Application of continuous thermodynamics to polymer fractionation

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Abstract - Continuous thermodynamics has been recently developed and applied to the liquid-liquid equilibrium of polydispersed polymer solutions. It uses the continuous distribution function directly in the thermodynamic equations to achieve a concise and convenient treatment of polydispersed systems. This paper presents the application of continuous thermodynamics to successive polymer fractionation procedures based on solubility differences. The method is then applied to describe Baker-Williams column fractionation. Lastly, it is used to model continuous polymer fractionation that splits the polymer into two fractions that can be fractionated again.

INTRODUCTION

Fractionation is one of the most important procedures of polymer characterization. From the thermodynamic point of view, it is the successive establishing of liquid-liquid equilibria for suitable polymer solutions. Schulz (refs. 1,2) was the first to present a mathematical treatment of successive fractionation experiments. Later Tung (ref. 3), Koningsveld and Staverman (ref. 4), Kamide et al. (refs. 5-8) simulated a number of successive fractionation processes. In all these papers, pseudocomponents were used to describe polymer polydispersity. In recent years, continuous thermodynamics has been developed (refs. 9,10) and has proved to be the most convenient method for treating the polydispersity of many industrially important mixtures. It has been applied to vapor-liquid equilibrium, especially of complex hydrocarbon systems (refs. 11-13), to liquid-liquid equilibrium, especially of polymer solutions (refs. 14-16) and of polymer blends (ref. 17), and to stability considerations (refs. 18,19). In continuous thermodynamics, the distribution functions describing polydispersity are directly used without arbitrary splitting into pseudocomponents. In this paper, continuous thermodynamics is applied to successive polymer fractionation, Baker-Williams column fractionation, and continuous polymer fractionation.

LIQUID–LIQUID EQUILIBRIUM

A solution of a solvent A and a polydispersed polymer B is considered. The individual species of polymer B are identified by their segment number, r, which is defined as the ratio of the hard-core volume of the species to that of an arbitrarily chosen standard segment. The essence of continuous thermodynamics consists in considering r as a continuously variable quantity. The composition of the polymer is described by the distribution function W(r), defined by the statement that W(r)dr gives the fraction of all segments from those species with segment numbers between r and r + dr. If r₀ is the lowest r₀ the highest occurring segment number, the normalization condition reads

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In continuous thermodynamics the condition for equilibrium between two phases  and  as expressed by the chemical potentials is written

\[ \mu_A' = \mu_A'' \]

\[ \mu_B'(r) = \mu_B''(r) \]

Eq. (3) is valid for all segment numbers from  to  . The chemical potentials may be written as follows

\[ \mu_A = \mu_A^*(T) + RT \left[ \ln (1 - \psi) + 1 - \frac{r}{r_A} \right] + r_A \ln \frac{A}{r} \]

\[ \mu_B(r) = \mu_B^*(r,T) + RT \left[ \ln \psi \frac{W(r)}{r} + 1 - \frac{r}{r_B} \right] + r \ln \frac{B(r)}{r} \]

The first term is the reference chemical potential, the second term is the well-known Flory-Huggins contribution (with  = 0), and the last term describes the deviation from such a Flory-Huggins mixture. The quantities  and  (r), named segment molar activity coefficients, are introduced for this purpose, and in the general case they depend on  ,  , and  .  is the number-average segment number for the phase considered, defined by

\[ \frac{1}{r} = \frac{1 - \psi}{r_A} + \frac{\psi}{r_B} ; \quad \frac{1}{r} = \int \frac{w(r)}{r} \, dr \]

Combination of Eqs. (2) and (3) with Eqs. (5) and (6) results in

\[ 1 - \psi'' = (1 - \psi') \exp \left( r_A \rho_A \right) \]

\[ \psi'' \frac{W'(r)}{r} = \psi' \frac{W'(r)}{r} \exp \left[ r \rho_B(r) \right] \]

with

\[ \rho_A = \frac{1}{r} - \frac{1}{r_A} + \ln \frac{A'}{A} - \ln \frac{A''}{A} \]

\[ \rho_B(r) = \frac{1}{r''} - \frac{1}{r'} + \ln \frac{B'(r)}{B} - \ln \frac{B''}{B} \]

In phase separation experiments, a feed phase  is split into the two coexisting phases  and  . The fraction of the feed volume that forms phase  is given by the quantity  . Hence, the mass balance for the polymer species in continuous thermodynamics reads

\[ \psi^F W^F(r) = (1 - \phi) \psi' W'(r) + \phi \psi'' W''(r) \]

and, after integration,

\[ \psi^F = (1 - \phi) \psi' + \phi \psi'' \]

Eq. (6) with Eqs. (11) and (12) leads to the relation

\[ \frac{1}{r'} = \frac{1}{r} - \phi \frac{\rho_B(r)}{r} \]

The composition of the feed (i.e.  and  ) is usually known. The relations between the quantities referring to phase  and those referring to phase  are provided by Eqs. (11) - (13), which permit elimination of the quantities of one of the two coexisting phases, e.g. of those referring to phase  . Combination of Eqs. (8) and (11) results in

\[ \psi' W'(r) = \frac{\psi^F W^F(r)}{\phi + (1 - \phi) \exp \left[ - r \rho_B(r) \right]} \]

The expressions for  and , are obtained from the excess Gibbs energy relation used. In the general case, the excess Gibbs energy depends
on $T, \psi$, and the distribution function $\bar{W}(r)$. But in many relations used in practice, the dependence on $W(r)$ is neglected as an acceptable approximation. Then the coefficients also do not depend on $W(r)$, and $\bar{p}_B$ and $p_B$ do not depend on the identification variable $r$. A simple example is provided by Huggins' $\chi$-parameter concept

$$r_A \ln \bar{p}_A = \chi^2; \quad r_A \ln p_B = \chi (1 - \psi)^2; \quad \chi = \chi(T)$$

(15)

In polymer fractionation, it is convenient to introduce the precipitation rate $K$. In the continuous case, $K$ is a continuous function of $r$ defined as the quotient of the amounts of segments of all species with segment numbers between $r$ and $r + dr$ in phase " and in the feed phase $F$, respectively:

$$K(r) = \frac{\phi \int W(r) dr}{W_F(r) dr} = \frac{\phi \int W(r) dr}{W(r) dr}$$

(16)

Eq. (14) permits us to write

$$K(r) = \frac{\phi}{\phi + (1 - \phi) \exp (- r \bar{p}_B(r))}$$

(17)

Introduction of $K(r)$ permits us to obtain from Eqs. (11) and (14) the simple relations

$$\psi' W'(r) = \frac{1 - K(r)}{1 - \phi} \psi F W_F(r)$$

(18)

$$\psi'' W''(r) = \frac{K(r)}{\phi} \psi F W_F(r)$$

(19)

These relations directly provide the unknown distribution functions $W'(r)$ and $W''(r)$. The other unknowns $\psi''$, $P''$, and $\phi$ (or $T$), may be calculated from the relations

$$1 - \psi'' = \frac{1 - \psi F}{\phi + (1 - \phi) \exp (- r_A \bar{p}_A)}$$

(20)

$$\psi'' = \frac{K(r)}{\phi} \psi F W_F(r) dr$$

(21)

$$\frac{1}{r''} = \frac{1 - \psi''}{r_A} + \frac{1}{r} \frac{K(r)}{\phi} \psi F W_F(r) dr$$

(22)

Eqs. (20) - (22) are obtained from Eqs. (7) and (12), Eqs. (1) and (19), and Eqs. (6) and (21), respectively.

SUCCESSIVE POLYMER FRACTIONATION

As an example, successive precipitation fractionation (SPF) is considered. A homogeneous polymer solution, called feed phase $F$, is split by lowering the temperature into two coexisting phases, a polymer-lean phase '" and a polymer-rich phase '" , which are then separated. The polymer is isolated from phase '" as fraction 1. Phase '" directly forms $F$ for the next step, etc. In the last step, the polymer of phase '" forms the final polymer fraction. All coexisting '" and '" pairs are assumed to be in equilibrium. Hence, it is possible to apply Eqs. (1) - (22). To indicate the different separation steps 1, 2, ... the corresponding number, in general $i, j$, or $k$, is added as a subscript.

Since phase '" from step $i$ is used directly as $F$ for step $(i + 1)$ the following relations are valid:

$$\psi_{i+1} = \psi'_i; \quad W_{i+1}^F(r) = W'_i(r); \quad \bar{p}_{i+1}^F = \bar{p}'_i$$

(23) - (25)

On adding the subscript $i$ Eq. (19) reads...
Use of Eqs. (18), (23), and (24) for successive substitution results in

\[ \psi'_1 \psi''_1(r) = \frac{K_1(r)}{\phi_1} \psi'_1 \psi'_1(r) \quad (26) \]

Eq. (27) permits the direct and explicit calculation of the distribution function of fraction \( i \), \( \psi''_1(r) \), from the distribution function \( \psi'_1(r) \) of the original polymer. The form of this relation corresponds to the fractionation scheme applied. In steps \( j = 1, \ldots, i-1 \) the polymer-lean phase \( \psi'_1 \) is taken to correspond to the occurrence of the factor \( (1 - K_1(r))/(1 - \phi_1) \)

\[ \psi'_1 \psi''_1(r) = \frac{K_1(r)}{\phi_1} \frac{1}{\phi_1} \prod_{j=1}^{i-1} \frac{1 - K_1(r)}{1 - \phi_1} \psi'_1 \psi'_1(r) \quad (27) \]

To perform the calculation, the composition of the original polymer solution, i.e., \( \psi''_1 \) and \( \psi'_1(r) \), must be given. Furthermore, Eq. (27) contains the unknowns \( \psi''_1 \), \( \psi'_1 \), and \( \phi_1 \) (or \( T_j \)) for \( j = 1, \ldots, i \). These quantities are to be calculated successively, i.e., at first for \( j = 1 \), then for \( j = 2 \) etc., from the relations

\[ 1 - \psi''_1 = \frac{1 - \psi'_1}{\phi_1} \prod_{j=1}^{i-1} \frac{1 - K_1(r)}{1 - \phi_1} \exp \left( - r_A \beta_j \right) \quad (28) \]

\[ \psi'_j = \int \frac{K_1(r)}{\phi_1} \prod_{k=1}^{j-1} \frac{1 - K_k(r)}{1 - \phi_k} \psi'_1 \psi'_1(r) \, dr \quad (29) \]

\[ \frac{1}{r_A} = \frac{1 - \psi''_1}{r_A} + \int \frac{1}{r} \frac{K_1(r)}{\phi_1} \prod_{k=1}^{j-1} \frac{1 - K_k(r)}{1 - \phi_k} \psi'_1 \psi'_1(r) \, dr \quad (30) \]

Eq. (28) is Eq. (20) as applied to step \( j \). Eq. (29) is obtained in an analogous way from Eq. (27) by integration, Eq. (30) is obtained analogously from Eq. (6) and Eq. (27).

**BAKER-WILLIAMS COLUMN FRACTIONATION**

Precipitation fractionation developed by Baker and Williams (ref. 20) is one of the most widely used column fractionation procedures. It is performed in a glass bead filled column with a temperature gradient down the column. To start fractionation, the total polymer is precipitated on the glass beads of a section at the entry of the column (or in a separate vessel). In a mixing vessel, a nonsolvent and a solvent are mixed to form a mixture with progressively more solvent power by continuous enrichment of the solvent. The polymer is dissolved by adding the solvent mixture. The resulting sol phase moves relatively to the column, and the polymer at a given increment of the liquid sol stream becomes less soluble due to the temperature gradient, and precipitates partially on the glass beads as a gel phase. Fractionation is achieved by repeated exchange of polymer molecules between the stationary gel phase and the mobile sol phase. Superposition of a solvent/nonsolvent gradient and a temperature gradient leads to very high efficiency.

Initially, a model is needed to describe the column fractionation by a number of local equilibria. In this paper, one similar to that of Smith (ref. 21) is used. The column is divided into stages labeled with \( m \) (\( m = 0,1,2,\ldots \)). The liquid stream is divided into increments with equal volumes, labeled with \( n \) (\( n = 0,1,2,\ldots \)). At time zero, the volume increment \( n = 0 \) fills stage \( m = 0 \), at time one the volume increment \( n = 0 \) occupies stage \( m = 1 \) and the volume increment \( n = 1 \) occupies stage \( m = 0 \) etc. Each volume increment \( n \) at each stage \( m \) is considered to form a
liquid-liquid equilibrium (nm) between the sol phase and the gel phase. The gel phases being coated on the surfaces of the small glass beads are stationary, i.e. they remain at the same stage m. However, the moving sol phases always remain in the same volume increment n.

At the start of fractionation, the total polymer is assumed to be precipitated at m = m_p = 0 or to be distributed evenly among the m_p + 1 stages from m = 0 to m = m_p. The temperature gradient is expressed by

\[ T_m = T_0 \quad ; \quad n \leq m_p \]
\[ T_m = T_0 - (n - m_p) \Delta T \quad ; \quad n > m_p \]

where \( T_m \) is the temperature of stage m and \( \Delta T \) is the constant temperature difference between neighbouring stages. The segment fraction \( Y \) of the solvent in the solvent/nonsolvent mixture supplied to the entry (*) of the column, \( Y_{n0}^* \), is assumed to be given by

\[ Y_{n0}^* = Y_{00}^* + \Delta Y^*[1 - \exp\left(-\frac{n}{n^*}\right)] \]

where \( Y_{00}^* \), \( \Delta Y^* \) and \( n^* \) are the parameters of the function. The polymer fractions are obtained from the sol phases of the last stage.

In contrast to the liquid-liquid equilibrium (LLE) discussed above, now a solvent A1, a nonsolvent A2 and a polydispersed polymer B are present. Therefore, some of Eqs. (1) - (22) must be reformulated. Eq. (6) now reads

\[ \frac{1}{r} = \frac{Y(1 - \psi)}{r_{A1}} + \frac{(1 - Y)(1 - \psi)}{r_{A2}} + \frac{\psi}{r_B} \quad ; \quad \frac{1}{r_B} = \int \frac{w(r)}{r} \, dr \]

\[ Y(1 - \psi) \] is the segment fraction of the solvent and \( (1 - Y)(1 - \psi) \) the segment fraction of the nonsolvent. In the phase equilibrium problem, there are now four unknown scalar quantities: \( Y^* \), \( \psi^* \), \( r^* \), and \( \phi \) which may be calculated from the equations (instead of Eqs. (20) - (22)) obtained by combining equilibrium conditions and mass balances:

\[ Y''(1 - \psi'') = \frac{Y^F(1 - \psi^F)}{\phi + (1 - \phi) \exp\left(-\frac{r_A \phi}{r_B}\right)} \]

\[ (1 - Y'')(1 - \psi'') = \frac{(1 - Y^F)(1 - \psi^F)}{\phi + (1 - \phi) \exp\left(-\frac{r_A \phi}{r_B}\right)} \]

\[ \psi'' = \int \frac{K(r)}{\phi} \psi^F \, w^F(r) \, dr \]

\[ \frac{1}{r^*} = \frac{Y''(1 - \psi'')}{r_{A1}} + \frac{(1 - Y'')(1 - \psi'')}{r_{A2}} + \int \frac{K(r)}{\phi} \psi^F \, w^F(r) \, dr \]

When applying the LLE equations to the Baker-Williams fractionation, the \( n \) and \( m \) will be indicated as subscripts, e.g. Eq. (18) now reads

\[ \psi_{nm} \, w_{nm}(r) = \frac{1 - \psi_{nm}(r)}{\psi_{nm}^F \, w_{nm}^F(r)} \]

If an equilibrium (nm) is established, the sol phase (nm) is moved to the next column stage and the gel phase (nm) is waiting for the next volume increment. The feed for an LLE does not exist as a homogeneous phase, i.e. the feed \( (n+1,m+1)^F \) for the LLE \( (n+1,m+1) \) is the union of the mobile sol phase \( (n+1,m)^F \) and the stationary gel phase \( (n,m+1)^* \). Accordingly the many occurring phase equilibria are to be interrelated by the mass balances reading for the polymer

\[ w_{n+1,m}^F(r) + w_{n,m+1}^F(r) = w_{n+1,m+1}^F(r) = w_{n+1,m+1}^F(r) + w''_{n+1,m+1}^F(r) \]
Here \( w(r) \) is the extensive distribution function, i.e., \( w(r) = W(r) \frac{\bar{n}}{n_B} \) where \( \bar{n} \) is the overall amount of segments of all polymer species in the phase considered. Similar treatment for successive polymer fractionation leads to equations permitting the direct and explicit calculation of the polymer distribution functions of all occurring phases from the distribution \( W_00(r) \) of the original polymer. The unknowns are \( Y_{ij} \), \( Y_{ij}^{c} \), \( Y_{ij}^{d} \) and \( \Phi_{ij} \) for \( i = 0,1,\ldots,n \) and \( j = 0,1,\ldots,m \). These quantities are to be calculated from Eqs. (34) - (37) as applied to the equilibrium (1j).

Some results will be presented based on the following specifications. The segment molar excess Gibbs energy \( \Delta G_E \) reads

\[
\frac{\Delta G_E}{RT} = Y(1 - Y)(1 - \Psi)^2 \chi_{A1,A2} + Y(1 - \Psi)\Psi \chi_{A1,B} + (1 - Y)(1 - \Psi)\Psi \chi_{A2,B}
\]

with \( \chi_{A1,A2} = 500K/T; \chi_{A1,B} = 150K/T; \) and \( \chi_{A2,B} = 250K/T. \) The distribution of the original polymer is assumed to be described by the Schulz-Florey function

\[
W_{00}(r) = \frac{r}{150^m} \exp \left( \frac{-r}{150} \right).
\]

Furthermore, the following values are applied: \( r_{A1} = 1, \ r_{A2} = 1, \Psi^F = 0.02, \ m_p = 2, \ T_0 = 340 K, \ \Delta T = 2.5 K, \ Y^* = 0.01, \ AY^* = 0.3, \ n^* = 30. \) To simulate a hypothetical column fractionation special software was developed in FORTRAN 77 for a personal computer in two separate program parts. One part permits the successive calculation of the local equilibria where the starting values are found by approximation routines or, if necessary, by a random procedure. The other part is needed to interpret these quantities and present the results in the desired manner.

A hypothetical Baker-Williams fractionation was then performed for a column with 13 stages: 3 stages (without temperature gradient) containing the polymer at the start, and 10 fractionation stages. The calculated distributions of the polymer in several selected increments of the liquid stream are considered at two points of the column. Fig. 1a gives some of these distributions after the dissolution process (on the first three stages), i.e., for the polymer in phase ' for \( m = 2 \) and various values of \( n \). The nonuniformity \( U \) is defined by the quotient of the weight average and the average segment number less 1. In Fig. 1b some distributions of polymer leaving the column are shown, i.e., of the polymer in phase ' at stage \( m = 12 \) and the indicated values of \( n \). Comparison of Figs. 1a and b shows the fractionation effect resulting from the temperature gradient of the column. For the first parts of the liquid stream, particularly for \( n = 0 \), this effect is small. The reason is that a repeated exchange of polymer between the phases is only possible if a stationary gel phase is already precipitated at the higher stages.

![Fig. 1.](image)
CONTINUOUS POLYMER FRACTIONATION

Continuous polymer fractionation (CPF) (ref. 22) involves the following counter-current extraction. A comparatively concentrated solution of the polymer (the feed - FD) is introduced into a pulsed sieve-bottom column at one end, and the same solvent but free from polymer (extracting agent - EA) is added at the other end. The CPF splits the polymer into two fractions leaving the column as sol and as gel. The theoretical treatment is similar to that of the Baker-Williams fractionation. The column is divided into a number of stages \( m \); the EA enters the column at stage \( m = m_{\text{max}} \) and leaves it (as sol) at stage \( m = 1 \). The stationary state is calculated by repeated calculation of stages \( m = 1, \ldots, m_{\text{max}} \). At start \(( j = 0 \) \) the column is filled with EA. For the first set of equilibria \(( j = 1 \) \) a certain amount of FD is added at stage \( m = 1 \), and the related phase \(^{"}\) is transferred downwards to the next stage \( m = 2 \) (filled with EA).

When phase \(^{"}\) has left the column at \( m_{\text{max}} \) as the first (non-stationary) gel phase, all phases \(^{"}\) are shifted by one stage upwards, and stage \( m_{\text{max}} \) is filled with pure EA again. The calculation is repeated for \( j = 2 \) and \( m = 1, \ldots, m_{\text{max}} \) etc. The stationary state is reached when the results for \( j \) and \( j-1 \) no longer change systematically.

Experimental data for the CPF of polyethylene (ref. 23) were compared with calculations based on the following specifications. The mass balance for the polymer transfer in Eq. (39) now reads

\[
W_{m+1,j-1}(r) + W_{m-1,j}(r) = W_{mj}(r) \quad (42)
\]

Usually a mixed solvent is applied. But here polyethylene was fractionated in the pure (theta) solvent diphenyl ether and hence Eqs. (1) - (22) can be used without reformulation for the second solvent. Eq. (40) is replaced by

\[
\frac{\delta E}{R T} = \psi (1 - \psi) g \quad ; \quad g = g_0 (1 + p \psi) \quad (43)
\]

Here \( p \) is a parameter expressing the effect of the composition \( \psi \) on \( g \). The parameters \( p \) and \( g_0 \) were adjusted to phase equilibria for the temperature \((133 ^\circ C) \) at which CPF is performed. The theoretical treatment allows determination of the number of theoretical stages of the CPF-experiment or - for a given number of physical stages - calculation of the stage efficiency. In the present calculation, the 19 sieve bottoms of the CPF-column are used as stages and the efficiency is fitted. The efficiency is defined as the quotient of the polymer amount transferred from one phase to the other and the polymer amount that must be transferred to reach phase equilibrium. Fig. 2 compares calculated and experimental fraction distribution functions. The good agreement demonstrates the applicability of this treatment.

![Fig. 2. Comparison of measured (points) and calculated (lines) molecular weight distributions for the two fractions (cf. Fig. 10 in ref. 23) of poly(ethylene) obtained by CPF. The calculation was performed for 19 stages with an efficiency of 0.2 (see text) and the parameters \( g_0 = 0.199 \) and \( p = -2.3 \).](image-url)
REFERENCES

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