'')\right] \tag{8}$$

The first equation results from the phase equilibrium condition for solvent A and is an equation for a scalar quantity (e.g., T, P, ψ', ψ''). The second equation results from the phase equilibrium condition for polymer B. Thus, it is valid for all M values within the molar mass interval occurring and permits the calculation of an unknown distribution function (e.g., W''(M) if W'(M) is known). The abbreviations ρ_A and ρ_B are given by

$$\left.\begin{aligned} \rho_A^{\alpha} &= \psi^{\alpha} \left(1 - \frac{M_S}{\overline{M}_B^{\alpha}}\right) + r_A \ln \bar{\bar{\gamma}}_A \qquad (9) \\ \rho_B^{\alpha} &= \psi^{\alpha} \left(1 - \frac{M_S}{\overline{M}_B^{\alpha}}\right) + r_A \ln \bar{\bar{\gamma}}_B \qquad (10) \end{aligned}\right\} \quad \alpha = {}', {}''$$

Here we use $r_B(M)/r_A = M/M_S$ where M_S is the molar mass of one polymer segment and $\overline{M}_B^{\alpha}$ is the mean value of the molar mass of the polymer in phase α.

The segment molar activity coefficients $\bar{\bar{\gamma}}_A$ and $\bar{\bar{\gamma}}_B$ may be calculated according to the well-known model theories based on statistical mechanics such as Huggins' χ-parameter concept, the UNIFAC model, or the Flory-Orwoll-Vrij theory. As long as we treat polymers and not oligomers, $\bar{\bar{\gamma}}_A$ and $\bar{\bar{\gamma}}_B$ may be assumed to be independent of W(M) and, furthermore, $\bar{\bar{\gamma}}_B$ and ρ_B may be considered to be independent of M. The reason is that endgroup effects may be neglected in this case. Thus, we have $\bar{\bar{\gamma}}_A = \bar{\bar{\gamma}}_A(T,P,\psi)$; $\bar{\bar{\gamma}}_B = \bar{\bar{\gamma}}_B(T,P,\psi)$. According to Huggins' χ-parameter concept, in the simplest case we obtain

$$r_A \ln \bar{\bar{\gamma}}_A = \chi\psi^2; \qquad r_A \ln \bar{\bar{\gamma}}_B = \chi(1 - \psi)^2; \qquad \chi = \chi(T,P) \tag{11}$$

CLOUD-POINT CURVE AND SHADOW CURVE

We assume the composition of phase ' (i.e., ψ' and $W'(M)$) and the pressure P to be specified. Thus, we wish to calculate the composition of the coexisting phase " (i.e., ψ'' and $W''(M)$) and the equilibrium temperature T. This corresponds to the problem of the cloud-point curve and the shadow curve.

The distribution function $W''(M)$ is immediately given by Eq. (8). In this relation, three unknown scalar quantities occur: ψ'', $\overline{M}_B''$, and T. Thus, we need three scalar equations. One of them is given by Eq. (7). The two others result from the normalization condition for $W''(M)$ and from the definition of $\overline{M}_B''$ (compare Eq. 6). Applying Eq. (8), these equations read

$$1 = \int_{M_O}^{M^O} \frac{\psi'}{\psi''} W'(M) \exp\left[\frac{M}{M_S}(\rho_B' - \rho_B'')\right] dM \tag{12}$$

$$\frac{1}{\overline{M}_B''} = \int_{M_O}^{M^O} \frac{1}{M} \frac{\psi'}{\psi''} W'(M) \exp\left[\frac{M}{M_S}(\rho_B' - \rho_B'')\right] dM \tag{13}$$

The solution of this system of three equations leads to the cloud-point curve $T(\psi')$ and to the shadow curve $T(\psi'')$. In performing the calculation, $\overline{M}_B''$ may be eliminated according to Eqs. (7) and (9).

The integrals in Eqs. (12) and (13) are usually calculated numerically. However, if $W'(M)$ is a Schulz-Flory distribution ($M_O = 0$, $M^O = \infty$),

$$W'(M) = \frac{k^{k+1}}{\overline{M}_B' \, \Gamma(k+1)} \left(\frac{M}{\overline{M}_B'}\right)^k \exp\left(-k\frac{M}{\overline{M}_B'}\right) \tag{14}$$

any integrations occurring may be performed analytically. The parameters in Eq. (14) are k and the mean value $\overline{M}_B'$ of the molar mass in phase '. Under the presumption $\overline{M}_B'(\rho_B' - \rho_B'')/(M_S k) < 1$, we obtain from Eqs. (12) and (13)

$$\psi'' = \frac{\psi'}{\left(1 - \frac{\overline{M}_B'}{M_S}\,\frac{\rho_B' - \rho_B''}{k}\right)^{k+1}}\,; \qquad \frac{\psi''}{\overline{M}_B} = \frac{\psi'/\overline{M}_B'}{\left(1 - \frac{\overline{M}_B'}{M_S}\,\frac{\rho_B' - \rho_B''}{k}\right)^{k}} \tag{15}$$

resulting in

$$\frac{\psi''}{(\overline{M}_B'')^{k+1}} = \frac{\psi'}{(\overline{M}_B')^{k+1}} \tag{16}$$

This symmetric equation does not depend on the real behavior of the coexisting phases but only on the presumption of a Schulz-Flory distribution. According to the symmetric relation (16), the distribution function W''(M) in the phase '' is also a Schulz-Flory distribution. It is characterized by the same value of k and by the mean value $\overline{M}_B''$ which may be calculated from $\overline{M}_B'$ by Eq. (16).

Similarly, analytic integrability is found if W'(M) is a linear combination of some Schulz-Flory distributions.

COEXISTENCE CURVES

A feed phase F splits into two coexisting phases ' and ''. In this case, the material balances also have to be accounted for. If ϕ is the total amount of segments in phase '' divided by the total amount of segments in the feed, the mass balance for the polymer species in continuous thermodynamics is

$$\psi^F W^F(M) = (1 - \phi)\,\psi' W'(M) + \phi\,\psi'' W''(M) \tag{17}$$

By dividing by M and integration, we obtain

$$\psi^F = (1 - \phi)\,\psi' + \phi\,\psi'' \tag{18}$$

$$\frac{\psi^F}{\overline{M}_B^F} = (1 - \phi)\,\frac{\psi'}{\overline{M}_B'} + \phi\,\frac{\psi''}{\overline{M}_B''} \tag{19}$$

In addition to the composition of the feed (i.e., ψ^F and $W^F(M)$), we assume T and P (or P and ϕ or T and ϕ) to be specified. The other variables are the unknowns. Applying Eqs. (17)-(19), the quantities referring to phase ' may be eliminated. Thus, the problem reduces to calculation of the unknown distribution function W''(M) and the unknown scalars ψ'', $\overline{M}_B''$, and ϕ (or T or P). By combining Eqs. (8) and (17) we obtain

$$W''(M) = \frac{\psi^F W^F(M)}{\psi'' \left\{ \phi + (1 - \phi) \exp\left[-\frac{M}{M_S} (\rho_B' - \rho_B'') \right] \right\}} \tag{20}$$

This relation permits the calculation of the unknown distribution function if we know the scalar unknowns. These may be calculated from

$$1 - \psi'' = \frac{1 - \psi^F}{\phi + (1 - \phi) \exp\left[-(\rho_A' - \rho_A'') \right]} \tag{21}$$

$$1 = \int_{M_O}^{M^O} \frac{\psi^F W^F(M)}{\psi'' \left\{ \phi + (1 - \phi) \exp\left[-\frac{M}{M_S} (\rho_B' - \rho_B'') \right] \right\}} \, dM \tag{22}$$

$$\frac{1}{\overline{M}_B''} = \int_{M_O}^{M^O} \frac{1}{M} \frac{\psi^F W^F(M)}{\psi'' \left\{ \phi + (1 - \phi) \exp\left[-\frac{M}{M_S} (\rho_B' - \rho_B'') \right] \right\}} \, dM \tag{23}$$

Relations (21)-(23) result from Eqs. (7), (18), (19), and (20) by applying arguments similar to those leading to Eqs. (12) and (13). The quantities referring to phase ' may easily be calculated from Eqs. (17)-(19) or by applying the equations for phase ' which are analogous to Eqs. (20)-(23).

EXAMPLE

As an example, consider a solution of polydisperse polyethylene wax in supercritical ethylene for different pressures at a temperature of 403.15 K. The model theory by Flory, Orwoll, and Vrij [20]

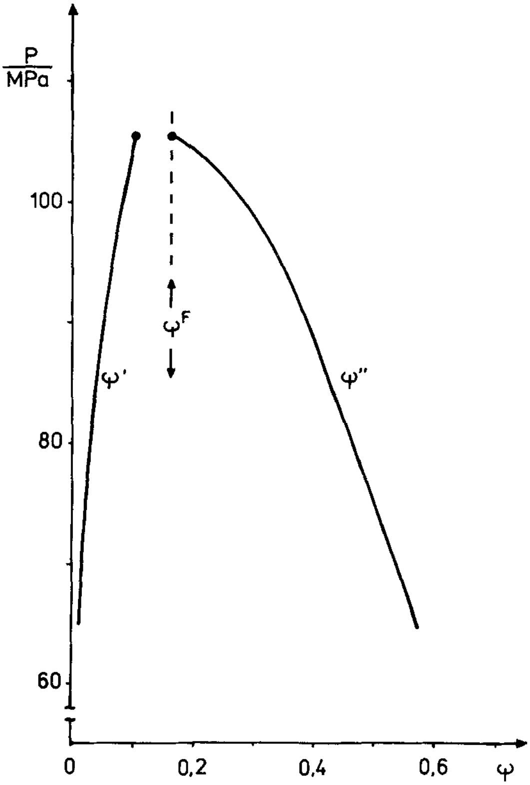

FIG. 2. Coexistence curve in the system ethylene + polyethylene at T = 403.15 K for $\psi^F = 0.168$.

is used to calculate $\bar{\bar{\gamma}}_A$ and $\bar{\bar{\gamma}}_B$. The parameter X_{AB} may be fitted to some experimental cloud-point curve data, leading to $X_{AB} = -8.61$ MPa. The polyethylene wax can be characterized by a Wesslau distribution

$$W^F(M) = \frac{1}{\beta\sqrt{\pi}\,M} \exp\left[-\left(\frac{\ln M - \ln M^*}{\beta}\right)^2\right] \tag{24}$$

where $M^* = 3880$ g/mol and $\beta = 1.362$. The calculated coexistence curves for a feed composition $\psi^F = 0.168$ are shown in Fig. 2. The corresponding means of the molar mass and the ϕ-values can be seen from Fig. 3. Finally, Fig. 4 gives the distribution functions for phase separation at 70.91 MPa.

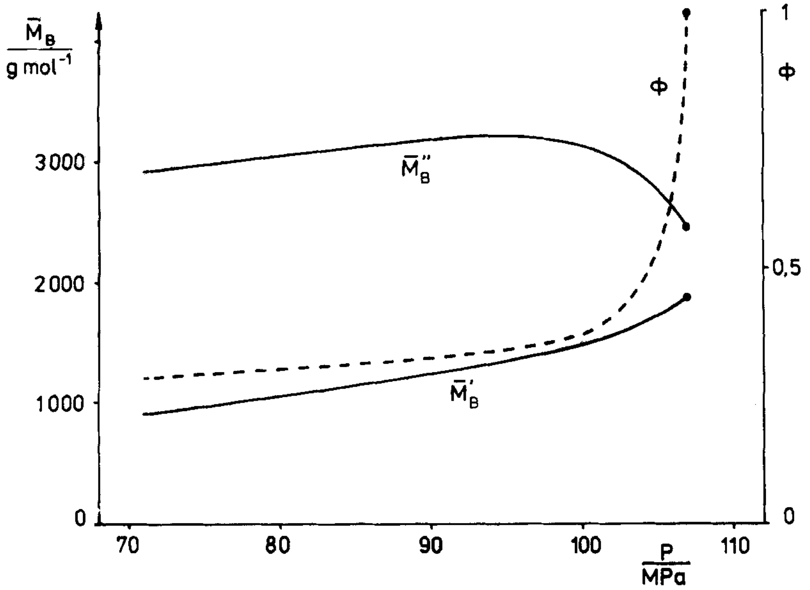

FIG. 3. Mean values of the molar mass $\overline{M}_B$ in the coexisting phases and amount ϕ of the polymer-rich phase in the system ethylene + polyethylene at T = 403.15 K for $\psi^F = 0.168$.

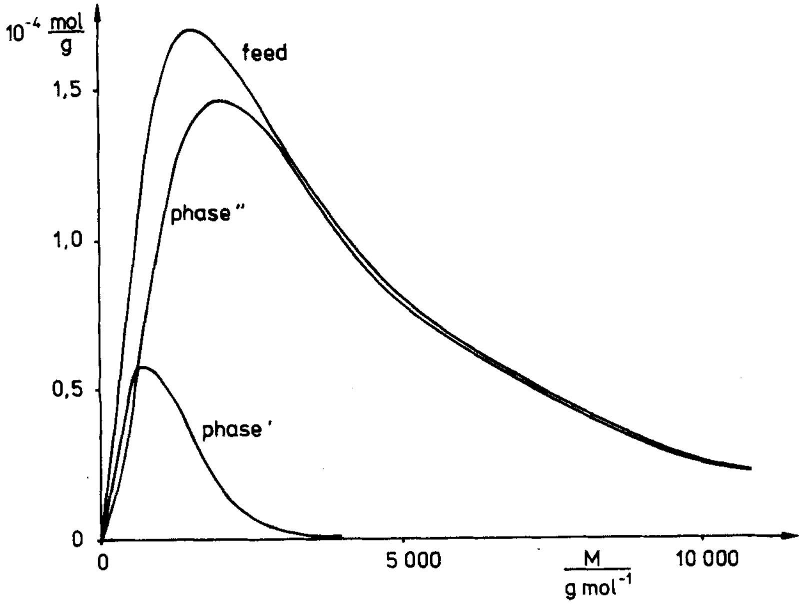

FIG. 4. Mass distribution functions in the system ethylene + polyethylene at T = 403.15 K for $\psi^F = 0.168$ and P = 70.91 MPa. To demonstrate the mass balance, the products $\psi^F W^F(M)$, $(1 - \phi)\psi' W'(M)$, and $\phi\psi'' W''(M)$ are plotted.

In comparison to the usual pseudocomponent approach, calculations on the basis of continuous thermodynamics require only 10 to 20% of the usual computer time. Furthermore, fewer convergence difficulties occur if continuous thermodynamics is applied.

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