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Liquid-Liquid Equilibrium of Polydisperse Copolymer Solutions. Multivariate Distribution Functions in Continuous Thermodynamics

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ABSTRACT

In addition to the usual polydispersity with respect to molar mass, copolymers show chemical polydispersity. Thus, the species present may not be adequately characterized by a single variable, and a divariate distribution function has to be applied for describing the composition of the copolymer. In continuous thermodynamics, such continuous distribution functions are used directly (without splitting into pseudocomponents) for describing the composition of complex multicomponent systems. Whereas until now usually only one distribution variable has been used in continuous thermodynamics, consideration of copolymers requires an extension to divariate distribution functions. Continuous thermodynamics is generalized to divariate distribution functions in this paper. The liquid-liquid equilibrium of copolymer solutions is considered as a specific example.

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INTRODUCTION

The theoretical treatment of phase equilibria is based on thermodynamics. Traditional thermodynamics describes the composition of a mixture by the mole fractions, or mass fractions, etc., of individual components. For synthetic polymers the number of species is much too large for numerical solution of the resulting system of equations. Thus, the usual procedure consists of combining several neighboring species to form a pseudocomponent. The number of these pseudocomponents is chosen in such a way that the cost of the numerical calculations may be tolerable. Clearly, this pseudocomponent method is an arbitrary and awkward procedure.

However, division into pseudocomponents proves to be unnecessary. In polymer chemistry, from the very beginning, continuous distribution functions have been applied for characterization. A version of thermodynamics was established in 1980 (Kehlen and Rätzsch [1], Salacuse and Stell [2], Gultieri et al. [3], Briano and Glandt [4]; for references to some earlier preliminary attempts, see Ref. 5) that uses such continuous distribution functions in the framework of thermodynamics directly without pseudocomponents. We call this extension "continuous thermodynamics." It has been successfully applied to the calculation of the vapor-liquid equilibria of petroleum and similar mixtures [6, 7] and of the liquid-liquid equilibria of polymer systems [5, 8, 9]. In those papers the distribution function was assumed to depend on only a single variable.

For characterizing copolymer species (at least) two variables are necessary. Thus, in this paper the treatment is generalized to divariate distribution functions. The further generalization to multivariate distribution functions is simple.

DIVARIATE DISTRIBUTION FUNCTIONS

Let us consider a copolymer consisting of two kinds of monomer units, α and β. We choose a standard segment and define the segment numbers r_α and r_β as the quotients of the hard core volumes of all α-monomer units or all β-monomer units, respectively, in a molecule and of this standard segment. For simplicity, we assume that each species of a polydisperse copolymer may be characterized sufficiently by the two variables r_α and r_β. To separate the effects of polydispersity with respect to molar mass and to chemical composition, we choose for characterization, instead of r_α and r_β, the total segment number r and the segment fraction Y of the α-monomer units within the molecules:

$$r = r_\alpha + r_\beta; \qquad Y = r_\alpha/r \tag{1}$$

Thus, the composition of a polydisperse copolymer may be described by a divariate distribution function W(r,Y). Generalizing the treatment in Refs. 5 and 9 to two variables, W(r,Y)drdY gives the segment fraction of all copolymer species with r-values between r and r + dr and Y-values between Y and Y + dY. Thus, we obtain by integration over the total domains of definition $r_0 \leq r \leq r^0$ and $0 \leq Y \leq 1$:

$$\int_r \int_Y W(r,Y)dYdr = 1; \qquad \int_r = \int_{r_0}^{r^0}; \qquad \int_Y = \int_0^1 \tag{2}$$

PHASE EQUILIBRIUM BY CONTINUOUS THERMODYNAMICS

We consider a system containing a solvent A and a copolymer B. The condition for phase equilibrium between two phases ' and '' is:

$$\begin{aligned} \mu_A' &= \mu_A'' \\ \mu_B'(r,Y) &= \mu_B''(r,Y) \end{aligned} \tag{3}$$

Here μ indicates the chemical potential. For the copolymer B, the phase equilibrium condition applies to all species present. In the traditional treatment, these are the individual pseudocomponents, but in continuous thermodynamics the copolymer is considered as a two-dimensional continuous ensemble. Two copolymer species may differ with respect to r and Y by as small amounts as we like. Of course, each such continuous copolymer species is present only in an infinitely small amount. Thus, the phase equilibrium condition for the copolymer B holds for all r- and Y-values within the domains of definition mentioned above.

To apply Eqs. (3), we need expressions for the chemical potentials in the continuous treatment. In earlier papers [5, 8, 9] the thermodynamic quantities were considered dependent on the distribution functions for only one variable. The generalization to divariate distribution functions is simple:

> In all relations, the single variable is to be replaced by two variables (r and Y).
> Single integrals are to be replaced by double integrals of type (2).

The relations for the chemical potentials read

$$\mu_A = \mu_A^* + RT\left[\ln(1-\psi) + 1 - r_A\left(\frac{1-\psi}{r_A} + \frac{\psi}{\bar{r}_B}\right)\right] + r_A RT \ln \bar{\bar{\gamma}}_A \tag{4}$$

$$\mu_B(r,Y) = \mu_{B,0}^*(r,Y) + RT\left[\ln \psi W(r,Y) + 1 - r\left(\frac{1-\psi}{r_A} + \frac{\psi}{\bar{r}_B}\right)\right]$$

$$+ rRT \ln \bar{\bar{\gamma}}_B(r,Y) \tag{4}$$

where R is the universal gas constant, T is the absolute temperature, ψ is the total segment fraction of all polymer species, and r_A is the segment number of the solvent molecules. The quantity $\bar{r}_B$ designates the number-average of the segment numbers of all polymer species, defined by

$$\frac{1}{\bar{r}_B} = \int_r\int_Y \frac{W(r,Y)}{r}\, dYdr \tag{5}$$

In Eqs. (4) the first terms on the right-hand side are standard terms independent of the composition of the mixture considered, i.e., independent of ψ and of W(r,Y). The second terms are the well-known Flory-Huggins terms, and the third terms describe the deviations from a Flory-Huggins mixture containing the so-called segment-molar activity coefficients $\bar{\bar{\gamma}}_A$ and $\bar{\bar{\gamma}}_B(r,Y)$.

Expressing the chemical potentials in Eqs. (3) according to Eqs. (4), we obtain, after rearranging,

$$(1 - \psi'') = (1 - \psi')\exp r_A\rho_A \tag{6}$$

$$W''(r,Y) = \frac{\psi'}{\psi''}W'(r,Y)\exp r\,\rho_B \tag{7}$$

where

$$\rho_A = -\frac{\psi'' - \psi'}{r_A} + \frac{\psi''}{\bar{r}_B''} - \frac{\psi'}{\bar{r}_B'} - \ln \bar{\bar{\gamma}}_A'' + \ln \bar{\bar{\gamma}}_A' \tag{8}$$

$$\rho_B = -\frac{\psi'' - \psi'}{r_A} + \frac{\psi''}{\bar{r}_B''} - \frac{\psi'}{\bar{r}_B'} - \ln \bar{\bar{\gamma}}_B''(r,Y) + \ln \bar{\bar{\gamma}}_B'(r,Y) \tag{9}$$

Further treatment depends on how the distribution function W(r,Y) influences the segment-molar activity coefficients $\bar{\bar{\gamma}}_A$ and $\bar{\bar{\gamma}}_B$. The logarithms of $\bar{\bar{\gamma}}_A$ and $\bar{\bar{\gamma}}_B$ are the partial segment-molar quantities with respect to the segment-molar excess Gibbs energy $\bar{\bar{G}}^E/RT$ (where "excess" means the deviation from a Flory-Huggins mixture). For homopolymers, one often may assume $\bar{\bar{G}}^E$ to be independent of the distribution function [5, 9]. Thus, for copolymers, $\bar{\bar{G}}^E$ should depend on W(r,Y) only through the weight-average $\tilde{Y}$ of the chemical composition Y of the copolymers

$$\tilde{Y} = \int_r \int_Y YW(r,Y)dYdr \tag{10}$$

as a reasonable assumption. Applying Huggins' χ-parameter concept and assuming χ to depend on $\tilde{Y}$ as a quadratic polynomial, we write

$$\bar{\bar{G}}^E/RT = \psi(1 - \psi)\,\chi; \qquad \chi = a + b\tilde{Y} + c\tilde{Y}^2 \tag{11}$$

Here the parameters a, b, and c of the polynomial depend only on the temperature (and eventually on the pressure).

Relation (11) may also be justified by molecular considerations (see Appendix). From Eq. (11) we obtain by the methods outlined in Refs. 1, 7, and 9:

$$\ln \bar{\bar{\gamma}}_A = \psi^2\,(a + b\tilde{Y} + c\tilde{Y}^2) \tag{12}$$

$$\ln \bar{\bar{\gamma}}_B = (1 - \psi)^2\,(a + b\tilde{Y} + c\tilde{Y}^2) + (1 - \psi)\,(b + 2c\tilde{Y})\,(Y - \tilde{Y})$$

Like $\bar{\bar{G}}^E$, the logarithms of the activity coefficients depend on W(r,Y) only through $\tilde{Y}$. Furthermore, ln $\bar{\bar{\gamma}}_B$ does not depend on r but on Y.

CLOUD-POINT CURVE AND SHADOW CURVE

To deal with this problem, the temperature of a given phase (') is changed at constant pressure P until a second phase (shadow phase, ") is formed. Thus, the unknowns of the problem are the equilibrium temperature T and the composition of phase ", i.e., ψ'' and the distribution function W"(r,Y).

To calculate them, the phase equilibrium conditions (6) and (7) and the normalization condition (2)—applied to W"(r,Y)—are used. In this system of equations, the unknown distribution function W"(r,Y) and the other unknowns T and ψ'' (which we will call scalar quantities to point out the difference) are interweaved. According to Eqs. (9) and (12), on the right-hand side of Eq. (7) the unknown distribution function W''(r,Y) occurs only by means of $\bar{r}_B''$ and $\tilde{Y}''$. Thus, we may achieve a separation of the problem of the unknown distribution function by considering $\bar{r}_B''$ and $\tilde{Y}''$ as additional scalar unknowns and their defining equations as additional scalar equations.

In this way the unknown distribution function W''(r,Y) is explicitly given by Eq. (7). According to Eqs. (9) and (12), four scalar unknowns occur in this relation: T, ψ'', $\bar{r}_B''$, and $\tilde{Y}''$. To calculate them, we need four equations. These are Eq. (6) and

$$\psi'' = \psi' \int_r \int_Y W'(r,Y) \exp(r\rho_B) dY dr$$

$$\frac{1}{\bar{r}_B''} = \frac{\psi'}{\psi''} \int_r \int_Y \frac{W'(r,Y)}{r} \exp(r\rho_B) dY dr \tag{13}$$

$$\tilde{Y}'' = \frac{\psi'}{\psi''} \int_r \int_Y Y W'(r,Y) \exp(r\rho_B) dY dr$$

Relations (13) result from Eqs. (2), (5), and (10)—applied to phase ''—by replacing W''(r,Y) according to Eq. (7). Thus, the complicated problem of calculating the cloud-point curve and the shadow curve for a polydisperse copolymer solution is reduced to solving a system of only four scalar equations. For the numerical calculation, furthermore, $\bar{r}_B''$ may be eliminated by means of Eqs. (6) and (8).

If $\bar{\bar{G}}^E/RT$ depends on W(r,Y) by means of scalars other than $\tilde{Y}$, we may proceed in an analogous manner.

ANALYTIC INTEGRABILITY

In the general case, the double integrals in Eqs. (13) have to be calculated numerically. But, if W'(r,Y) has an appropriate structure, the double integrals can be calculated analytically, an important simplification.

For instance, analytic integrability is found for a (generalized) Stockmayer distribution [10]

$$W'(r,Y) = \left\{ \frac{k^{k+1}}{\bar{r}_B' \Gamma(k+1)} \left(\frac{r}{\bar{r}_B'} \right)^k \exp\left(-k \frac{r}{\bar{r}_B'}\right) \right\} \cdot \left\{ \frac{\sqrt{r}}{\sqrt{2\pi\epsilon}} \exp\left[- \frac{r(Y - \tilde{Y}')^2}{2\epsilon} \right] \right\} \qquad (14)$$

The first factor is a generalized Schulz-Flory distribution with respect to r ($r_0 = 0$, $r^0 = \infty$). The parameters are k and $\bar{r}_B'$. Γ is the Γ function. The second factor is a Gaussian distribution with respect to Y, with a standard deviation of $\sqrt{\epsilon/r}$. The parameters are $\tilde{Y}'$ and ϵ. The Gaussian function is assumed to be so narrow that its limits of definition, $-\infty$ and ∞, may be replaced by 0 and 1, respectively, with a very small error. Many industrial copolymers obey this requirement. For random copolymers we have $\epsilon \leqq 1/4$.

Applying Eq. (14), the double integrals in Eqs. (13) may be calculated exactly, and we obtain from Eqs. (6) and (13), after rearranging:

$$[1 + 2\epsilon c(1 - \psi'')]^2 \left\{ \ln \frac{1 - \psi''}{1 - \psi'} - \frac{r_A}{\bar{r}_B'} k \left[1 - \left(\frac{\psi'}{\psi''} \right)^{1/(k+1)} \right] + 2r_A[a + b\tilde{Y}' + c\tilde{Y}'^2](\psi'' - \psi') \right\} + r_A\epsilon(b + 2c\tilde{Y}')^2 (\psi'' - \psi') \left\{ \frac{1}{2}(1 + 2\epsilon c)(\psi'' - \psi') + \psi''[1 + 2\epsilon c(1 - \psi'')] \right\} = 0 \qquad (15)$$

$$[1 + 2\epsilon c(1 - \psi'')]^2 \left\{ \ln \frac{1 - \psi''}{1 - \psi'} + \frac{r_A}{\bar{r}_B'} \psi' \left[1 - \left(\frac{\psi''}{\psi'} \right)^{k/(k+1)} \right] + (\psi'' - \psi') + r_A(a + bY' + cY'^2)(\psi''^2 - \psi'^2) \right\} + r_A\epsilon(b + 2c\tilde{Y}')^2 \psi''^2 (\psi'' - \psi')[1 + \epsilon c(2 - \psi' - \psi'')] = 0 \qquad (16)$$

$$\bar{r}_B'' = \bar{r}_B' \left(\frac{\psi''}{\psi'} \right)^{1/(k+1)} \qquad (17)$$

$$\tilde{Y}'' = \tilde{Y}' + \frac{\epsilon(b + 2c\tilde{Y}')(\psi'' - \psi')}{1 + 2\epsilon c(1 - \psi'')} \tag{18}$$

Because a, b, c depend on T, Eqs. (15) and (16) permit the calculation of T and ψ''. Then, $\bar{r}_B''$ and Y'' are given directly by Eqs. (17) and (18). Furthermore, according to Eq. (7), $W''(r,Y)$ also proves to be a generalized Stockmayer distribution of type (14) with the same values of k and ϵ and averages $\bar{r}_B''$ and $\tilde{Y}''$, which are to be calculated by Eqs. (17) and (18).

COEXISTENCE CURVES

To calculate the coexistence curves we consider a feed phase F splitting into the coexisting phases ' and ''. Thus, the mass balance [5]

$$\psi^F W^F(r,Y) = (1 - \phi)\,\psi' W'(r,Y) + \phi\psi'' W''(r,Y) \tag{19}$$

is to be combined with the phase equilibrium conditions. Here ϕ is the quotient of the total amount of segments in the phase '' and in the feed phase. From Eq. (19) we obtain, according to (2), (5), and (10),

$$\begin{aligned} \psi^F &= (1 - \phi)\,\psi' + \phi\psi'' \\ \psi^F/\bar{r}_B{}^F &= (1 - \phi)\,\psi'/\bar{r}_B{}' + \phi\psi''/\bar{r}_B{}'' \\ \psi^F\tilde{Y}^F &= (1 - \phi)\,\psi'\tilde{Y}' + \phi\psi''\tilde{Y}'' \end{aligned} \tag{20}$$

Besides the feed, two of the three variables T, P, and ϕ are assumed to be specified. Starting with the phase equilibrium conditions (6) and (7), the balances (19) and (20) may be applied to eliminate the quantities referring to one of the two coexisting phases (we choose phase '), which leads to

$$W''(r,Y) = \frac{\psi^F}{\psi''}\,\frac{W^F(r,Y)}{\phi + (1 - \phi)\exp(-r\rho_B)} \tag{21}$$

$$(1 - \psi'') = \frac{1 - \psi^F}{\phi + (1 - \phi)\exp(-r_A\rho_A)} \tag{22}$$

$$1 = \frac{\psi^F}{\psi''} \int_r \int_Y \frac{W^F(r,Y)}{\phi + (1 - \phi) \exp(-r\rho_B)} \, dYdr \qquad (23)$$

$$\frac{1}{r_B''} = \frac{\psi^F}{\psi''} \int_r \int_Y \frac{1}{r} \frac{W^F(r,Y)}{\phi + (1 - \phi) \exp(-r\rho_B)} \, dYdr \qquad (24)$$

$$\tilde{Y}'' = \frac{\psi^F}{\psi''} \int_r \int_Y Y \frac{W^F(r,Y)}{\phi + (1 - \phi) \exp(-r\rho_B)} \, dYdr \qquad (25)$$

In complete analogy to the treatment of the cloud-point and shadow curves, a separation of the problem of the unknown distribution function $W''(r,Y)$ is achieved by considering $\bar{r}_B''$ and $\tilde{Y}''$ as additional scalar unknowns and their defining relations as additional scalar equations. Thus, $W''(r,Y)$ is explicitly given by Eq. (21). This relation contains four scalar unknowns: ψ'', $\bar{r}_B''$, $\tilde{Y}''$, and the unspecified of the three quantities T, P, and ϕ. These unknowns may be calculated from the four scalar equations (22)-(25). Then, the quantities referring to phase' may be easily obtained, e.g., from Eqs. (19) and (20).

EXAMPLE

As an example, we consider the cloud-point curve for the solution of a random copolymer, e.g., ethylene/vinyl acetate copolymer, which shall be characterized by the Stockmayer distribution (14), i.e., the relations (15)-(18) apply. We choose $r_A = 1$, $\bar{r}_B' = 100$, $k = 1$, $\tilde{Y}' = 0.5$, and, according to the randomness, $\epsilon = \tilde{Y}'(1 - \tilde{Y}')$. Furthermore, we assume a, b, and c, and, therefore, according to Eq. (11), also χ, to be proportional to T^{-1}. Thus, the plot of χ^{-1} against ψ' corresponds to the cloud-point curve.

To illustrate the influence of chemical polydispersity, in Fig. 1 the cloud-point curves are shown for three different sets of the parameters a, b, and c. If we choose $b = 0$ and $c = 0$, the influence of chemical polydispersity is eliminated, and we obtain the same curve as for a homopolymer. The case $b = 0$, $c = a$ approximately describes many real copolymer solutions. Figure 1 shows that, for solutions of random copolymers, the influence of the chemical polydispersity on the liquid-liquid equilibrium is small. To give an idea of how large this influence may be in an unusual case, the cloud-point curve for $b = -a$, $c = 0$ is shown too. These parameter values correspond to an unusual case because they imply the interactions of the α- and of the β-segments of the copolymer with the solvent molecules to be very different.

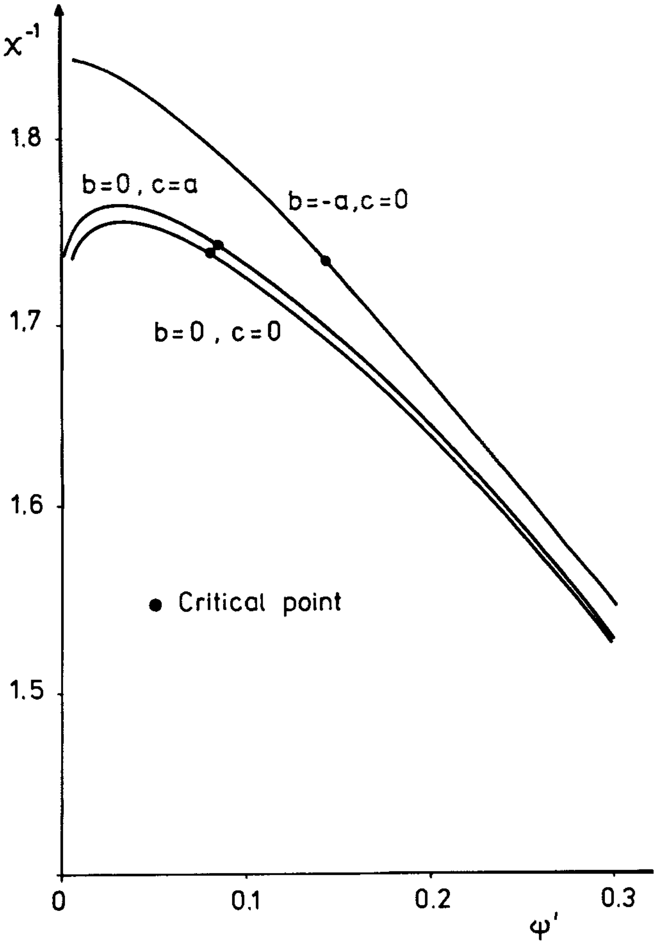

FIG. 1. Cloud-point curves for solutions of a random copolymer with different parameter sets.

APPENDIX: DERIVATION OF EQ. (11) FROM LATTICE THEORY

In addition to the well-known assumptions of Barker's lattice theory [11], we assume:

(a) The combinatorial part of the Gibbs free energy is given by the Flory-Huggins relation.
(b) The contact pair numbers are calculated by the random mixture assumption.
(c) For each segment, all z contact points are available for intermolecular interactions.

Considering homopolymers, these assumptions result in the well-known Huggins χ-parameter concept. For copolymers a modified Huggins theory is obtained that accounts for the chemical polydispersity.

The residual part of the change in the Gibbs free energy of mixing Δg_{res} reads

$$\Delta g_{res} = N_{A\alpha}^{*}\Delta u_{A\alpha} + N_{A\beta}^{*}\Delta u_{A\beta} + (N_{\alpha\beta}^{*} - N_{\alpha\beta 1}^{*})\,\Delta u_{\alpha\beta}$$

$N_{A\alpha}^{*}$, $N_{A\beta}^{*}$, and $N_{\alpha\beta}^{*}$ are contact pair numbers for contacts between solvent segments A and/or between copolymer segments α and β. $\Delta u_{A\alpha}$, $\Delta u_{A\beta}$, and $\Delta u_{\alpha\beta}$ are differences of interaction parameters of type

$$\Delta u_{A\alpha} = u_{A\alpha} - \frac{1}{2}\,(u_{AA} + u_{\alpha\alpha})$$

$N_{\alpha\beta 1}^{*}$ is the value of $N_{\alpha\beta}^{*}$ for the pure copolymer.

According to Assumptions (a)-(c), the contact pair numbers are given by

$$N_{A\alpha}^{*} = (1 - \psi)\, z\sum_{i}\sum_{j} r_i Y_j N_{ij}$$

$$N_{A\beta}^{*} = (1 - \psi)\, z\sum_{i}\sum_{j} r_i (1 - Y_j) N_{ij}$$

$$N_{\alpha\beta}^{*} = \psi z\, \frac{\left[\sum_{i}\sum_{j} r_i Y_j N_{ij}\right]\left[\sum_{i}\sum_{j} r_i (1 - Y_j) N_{ij}\right]}{\sum_{i}\sum_{j} r_i N_{ij}}$$

where N_{ij} is the number of copolymer molecules characterized by the segment number r_i and the segment fraction of α-monomers Y_j. Applying a continuous description, we obtain

$$\bar{\bar{G}}^E/RT = \psi(1-\psi)z \left[\frac{\Delta u_{A\alpha}}{kT} \int_r \int_Y YW(r,Y)dYdr \right.$$

$$+ \frac{\Delta u_{A\beta}}{kT} \int_r \int_Y (1-Y)W(r,Y)dYdr$$

$$\left. - \frac{\Delta u_{\alpha\beta}}{kT} \int_r \int_Y YW(r,Y)dYdr \int_r \int_Y (1-Y)W(r,Y)dYdr \right]$$

where k is Boltzmann's constant. With Eq. (10) we get immediately Eq. (11) where

$$a = \frac{z\Delta_{A\beta}}{kT}; \quad b = \frac{z(\Delta u_{A\alpha} - \Delta u_{A\beta} - \Delta u_{\alpha\beta})}{kT}; \quad c = \frac{z\Delta u_{\alpha\beta}}{kT}$$

In practice, the parameters a, b, and c are to be fitted to experimental data.

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