

Statistical thermodynamics of polydisperse polymer mixtures

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A statistical thermodynamics theory of polydisperse polymer blends based on a lattice model description of a fluid is formulated. Characterization of a binary polydisperse polymer mixture requires a knowledge of the pure polymer system and the interaction energy. It is assumed that the intrinsic and interactive properties of polymer (for example, T^* , P^* , ρ^* , and ϵ_{ij}^*) are independent of molecular size. Thermodynamic properties of ternary and higher order mixtures are completely defined in terms of the pure fluid polymer parameters and the binary interaction energies. Thermodynamic stability criteria for the phase transitions of a binary mixture are shown. The binodal and spinodal of general binary systems and of special binary systems are discussed.

(Keywords: statistical thermodynamics; polymer blends; polydispersity; equation of state)

INTRODUCTION

At different times in the history of polymer science, specific subjects have come to 'centre stage' for intense investigation because they represented new and important intellectual challenges as well as technological opportunities. Polymer blends have now come to the fore as a topic of major endeavour. In the field of polymer blends, polymer-polymer compatibility is always very important, especially the statistical thermodynamics theory of compatibility.

Scott¹ and Tompa² were the first to apply the Flory-Huggins theory of polymer solutions³⁻⁶ to mixtures of polymers, with or without added solvent, and found the critical conditions⁷ in such systems. The Flory-Huggins theory gives remarkably good results in calculations of polymer compatibility when it is used with care. However, it completely fails to describe the lower critical solution temperature (LCST)⁸ behaviour. After the discovery of the universality of LCST behaviour in polymer solutions and blends, Flory and co-workers⁹⁻¹² developed a new theory of solutions which incorporated the 'equation of state' properties of the pure components. This new theory of solutions (hereafter referred to as the Flory theory) demonstrated that the thermodynamic properties of the mixture depend on the thermodynamic properties of the pure components, and the LCST behaviour is related to the dissimilarity of the equation of state of the properties of polymer and solvent. After this, Sanchez and

Lacombe¹³⁻¹⁵ suggested their lattice-fluid (LF) model and obtained fairly good results in describing LCST behaviour of polymer solutions. The Flory theory and the LF model are also quite successful in explaining the LCST behaviour of non-polar polymer-polymer blends^{14,16}. When strong or specific interactions take place between components in a polymer blend system, it is not very accurate to apply the original Flory theory and LF model to analyse LCST behaviour. Using quasi-chemical approaches to treat the non-random character of a solution, Panayiotou and Vera¹⁷ and Renuncio and Prausnitz¹⁸ developed improved modifications of the Flory theory. Sanchez and Balazs¹⁹ adopted a simpler approach which is quite similar to that of ten Brinke and Karasz²⁰, who developed an incompressible model of binary mixtures with specific interactions, to perfect the LF model; these workers have obtained good results.

Koningsveld, Kleintjens and co-workers²¹⁻²⁵ have dealt with the influence of polydispersity on a polymer solution based on the Flory-Huggins theory. Their results reveal that the spinodal depends on the mass-average chain length alone and that the critical conditions are determined by the mass-average chain length and z -average chain length only. They used mean-field lattice gas model for a multicomponent polymer system²⁶⁻²⁹ and obtained the same conclusions as those mentioned above. Although the results of Koningsveld and Kleintjens are significant, the influences of polydispersity on phase separation are not thoroughly solved.

The general objective in the present paper is to discuss the statistical thermodynamics of polydisperse polymer blends on the basis of LF theory and the influences of

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polydispersity of the polymer on compatibility. The thermodynamics of polydispersity can be reduced to the LF theory of Sanchez when every component is changed into a monodisperse polymer.

THEORY

Mixture of polymer fluids

A statistical mechanical model of pure, polydisperse polymer fluids has been developed³⁰. The basic simplicity and structure of the theory enables it to be readily extended to mixed polymer fluids.

A lattice is used to enumerate the number of configurations available to a system of $N_1 r_1$ -mers, $N_2 r_2$ -mers, ..., $N_m r_m$ -mers and N_0 empty sites (holes). An r_i -mer is a molecule that occupies an average of r_i sites on a lattice of coordination number z . The polymer molecules consist of a series of different chain-length molecules, i.e.

$$N_i = N_{i1} + N_{i2} + \dots + N_{in} = \sum_{j=1}^n N_{ij} \quad (1)$$

$$r_i = \sum_{j=1}^n r_{ij} N_{ij} / N_i \quad (2)$$

$$(i = 1, 2, \dots, m; \quad 1, 2, \dots, n)$$

where N_{ij} is the number of molecules whose chain length is r_{ij} in the i component.

The number of configurations Ω available to this system is given approximately by³¹⁻³³:

$$\Omega = \frac{N_r!}{N_0!} \left(\frac{N_q!}{N_r!} \right)^{z/2} \prod_{ij} \left(\frac{\delta_{ij}}{\sigma_{ij}} \right)^{N_{ij}} \frac{1}{N_{ij}!} \quad (3)$$

where

$$N_r = N_0 + \sum_{ij} r_{ij} N_{ij} \quad (4)$$

$$N_q = N_0 + \sum_{ij} q_{ij} N_{ij} \quad (5)$$

$$q_{ij} z = r_{ij} (z - 2) + 2 \quad (6)$$

$$(z/2) N_q = (z/2 - 1) N_r + N_0 + \sum_{ij} N_{ij} \quad (7)$$

where σ_{ij} is a symmetry number and δ_{ij} is a flexibility parameter characteristic of chain length r_{ij} . A full description of these parameters is given in ref. 13.

As the coordination number of the lattice gets larger, Ω approaches a limiting and simpler form (the Flory approximation⁴):

$$\lim_{z \rightarrow \infty} \Omega = \left(\frac{1}{f_0} \right)^{N_0} \prod_{ij} \left(\frac{\omega_{ij}}{f_{ij}} \right)^{N_{ij}} \quad (8)$$

$$\omega_{ij} = \delta_{ij} r_{ij} / \sigma_{ij} e^{r_{ij} - 1} \quad (9)$$

$$f_0 = N_0 / N_r; \quad f_{ij} = r_{ij} N_{ij} / N_r \quad (10)$$

where ω_{ij} is the number of configurations available to a r_{ij} -mer in the close-packed pure state. The fraction of sites occupied by r_{ij} -mers is f_{ij} and the empty site fraction is f_0 .

The lattice energy (attractive) depends only on nearest-neighbour interactions. If hole-mer and hole-hole interactions are assigned a zero energy and random mixing of the component is assumed, then the lattice

energy in the large z limit becomes ($z\epsilon_{ij}$ remains finite):

$$E = -N_r \sum_{l=1}^m \sum_{k=1}^m f_l f_k \epsilon_{lk}^* \quad (11)$$

$$\epsilon_{lk}^* = (z/2) \epsilon_{lk} \quad (12)$$

$$f_l = \frac{r_l N_l}{N_r} = \frac{\sum_{j=1}^n r_{lj} N_{lj}}{N_r} = \sum_{j=1}^n f_{lj} \quad (13)$$

$$f_k = \frac{r_k N_k}{N_r} = \frac{\sum_{j=1}^n r_{kj} N_{kj}}{N_r} = \sum_{j=1}^n f_{kj} \quad (14)$$

where ϵ_{lk}^* is the interaction energy of a mer belonging to component l when it is surrounded by z mers belonging to component k . The interaction energies are symmetrical ($\epsilon_{lk}^* = \epsilon_{kl}^*$).

The volume of the mixture is:

$$V = N_r v^* = (N_0 + rN) v^* \quad (15)$$

where

$$r = \sum_{ij} x_{ij} r_{ij} = \sum_i x_i r_i \quad (16)$$

$$x_{ij} = N_{ij} / N; \quad x_i = N_i / N = \sum_{j=1}^n x_{ij} \quad (17)$$

$$N = \sum_{ij} N_{ij} = \sum_i N_i \quad (18)$$

and v^* is the average close-packed volume of a mer in the mixture.

The close-packed volume of the mixture is

$$V^* = v^* \sum_{ij} r_{ij} N_{ij} = rN v^* \quad (19)$$

Note that the reduced volume of the mixture \tilde{v} is independent of v^* :

$$\tilde{v} = \frac{V}{V^*} = (N_0 + rN) / rN \quad (20)$$

In general, v^* is some unknown function of the pure component v_i^* and the composition of the mixture. This presents a problem because there is no *ab initio* method of determining v^* . Determination of v^* is tantamount to determining how molecules of arbitrary geometry and size will randomly close-pack, which is a unique and difficult problem in itself. Further progress here requires the introduction of the following two 'combining rules' for the close-packed mixture.

1. The close-packed molecular volume of each component is conserved. If an (ij) molecule occupies r_{ij}^0 sites in the pure state and has a close-packed molecular volume of $r_{ij}^0 v_i^*$, then it will occupy r_{ij} sites in the mixture where:

$$r_{ij} = r_{ij}^0 (v_i^* / v^*) \quad (21)$$

This rule guarantees additivity of the close-packed volumes:

$$\sum_{ij} r_{ij}^0 N_{ij} v_i^* = \sum_{ij} r_{ij} N_{ij} v^* = V^* \quad (22)$$

2. The total number of pair interactions in the close-packed mixture is equal to the sum of the pair interactions of the components in their close-packed

pure states, i.e.

$$(z/2) \sum_{ij} r_{ij}^0 N_{ij} = (z/2) \sum_{ij} r_{ij} N_{ij} = (z/2) r N \quad (23)$$

Equations (21) and (23) yield the following relationship for the average close-packed mer volume:

$$v^* = \sum_{ij} \varphi_{ij}^0 v_i^* = \sum_i \varphi_i^0 v_i^* \quad (24)$$

where

$$\varphi_{ij}^0 = \frac{r_{ij}^0 N_{ij}}{\sum_{ij} r_{ij}^0 N_{ij}} = \frac{r_{ij}^0 N_{ij}}{r N} \quad (25)$$

$$\varphi_i^0 = \frac{r_i^0 N_i}{r N} = \sum_j \varphi_{ij}^0 \quad (26)$$

$$r_i^0 = \frac{\sum_j r_{ij}^0 N_{ij}}{N_i} \quad (27)$$

The net effect of combining rules is to introduce a surface area effect. A component in a binary mixture with a larger mer volume is capable of more interactions per mer in the mixture than in the pure state. For example, if $v_1^* > v_2^*$ then $r_1 > r_1^0$ and $r_2 < r_2^0$ (where r_i and r_i^0 can be given by equations (2) and (27)). Thus, a molecule of component 1 has, on average, $(z/2)r_1$ pair interactions in the close-packed mixture instead of the smaller $(z/2)r_1^0$. The increase in interactions of the first component is at the expense of the second component, since the total number of interactions is conserved.

In the pressure ensemble, the partition function for this model can be written as

$$Z(T, P) = \sum_{N_0=0}^{\infty} \Omega \exp[-\beta(E + PV)] \quad (28)$$

The above sum can be replaced by its maximum term. Since the Gibbs free energy G is given by

$$G = -kT \ln Z(T, P) \quad (29)$$

finding the maximum term is equivalent to equating the free energy to the logarithm of the generic term in the sum and then finding the minimum value of the free energy. Thus

$$G = E + PV - kT \ln \Omega \quad (30)$$

Using equations (8), (11), (15) and (20), the free energy can also be expressed in terms of reduced variables:

$$\begin{aligned} \tilde{G} &= G/(rN\varepsilon^*) \\ &= -\tilde{\rho} + \tilde{P}\tilde{v} \\ &+ \tilde{T} \left[(\tilde{v}-1) \ln(1-\tilde{\rho}) + \frac{1}{r} \ln \tilde{\rho} + \sum_{ij} \left(\frac{\varphi_{ij}}{r_{ij}} \right) \ln \left(\frac{\varphi_{ij}}{\omega_{ij}} \right) \right] \end{aligned} \quad (31)$$

where

$$\tilde{T} = T/T^* \quad T^* = \varepsilon^*/k \quad (32)$$

$$\tilde{P} = P/P^* \quad P^* = \varepsilon^*/v^* \quad (33)$$

$$\tilde{v} = \frac{V}{V^*} = \frac{1}{\tilde{\rho}} \quad (34)$$

$$\varepsilon^* = \sum_{l=1}^m \sum_{k=1}^m \varphi_l \varphi_k \varepsilon_{lk}^* = \sum_{l=1}^m \varphi_l \varepsilon_{ll}^* - kT \sum_{l=1}^m \sum_{k=1}^m \varphi_l \varphi_k \chi_{lk} \quad (35)$$

$$\chi_{lk} = (\varepsilon_{ll}^* + \varepsilon_{kk}^* - 2\varepsilon_{lk}^*)/kT \quad (36)$$

$$\varphi_{ij} = \frac{r_{ij} N_{ij}}{\sum_{ij} r_{ij} N_{ij}} = \frac{r_{ij} N_{ij}}{r N} \quad (37)$$

$$1/r = \sum_{ij} \frac{\varphi_{ij}}{r_{ij}} = \sum_{ij} \frac{\varphi_{ij}^0}{r_{ij}^0} \quad (38)$$

$$f_0 = 1 - \tilde{\rho} \quad f_{ij} = \tilde{\rho} \varphi_{ij} \quad (39)$$

Minimization of the free energy with respect to N_0 , or equivalently the reduced volume \tilde{v} , yields:

$$\left. \frac{\partial \tilde{G}}{\partial \tilde{v}} \right|_{T, \tilde{P}} = 0 \quad (40)$$

or

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r}\right) \tilde{\rho} \right] = 0 \quad (41)$$

$$PV/NkT = r\tilde{P}\tilde{v}/\tilde{T} = 1 - r[1 + \ln(1-\tilde{\rho})/\tilde{\rho} + \tilde{\rho}/\tilde{T}] \quad (42)$$

Equations (41) and (42) are the equation of state of the mixture. It is identical in form with the equation of state of a pure fluid³⁰.

As a special case, if the mixture consists of two pure polymer fluids and every pure polymer fluid obeys a Flory distribution³⁴ in the system, i.e.

$$N_{r_{1j}} = N_1^* (1-p_1)^2 p_1^{r_{1j}-1} \quad (43)$$

$$N_{r_{2j}} = N_2^* (1-p_2)^2 p_2^{r_{2j}-1} \quad (44)$$

where N_1^* and N_2^* are the numbers of 1st-mers and 2nd-mers, and p_1 and p_2 are the parameters of reaction extent of 1st-mers and 2nd-mers and the independent variables, respectively, in the system, then \tilde{G} is

$$\begin{aligned} \tilde{G} &= -\tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T} \left\{ (\tilde{v}-1) \ln(1-\tilde{\rho}) \right. \\ &+ [\varphi_1(1-p_1) + \varphi_2(1-p_2)] \ln \tilde{\rho} \\ &+ \varphi_1(1-p_1) \ln \varphi_1(1-p_1)^2 + \varphi_1 p_1 \ln p_1 + \varphi_1 p_1 \\ &+ \varphi_1(1-p_1)^2 \sum_{r_{1j}=1}^{\infty} p_1^{r_{1j}-1} \ln \left(\frac{\sigma_{r_{1j}}}{\delta_{r_{1j}}} \right) \\ &+ \varphi_2(1-p_2) \ln \varphi_2(1-p_2)^2 + \varphi_2 p_2 \ln p_2 + \varphi_2 p_2 \\ &+ \left. \varphi_2(1-p_2)^2 \sum_{r_{2j}=1}^{\infty} p_2^{r_{2j}-1} \ln \left(\frac{\sigma_{r_{2j}}}{\delta_{r_{2j}}} \right) \right\} \end{aligned} \quad (45)$$

and the equation of state is

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} [\ln(1-\tilde{\rho}) + (\varphi_1 p_1 + \varphi_2 p_2) \tilde{\rho}] = 0 \quad (46)$$

Chemical potentials

Chemical potentials μ_i are related to the Gibbs free energy by:

$$\mu_i \equiv \left. \frac{\partial G}{\partial N_i} \right|_{T, P, N'} \quad (47)$$

$$G = \sum N_i \mu_i \quad (48)$$

where the subscript N' indicates that all other mole

numbers except N_i are to be held constant.

$$\text{In the mixing system, } N_i = N_{i1} + N_{i2} + \dots + N_{in} = \sum_j N_{ij}.$$

If it is assumed that

$$N_{i1}:N_{i2}:\dots:N_{in} = q_{i1}:q_{i2}:\dots:q_{in} \quad (49)$$

then

$$N_{ij} = N_{i1}q_{ij}/q_{i1} \quad (50)$$

From the above, we have

$$\begin{aligned} N_i &= \sum_j N_{ij} = \sum_j N_{i1}q_{ij}/q_{i1} \\ &= N_{i1} \sum_j q_{ij}/q_{i1} = N_{i1}q_i/q_{i1} \end{aligned} \quad (51)$$

where

$$q_i = q_{i1} + q_{i2} + \dots + q_{in} = \sum_j q_{ij} \quad (52)$$

Thus

$$N_{i1} = \frac{q_{i1}}{q_i} N_i \quad (53)$$

From equation (53), we obtain:

$$N_{ij} = \frac{q_{ij}}{q_i} N_i \quad (54)$$

Using equation (54), we have the following equations:

$$\varphi_{ij} = \frac{1}{rN} r_{ij} \frac{q_{ij}}{q_i} N_i \quad (55)$$

$$rN = \sum_{ij} r_{ij} N_{ij} = \sum_i r_i N_i \quad (56)$$

$$\begin{aligned} \varepsilon^* &= \sum_k \sum_l \varphi_k \varphi_l \varepsilon_{kl}^* \\ &= \frac{1}{(rN)^2} \sum_k r_k N_k \sum_l r_l N_l \varepsilon_{kl}^* \end{aligned} \quad (57)$$

$$\begin{aligned} \tilde{G} &= -\tilde{p} + \frac{\tilde{P}}{\tilde{p}} \\ &+ \tilde{T} \left[\frac{1-\tilde{p}}{\tilde{p}} \ln(1-\tilde{p}) + \frac{1}{r} \ln \tilde{p} + \sum_{ij} \frac{q_{ij}}{r_i q_i} \varphi_i \ln \left(\frac{r_{ij} q_{ij}}{\omega_{ij} r_i q_i} \varphi_i \right) \right] \end{aligned} \quad (58)$$

where

$$r_i = \sum_j r_{ij} q_{ij}/q_i \quad (59)$$

$$\varphi_\beta = \sum_j \varphi_{\beta j} = \sum_j \frac{1}{rN} r_{\beta j} \frac{q_{\beta j}}{q_\beta} N_\beta = \frac{1}{rN} r_\beta N_\beta \quad (\beta = k, l) \quad (60)$$

$$\begin{aligned} \frac{1}{r} &= \sum_{ij} N_{ij} / \sum_{ij} r_{ij} N_{ij} = \sum_i N_i / \sum_i r_i N_i \\ &= \sum_{ij} \varphi_{ij} / r_{ij} = \sum_i \varphi_i / r_i \end{aligned} \quad (61)$$

Thus, the chemical potential μ_i is obtained by:

$$\mu_i = \frac{\partial G}{\partial N_i} \Big|_{T,P,N'} = \frac{\partial}{\partial N_i} (rN\varepsilon^* \tilde{G})$$

$$= \varepsilon^* \tilde{G} \frac{\partial}{\partial N_i} (rN) + rN \tilde{G} \frac{\partial \varepsilon^*}{\partial N_i} + rN \varepsilon^* \frac{\partial \tilde{G}}{\partial N_i} \quad (62)$$

where $\partial(rN)/\partial N_i$, $\partial\varepsilon^*/\partial N_i$ and $\partial\tilde{G}/\partial N_i$ are calculated in Appendix A. For a binary mixture, i , l and k are equal to 1 or 2.

If both pure components (polymer fluid) possess the Flory distribution³⁴ in the binary mixture, then:

$$\begin{aligned} \mu_1 &= \frac{\partial G}{\partial \sum_{r_{ij}} N_{r_{ij}}} \Big|_{T,P, \sum_{r_{ij}} N_{r_{ij}}} = \frac{\partial G}{\partial N_{I1}} \Big|_{T,P, N_{II}} \\ &= \varepsilon^* \tilde{G} \frac{\partial}{\partial N_1} (rN) + rN \tilde{G} \frac{\partial \varepsilon^*}{\partial N_1} + rN \varepsilon^* \frac{\partial \tilde{G}}{\partial N_1} \end{aligned} \quad (63)$$

and

$$\begin{aligned} \mu_2 &= \frac{\partial G}{\partial \sum_{r_{ij}} N_{r_{ij}}} \Big|_{T,P, \sum_{r_{ij}} N_{r_{ij}}} = \frac{\partial G}{\partial N_{II}} \Big|_{T,P, N_I} \\ &= \varepsilon^* \tilde{G} \frac{\partial}{\partial N_{II}} (rN) + rN \tilde{G} \frac{\partial \varepsilon^*}{\partial N_{II}} + rN \varepsilon^* \frac{\partial \tilde{G}}{\partial N_{II}} \end{aligned} \quad (64)$$

where

$$N_I = \sum_{r_{ij}} N_{r_{ij}} \quad N_{II} = \sum_{r_{ij}} N_{r_{ij}} \quad (65)$$

$$\varepsilon^* = \varphi_1^2 \varepsilon_{11}^* + 2\varphi_1 \varphi_2 \varepsilon_{12}^* + \varphi_2^2 \varepsilon_{22}^* \quad (66)$$

and $\partial(rN)/\partial N_1$, $\partial\varepsilon^*/\partial N_1$, $\partial\tilde{G}/\partial N_1$, $\partial(rN)/\partial N_{II}$, $\partial\varepsilon^*/\partial N_{II}$ and $\partial\tilde{G}/\partial N_{II}$ are calculated in Appendix B.

BINARY MIXTURES

General binary mixture

Stability criteria. The thermodynamic stability of a homogeneous phase of a single component system requires that the compressibility and constant volume heat capacity be positive, i.e.

$$-\frac{\partial V}{\partial P} \Big|_T > 0; \quad -\frac{\partial E}{\partial T} \Big|_V > 0 \quad (67)$$

The stability of a homogeneous phase in a binary mixture requires, in addition to the above two conditions, the following:

$$\frac{\partial \mu_1}{\partial x_1} > 0; \quad \frac{\partial \mu_2}{\partial x_2} > 0; \quad \frac{\partial \mu_1}{\partial x_2} = \frac{\partial \mu_2}{\partial x_1} < 0 \quad (68)$$

According to the stability conditions (68), we have the same stability criteria as equation (69), i.e.

$$\frac{\partial \mu_1}{\partial N_1} > 0 \quad \text{or} \quad \frac{\partial \mu_2}{\partial N_2} > 0 \quad (69)$$

where

$$\begin{aligned} \frac{\partial \mu_1}{\partial N_1} &= 2\tilde{G} \frac{\partial \varepsilon^*}{\partial N_1} \frac{\partial}{\partial N_1} (rN) + 2\varepsilon^* \frac{\partial \tilde{G}}{\partial N_1} \frac{\partial}{\partial N_1} (rN) \\ &+ 2rN \frac{\partial \tilde{G}}{\partial N_1} \frac{\partial \varepsilon^*}{\partial N_1} + rN \tilde{G} \frac{\partial^2 \varepsilon^*}{\partial N_1^2} + rN \varepsilon^* \frac{\partial^2 \tilde{G}}{\partial N_1^2} \end{aligned} \quad (70)$$

$$\begin{aligned} \frac{\partial \mu_2}{\partial N_2} = & 2\tilde{G} \frac{\partial \varepsilon^*}{\partial N_2} \frac{\partial}{\partial N_2} (rN) + 2\varepsilon^* \frac{\partial \tilde{G}}{\partial N_2} \frac{\partial}{\partial N_2} (rN) \\ & + 2rN \frac{\partial \tilde{G}}{\partial N_2} \frac{\partial \varepsilon^*}{\partial N_2} + rN\tilde{G} \frac{\partial^2 \varepsilon^*}{\partial N_2^2} + rN\varepsilon^* \frac{\partial^2 \tilde{G}}{\partial N_2^2} \end{aligned} \quad (71)$$

and $\partial^2 \varepsilon^*/\partial N_1^2$, $\partial^2 \tilde{G}/\partial N_1^2$, $\partial^2 \varepsilon^*/\partial N_2^2$ and $\partial^2 \tilde{G}/\partial N_2^2$ are calculated in Appendix A.

Instability and the spinodal. If the above inequality (69) is not satisfied, a binary fluid mixture will phase-separate into two fluid phases. The curve that separates (meta)stable and unstable regimes is called the spinodal, i.e.

$$\begin{aligned} \frac{\partial \mu_1}{\partial N_1} = & 2\tilde{G} \frac{\partial \varepsilon^*}{\partial N_1} \frac{\partial}{\partial N_1} (rN) + 2\varepsilon^* \frac{\partial \tilde{G}}{\partial N_1} \frac{\partial}{\partial N_1} (rN) + 2rN \frac{\partial \tilde{G}}{\partial N_1} \frac{\partial \varepsilon^*}{\partial N_1} \\ & + rN\tilde{G} \frac{\partial^2 \varepsilon^*}{\partial N_1^2} + rN\varepsilon^* \frac{\partial^2 \tilde{G}}{\partial N_1^2} = 0 \end{aligned} \quad (72)$$

or

$$\begin{aligned} \frac{\partial \mu_2}{\partial N_2} = & 2\tilde{G} \frac{\partial \varepsilon^*}{\partial N_2} \frac{\partial}{\partial N_2} (rN) + 2\varepsilon^* \frac{\partial \tilde{G}}{\partial N_2} \frac{\partial}{\partial N_2} (rN) + 2rN \frac{\partial \tilde{G}}{\partial N_2} \frac{\partial \varepsilon^*}{\partial N_2} \\ & + rN\tilde{G} \frac{\partial^2 \varepsilon^*}{\partial N_2^2} + rN\varepsilon^* \frac{\partial^2 \tilde{G}}{\partial N_2^2} = 0 \end{aligned} \quad (73)$$

In the above spinodal, we can obtain:

$$T = T(P, \varphi_1, \varphi_2) \quad (74)$$

$$\varphi_1 + \varphi_2 = 1 \quad (75)$$

Thus, when P is known, the functional relation of T and φ_1 or T and φ_2 can be obtained because there are three unknown variables and two equations. According to the above description, the spinodal curve ($T \sim \varphi_1$ or φ_2) can be drawn. The spinodal curve is the boundary of metastable and unstable regimes in a fluid mixture.

Phase equilibrium and the binodal. Equilibrium between two phases in a binary fluid mixture is determined by the following conditions on the chemical potentials:

$$\mu'_1 = \mu''_1 \quad (76)$$

$$\mu'_2 = \mu''_2 \quad (77)$$

where the prime denotes one phase and double prime denotes the second phase. The locus of points (a surface) that satisfy these conditions is called the binodal. The chemical potentials in both phases must also satisfy inequality (69).

Equations (76) and (77) can be used to evaluate the binodal curve for two polydisperse polymers. Setting the chemical potentials of each component equal in both phases, one obtains two equations:

$$\mu'_1(T, P, \varphi'_1) = \mu''_1(T, P, \varphi''_1) \quad (78)$$

$$\mu'_2(T, P, \varphi'_2) = \mu''_2(T, P, \varphi''_2) \quad (79)$$

where

$$\varphi'_1 + \varphi'_2 = 1 \quad \varphi''_1 + \varphi''_2 = 1 \quad (80)$$

If there are different T values when P is fixed, relevant

φ'_1 , φ''_1 , φ'_2 and φ''_2 can be solved by equations (78), (79) and (80). Besides the above discussion, it is essential to consider the following

$$\frac{\partial \mu_1}{\partial N_1} = 0 \quad \text{or} \quad \frac{\partial \mu_2}{\partial N_2} = 0 \quad (81)$$

From equation (81), φ_b and φ_c can be solved and let $\varphi_b < \varphi_c$. If the following equations are given:

$$\mu'_1(T, P, \varphi_1) = \mu''_1(T, P, \varphi_c) \quad (82)$$

$$\mu'_2(T, P, 1 - \varphi_1) = \mu''_2(T, P, 1 - \varphi_b) \quad (83)$$

From equation (82) we obtain $\varphi_1 = \varphi_a$ and let $\varphi_a < \varphi_b$. From equation (83) we also obtain $\varphi_1 = \varphi_d$ and let $\varphi_c < \varphi_d$.

Let φ'_1 and φ''_1 be such that $\varphi_a \leq \varphi'_1 \leq \varphi_b$ and $\varphi_c \leq \varphi''_1 \leq \varphi_d$. Then, according to equations (78), (79) and (80), φ'_1 and φ''_1 or φ'_2 and φ''_2 are solved. In general, $\varphi'_1 \neq \varphi''_1$ or $\varphi'_2 \neq \varphi''_2$ (where $\varphi'_1 \leq \varphi''_1$ or $\varphi'_2 \leq \varphi''_2$). However, when the critical point is approached, $\varphi'_1 = \varphi''_1$ or $\varphi'_2 = \varphi''_2$. The curve of $T \sim \varphi'_1(\varphi''_1)$ or $T \sim \varphi'_2(\varphi''_2)$ is called the binodal curve. For the above reason, the binodal curves are very difficult to solve even with a computer.

Special binary mixture

Stability criteria. If both pure components obey the Flory distribution in the binary mixture, then according to the above discussion we can derive the following stability criteria:

$$\begin{aligned} \frac{\partial \mu_1}{\partial N_1} = & 2\tilde{G} \frac{\partial \varepsilon^*}{\partial N_1} \frac{\partial}{\partial N_1} (rN) + 2\varepsilon^* \frac{\partial \tilde{G}}{\partial N_1} \frac{\partial}{\partial N_1} (rN) + 2rN \frac{\partial \tilde{G}}{\partial N_1} \frac{\partial \varepsilon^*}{\partial N_1} \\ & + rN\tilde{G} \frac{\partial^2 \varepsilon^*}{\partial N_1^2} + rN\varepsilon^* \frac{\partial^2 \tilde{G}}{\partial N_1^2} > 0 \end{aligned} \quad (84)$$

or

$$\begin{aligned} \frac{\partial \mu_2}{\partial N_{II}} = & 2\tilde{G} \frac{\partial \varepsilon^*}{\partial N_{II}} \frac{\partial}{\partial N_{II}} (rN) + 2\varepsilon^* \frac{\partial \tilde{G}}{\partial N_{II}} \frac{\partial}{\partial N_{II}} (rN) + 2rN \frac{\partial \tilde{G}}{\partial N_{II}} \frac{\partial \varepsilon^*}{\partial N_{II}} \\ & + rN\tilde{G} \frac{\partial^2 \varepsilon^*}{\partial N_{II}^2} + rN\varepsilon^* \frac{\partial^2 \tilde{G}}{\partial N_{II}^2} > 0 \end{aligned} \quad (85)$$

where $\partial^2 \varepsilon^*/\partial N_1^2$, $\partial^2 \tilde{G}/\partial N_1^2$, $\partial^2 \varepsilon^*/\partial N_{II}^2$ and $\partial^2 \tilde{G}/\partial N_{II}^2$ are calculated in Appendix B.

Instability and the spinodal. As above, the spinodal is

$$\begin{aligned} 2\tilde{G} \frac{\partial \varepsilon^*}{\partial N_1} \frac{\partial}{\partial N_1} (rN) + 2\varepsilon^* \frac{\partial \tilde{G}}{\partial N_1} \frac{\partial}{\partial N_1} (rN) + 2rN \frac{\partial \tilde{G}}{\partial N_1} \frac{\partial \varepsilon^*}{\partial N_1} \\ + rN\tilde{G} \frac{\partial^2 \varepsilon^*}{\partial N_1^2} + rN\varepsilon^* \frac{\partial^2 \tilde{G}}{\partial N_1^2} = 0 \end{aligned} \quad (86)$$

or

$$\begin{aligned} 2\tilde{G} \frac{\partial \varepsilon^*}{\partial N_{II}} \frac{\partial}{\partial N_{II}} (rN) + 2\varepsilon^* \frac{\partial \tilde{G}}{\partial N_{II}} \frac{\partial}{\partial N_{II}} (rN) + 2rN \frac{\partial \tilde{G}}{\partial N_{II}} \frac{\partial \varepsilon^*}{\partial N_{II}} \\ + rN\tilde{G} \frac{\partial^2 \varepsilon^*}{\partial N_{II}^2} + rN\varepsilon^* \frac{\partial^2 \tilde{G}}{\partial N_{II}^2} = 0 \end{aligned} \quad (87)$$

According to equations (86) or (87), we can obtain the functional relation of T and φ_1 or T and φ_2 when P is fixed. The $T-\varphi_1$ or $T-\varphi_2$ curve is called the spinodal curve.

Phase equilibrium and the binodal. The binodal is easily obtained by interchanging the equations concerning general binary mixture and the equations

concerning special binary mixture in the derivation process.

DISCUSSION AND CONCLUSION

From the above derivation, it is known that a binary polydisperse polymer mixture is characterized by a knowledge of the pure polydisperse polymer system and the interaction energy, and the thermodynamic properties of ternary and higher order mixtures are completely defined in terms of the pure fluid polymer parameters and the binary interaction energies. At the same time, it can also be seen that the introduction of polydispersity makes the statistical thermodynamics complicated and some equations, e.g. chemical potentials, spinodals and binodals, become very complex. Though it is very difficult to see directly the influence of polydispersity on them, we can be sure that it has no effect in solving the thermodynamic questions of polydisperse polymer blends even if a correction factor is introduced to reduce it to a monodisperse blend.

When every component is turned into a monodisperse fluid, all the above results can be reduced to the LF theory for monodisperse fluid mixtures¹⁴. For example, when $r_{ij}=r_i$, $\sigma_{ij}=\sigma_i$, $\delta_{ij}=\delta_i$, $\varphi_{ij}=\varphi_i$ and the summation of j is deprived, the following results are obtained¹⁴. For the system of n components, we have:

$$\tilde{G} = -\tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T} \left[(\tilde{v}-1) \ln(1-\tilde{\rho}) + \frac{1}{r} \ln \tilde{\rho} + \sum_i \frac{\varphi_i}{r_i} \ln \frac{\varphi_i}{\omega_i} \right] \quad (88)$$

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r}\right) \tilde{\rho} \right] = 0 \quad (\text{equation of state}) \quad (89)$$

and

$$\mu_i = \left. \frac{\partial G}{\partial N_i} \right|_{T,P,N'} \quad (90)$$

where

$$r = \sum_i r_i x_i \quad (91)$$

For the binary mixture, the spinodal is given by:

$$\frac{\partial^2 g}{\partial \varphi_1^2} = 0 \quad (92)$$

where

$$g = \varepsilon^* \tilde{G} \quad (93)$$

As another example, when $p_1=p_2=0$ in the binary mixture with Flory distribution ($p_1=p_2=0$, then both components are monodisperse), we have:

$$\begin{aligned} \tilde{G} = & -\tilde{\rho} + \tilde{P}\tilde{v} \\ & + \tilde{T} \left[(\tilde{v}-1) \ln(1-\tilde{\rho}) + \ln \tilde{\rho} + \varphi_1 \ln \frac{\varphi_1}{\omega_1} + \varphi_2 \ln \frac{\varphi_2}{\omega_2} \right] \end{aligned} \quad (94)$$

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \ln(1-\tilde{\rho}) = 0 \quad (\text{equation of state}) \quad (95)$$

where $r_1=r_2=r=1$. The chemical potentials and spinodal are the same as above.

The main conclusions of this paper are summarized as follows:

1. Thermodynamic properties of polydisperse polymer blends are completely defined in terms of the pure polydisperse fluid polymer parameters and the binary interaction energies.
2. The polydispersity has a great influence on the thermodynamic treatment of mixtures. However, the magnitude of its effect is far from clear due to the complexity of the relevant equations.
3. Our theory is a generalized theory and the LF theory of Sanchez for a monodisperse fluid mixture is a special case of our theory.

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REFERENCES

- 1 Scott, R. L. *J. Chem. Phys.* 1949, **17**, 279
- 2 Tompa, H. *Trans. Faraday Soc.* 1949, **45**, 1142
- 3 Flory, P. J. *J. Chem. Phys.* 1941, **9**, 660
- 4 Flory, P. J. *J. Chem. Phys.* 1942, **10**, 51
- 5 Huggins, M. L. *J. Chem. Phys.* 1941, **9**, 440
- 6 Huggins, M. L. *Ann. NY Acad. Sci.* 1942, **43**, 1
- 7 Tompa, H. 'Polymer Solutions', Butterworth, London, 1956
- 8 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1953, Ch. 12
- 9 Flory, P. J., Orwoll, R. A. and Vrij, A. *J. Am. Chem. Soc.* 1964, **86**, 3515
- 10 Flory, P. J. *J. Am. Chem. Soc.* 1965, **87**, 1833
- 11 Eichinger, B. E. and Flory, P. J. *Trans. Faraday Soc.* 1968, **64**, 2035
- 12 Flory, P. J. *Discuss. Faraday Soc.* 1970, **49**, 7
- 13 Sanchez, I. C. and Lacombe, R. H. *J. Phys. Chem.* 1976, **80**, 2352
- 14 Lacombe, R. H. and Sanchez, I. C. *J. Phys. Chem.* 1976, **80**, 2568
- 15 Sanchez, I. C. and Lacombe, R. H. *Macromolecules* 1978, **11**, 1145
- 16 McMaster, L. P. *Macromolecules* 1973, **6**, 760
- 17 Panayiotou, C. and Vera, J. H. *Fluid Phase Equilib.* 1980, **5**, 55
- 18 Renuncio, J. A. R. and Prausnitz, J. M. *Macromolecules* 1976, **9**, 895
- 19 Sanchez, I. C. and Balazs, A. C. *Macromolecules* 1989, **22**, 2325
- 20 ten Brinke, G. and Karasz, F. E. *Macromolecules* 1984, **17**, 815
- 21 Koningsveld, R. and Staverman, A. J. *J. Polym. Sci., A-2* 1968, **6**, 325
- 22 Koningsveld, R. and Kleintjens, L. A. *Macromolecules* 1971, **4**, 637
- 23 Koningsveld, R., Chermin, H. A. G. and Gordon, M. *Proc. R. Soc. London* 1973, **A319**, 331
- 24 Koningsveld, R. and Kleintjens, L. A. 'Macromolecular Chemistry', Vol. I, Butterworth, London, 1973
- 25 Joanny, J. F. *Comptes Rendus Seanc. Sci.* 1978, **B286**, 89
- 26 Kleintjens, L. A. and Koningsveld, R. *Colloid Polym. Sci.* 1980, **258**, 711
- 27 Kleintjens, L. A. and Koningsveld, R. *J. Electrochem. Soc.* 1980, **127**, 2352
- 28 Kleintjens, L. A. *Fluid Phase Equilib.* 1983, **10**, 183
- 29 Koningsveld, R., Kleintjens, L. A. and Leblans-Vinck, A. M. *J. Phys. Chem.* 1987, **91**, 6423
- 30 An, L., Ma, R., Kou, X., Tang, X. and Jing, B. *Polymer* 1992, **33**, 2855
- 31 Guggenheim, E. A. 'Mixtures', Oxford University Press, London, 1952, Ch. X and XI
- 32 Guggenheim, E. A. *Proc. R. Soc. London, Ser. A* 1944, **183**, 203
- 33 Guggenheim, E. A. 'Application of Statistical Mechanics', Oxford University Press, London, 1966, Ch. 4 and 7
- 34 Flory, P. J. *J. Am. Chem. Soc.* 1936, **58**, 1877

APPENDIX A

According to equations (55), (56), (57), (58) and (61) we obtain:

$$\frac{\partial}{\partial N_i}(rN) = r_i \quad (\text{A1})$$

$$\frac{\partial \varepsilon^*}{\partial N_i} = \frac{2r_i}{rN} \left(\sum \varphi_l \varepsilon_{il}^* - \varepsilon^* \right) \quad (\text{A2})$$

$$\begin{aligned} \frac{\partial \tilde{G}}{\partial N_i} = & \left[-1 - \frac{\tilde{P}}{\tilde{\rho}^2} - \frac{\tilde{T}}{\tilde{\rho}^2} \ln(1-\tilde{\rho}) - \frac{\tilde{T}}{\tilde{\rho}} + \frac{\tilde{T}}{r\tilde{\rho}} \right] \frac{\partial \tilde{\rho}}{\partial N_i} + \frac{1}{\tilde{\rho}} \frac{\partial \tilde{P}}{\partial N_i} \\ & + \left[\frac{1-\tilde{\rho}}{\tilde{\rho}} \ln(1-\tilde{\rho}) + \frac{1}{r} \ln \tilde{\rho} + \sum_i \frac{\varphi_i}{r_i} \ln \varphi_i \right. \\ & + \sum_i \varphi_i \sum_j \frac{q_{ij}}{r_i q_i} \ln \left(\frac{r_{ij} q_{ij}}{\omega_{ij} r_i q_i} \right) \left. \right] \frac{\partial \tilde{T}}{\partial N_i} \\ & + \frac{\tilde{T}}{rN} \left[\left(1 - \frac{r_i}{r} \right) \ln \tilde{\rho} - r_i \sum_l \frac{\varphi_l}{r_l} \sum_j \frac{q_{lj}}{q_l} \ln \left(\frac{r_{lj} q_{lj}}{\omega_{lj} r_l q_l} \right) \right. \\ & \left. - r_i \sum_l \frac{\varphi_l}{r_l} (\ln \varphi_l + 1) + \sum_j \frac{q_{ij}}{q_i} \ln \left(\frac{r_{ij} q_{ij}}{\omega_{ij} r_i q_i} \right) + (\ln \varphi_i + 1) \right] \end{aligned} \quad (\text{A3})$$

From the equation of state (equation (41)), we have:

$$\frac{\partial \tilde{\rho}}{\partial N_i} = \frac{\frac{\tilde{T}\tilde{\rho}}{rN} \left(1 - \frac{r_i}{r} \right) - \frac{\partial \tilde{P}}{\partial N_i} - \left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r} \right) \tilde{\rho} \right] \frac{\partial \tilde{T}}{\partial N_i}}{2\tilde{\rho} - \frac{\tilde{T}}{1-\tilde{\rho}} + \tilde{T} \left(1 - \frac{1}{r} \right)} \quad (\text{A4})$$

where

$$\frac{\partial \tilde{P}}{\partial N_i} = \frac{1}{rN} \frac{P}{\varepsilon^{*2}} \left[r_i \varepsilon^* v^* - 2r_i v^* \sum_l \varphi_l \varepsilon_{il}^* + r_i^0 \varepsilon^* v_i^* \right] \quad (\text{A5})$$

$$\frac{\partial \tilde{T}}{\partial N_i} = -\frac{r_i}{rN} \frac{2kT}{\varepsilon^{*2}} \left(\sum_l \varphi_l \varepsilon_{il}^* - \varepsilon^* \right) \quad (\text{A6})$$

For a binary mixture, i and l are equal to 1 or 2 in equations (A1)–(A6).

According to equations (A2) and (A3), we have the following equations when $i=1$ or 2:

$$\frac{\partial^2 \varepsilon^*}{\partial N_a^2} = \frac{2r_a^2}{(rN)^2} (3\varepsilon^* + \varepsilon_{aa}^* - 4\varphi_1 \varepsilon_{a1}^* - 4\varphi_2 \varepsilon_{a2}^*) \quad (\text{A7})$$

$$\begin{aligned} \frac{\partial^2 \tilde{G}}{\partial N_a^2} = & \left[-1 - \frac{\tilde{T}}{\tilde{\rho}^2} \ln(1-\tilde{\rho}) - \frac{\tilde{P}}{\tilde{\rho}^2} - \frac{\tilde{T}}{\tilde{\rho}} + \frac{\tilde{T}}{r\tilde{\rho}} \right] \frac{\partial^2 \tilde{\rho}}{\partial N_a^2} + \frac{1}{\tilde{\rho}} \frac{\partial^2 \tilde{T}}{\partial N_a^2} \\ & + \left[\frac{1-\tilde{\rho}}{\tilde{\rho}} \ln(1-\tilde{\rho}) + \frac{1}{r} \ln \tilde{\rho} + \frac{\varphi_1}{r_1} \ln \varphi_1 \right. \\ & + \frac{\varphi_1}{r_1} \sum_j \frac{q_{1j}}{q_1} \ln \left(\frac{r_{1j} q_{1j}}{\omega_{1j} r_1 q_1} \right) + \frac{\varphi_2}{r_2} \ln \varphi_2 \\ & + \frac{\varphi_2}{r_2} \sum_j \frac{q_{2j}}{q_2} \ln \left(\frac{r_{2j} q_{2j}}{\omega_{2j} r_2 q_2} \right) \left. \right] \frac{\partial^2 \tilde{T}}{\partial N_a^2} \\ & + \left[\frac{2\tilde{P}}{\tilde{\rho}^3} + \frac{2\tilde{T} \ln(1-\tilde{\rho})}{\tilde{\rho}^3} + \frac{\tilde{T}}{\tilde{\rho}^2(1-\tilde{\rho})} + \frac{\tilde{T}}{\tilde{\rho}^2} - \frac{\tilde{T}}{r\tilde{\rho}^2} \right] \left(\frac{\partial \tilde{\rho}}{\partial N_a} \right)^2 \\ & - \frac{2}{\tilde{\rho}^2} \frac{\partial \tilde{\rho}}{\partial N_a} + 2 \left[-\frac{\ln(1-\tilde{\rho})}{\tilde{\rho}^2} - \frac{1}{\tilde{\rho}} + \frac{1}{r\tilde{\rho}} \right] \frac{\partial \tilde{\rho}}{\partial N_a} \frac{\partial \tilde{T}}{\partial N_a} \\ & + \frac{2}{rN} \frac{\tilde{T}}{\tilde{\rho}} \left(1 - \frac{r_a}{r} \right) \frac{\partial \tilde{\rho}}{\partial N_a} \end{aligned}$$

$$\begin{aligned} & + \frac{2}{rN} \left[\left(1 - \frac{r_a}{r} \right) \ln \tilde{\rho} - r_a \sum_{k=1}^2 \frac{\varphi_k}{r_k} \sum_j \frac{q_{kj}}{q_k} \ln \left(\frac{r_{kj} q_{kj}}{\omega_{kj} r_k q_k} \right) \right. \\ & \left. - r_a \sum_{k=1}^2 \frac{\varphi_k}{r_k} (\ln \varphi_k + 1) \right. \\ & \left. + \sum_j \frac{q_{aj}}{q_a} \ln \left(\frac{r_{aj} q_{aj}}{\omega_{aj} r_a q_a} \right) + (\ln \varphi_a + 1) \right] \\ & + \tilde{T} \left\{ \frac{\partial^2 \left(\frac{1}{r} \right)}{\partial N_a^2} \ln \tilde{\rho} + \frac{\partial^2}{\partial N_a^2} \left[\left(\sum_j \frac{\varphi_{1j}}{r_{1j}} \ln \frac{\varphi_{1j}}{\omega_{1j}} \right) \right. \right. \\ & \left. \left. + \left(\sum_j \frac{\varphi_{2j}}{r_{2j}} \ln \frac{\varphi_{2j}}{\omega_{2j}} \right) \right] \right\} \end{aligned} \quad (\text{A8})$$

where

$$\frac{\partial}{\partial N_a^2} \left(\frac{1}{r} \right) = -\frac{2r_a}{(rN)^2} \left(1 - \frac{r_a}{r} \right) \quad (\text{A9})$$

$$\begin{aligned} & \frac{\partial^2}{\partial N_a^2} \left[\left(\sum_j \frac{\varphi_{1j}}{r_{1j}} \ln \frac{\varphi_{1j}}{\omega_{1j}} \right) + \left(\sum_j \frac{\varphi_{2j}}{r_{2j}} \ln \frac{\varphi_{2j}}{\omega_{2j}} \right) \right] \\ & = \frac{r_a}{(rN)^2} \left[2r_a \sum_{k=1}^2 \frac{\varphi_k}{r_k} \sum_j \frac{q_{kj}}{q_k} \ln \left(\frac{r_{kj} q_{kj}}{\omega_{kj} r_k q_k} \right) + 2r_a \sum_{k=1}^2 \frac{\varphi_k}{r_k} (\ln \varphi_k + 1) \right. \\ & \left. - 2 \sum_j \frac{q_{aj}}{q_a} \ln \left(\frac{r_{aj} q_{aj}}{\omega_{aj} r_a q_a} \right) - 2(\ln \varphi_a + 1) + \frac{r_a}{r} + \frac{1-2\varphi_a}{\varphi_a} \right] \end{aligned} \quad (\text{A10})$$

From equations (A4) to (A6), we have:

$$\begin{aligned} \frac{\partial^2 \tilde{\rho}}{\partial N_a^2} = & \left\{ \frac{\partial^2 \tilde{P}}{\partial N_a^2} - \frac{\partial^2 \tilde{T}}{\partial N_a^2} \left[\ln(1-\tilde{\rho}) + \left(1 - \frac{1}{r} \right) \tilde{\rho} \right] \right. \\ & - \left[2 - \frac{\tilde{T}}{(1-\tilde{\rho})^2} \right] \left(\frac{\partial \tilde{\rho}}{\partial N_a} \right)^2 \\ & + 2 \left[\frac{1}{1-\tilde{\rho}} - \left(1 - \frac{1}{r} \right) \right] \frac{\partial \tilde{\rho}}{\partial N_a} \frac{\partial \tilde{T}}{\partial N_a} + \frac{2\tilde{T}}{rN} \left(1 - \frac{r_a}{r} \right) \frac{\partial \tilde{\rho}}{\partial N_a} \\ & + \frac{2\tilde{\rho}}{rN} \left(1 - \frac{r_a}{r} \right) \frac{\partial \tilde{T}}{\partial N_a} - \frac{2r_a}{(rN)^2} \tilde{T} \tilde{\rho} \left(1 - \frac{r_a}{r} \right) \left. \right\} \\ & \times \left\{ 2\tilde{\rho} - \frac{\tilde{T}}{1-\tilde{\rho}} + \tilde{T} \left(1 - \frac{1}{r} \right) \right\}^{-1} \end{aligned} \quad (\text{A11})$$

$$\begin{aligned} \frac{\partial^2 \tilde{P}}{\partial N_a^2} = & \frac{r_a P}{(rN \varepsilon^{*2})^2} \left[\left(3 - \frac{4}{\varepsilon^*} \sum_{l=1}^2 \varphi_l \varepsilon_{al}^* \right) \left(r_a \varepsilon^* v^* - 2r_a v^* \sum_{l=1}^2 \varphi_l \varepsilon_{al}^* \right. \right. \\ & \left. \left. + r_a^0 \varepsilon^* v_a^* \right) + 2 \left(\sum_{l=1}^2 \varphi_l \varepsilon_{al}^* - \varepsilon^* \right) (r_a v^* + r_a^0 v_a^*) \right. \\ & \left. + (r_a^0 v_a^* - r_a v^*) \left(\varepsilon^* - 2 \sum_{l=1}^2 \varphi_l \varepsilon_{al}^* \right) \right. \\ & \left. - 2r_a v^* \left(\varepsilon_{aa}^* - \sum_{l=1}^2 \varphi_l \varepsilon_{al}^* \right) \right] \end{aligned} \quad (\text{A12})$$

$$\begin{aligned} \frac{\partial^2 \tilde{T}}{\partial N_a^2} = & \frac{2kT r_a^2}{(rN \varepsilon^{*2})^2} \left[\frac{4}{\varepsilon^*} \left(\sum_{l=1}^2 \varphi_l \varepsilon_{al}^* - \varepsilon^* \right)^2 \right. \\ & \left. + 3 \left(\sum_{l=1}^2 \varphi_l \varepsilon_{al}^* - \varepsilon^* \right) - \left(\varepsilon_{aa}^* + \sum_{l=1}^2 \varphi_l \varepsilon_{al}^* \right) \right] \end{aligned} \quad (\text{A13})$$

In equations (A7)–(A13), $a=1$ or 2.

APPENDIX B

For a binary mixture of the Flory distribution, the following can be given by:

$$rN = N_1^* + N_2^* \tag{B1}$$

$$N_1 = N_1^*(1 - p_1) \quad N_{II} = N_2^*(1 - p_2) \tag{B2}$$

$$\varphi_1 = \frac{N_1^*}{rN} \quad \varphi_2 = \frac{N_2^*}{rN} \tag{B3}$$

Then, we can obtain the following functional relations:

$$rN = f_1(T, P, N_1, N_{II}) \tag{B4}$$

$$\varepsilon^* = f_2(T, P, N_1, N_{II}) \tag{B5}$$

$$\tilde{G} = f_3(T, P, N_1, N_{II}) \tag{B6}$$

Thus, we have:

$$\frac{\partial}{\partial N_1}(rN) = \frac{1}{1 - p_1} \tag{B7}$$

$$\frac{\partial \varepsilon^*}{\partial N_1} = \frac{2\varphi_2}{rN(1 - p_1)} [\varphi_1(\varepsilon_{11}^* - \varepsilon_{12}^*) + \varphi_2(\varepsilon_{12}^* - \varepsilon_{22}^*)] \tag{B8}$$

$$\begin{aligned} \frac{\partial \tilde{G}}{\partial N_1} = & \left\{ -1 - \frac{\tilde{P}}{\tilde{\rho}^2} - \frac{\tilde{T} \ln(1 - \tilde{\rho})}{\tilde{\rho}^2} - \frac{\tilde{T}}{\tilde{\rho}} \right. \\ & + \left. \frac{\tilde{T}[\varphi_1(1 - p_1) + \varphi_2(1 - p_2)]}{\tilde{\rho}} \right\} \frac{\partial \tilde{\rho}}{\partial N_1} \\ & + \frac{1}{\tilde{\rho}} \frac{\partial \tilde{P}}{\partial N_1} + \frac{\partial \tilde{T}}{\partial N_1} \left\{ \frac{1 - \tilde{\rho}}{\tilde{\rho}} \ln(1 - \tilde{\rho}) \right. \\ & + [\varphi_1(1 - p_1) + \varphi_2(1 - p_2)] \ln \tilde{\rho} \\ & + \varphi_1(1 - p_1) \ln \varphi_1(1 - p_1)^2 + \varphi_1 p_1 \ln p_1 \\ & + \varphi_1 p_1 + \varphi_1(1 - p_1)^2 \sum_{r_{1j}=1}^{\infty} p_1^{r_{1j}-1} \ln \frac{\sigma_{r_{1j}}}{\delta_{r_{1j}}} \\ & + \varphi_2(1 - p_2) \ln \varphi_2(1 - p_2)^2 + \varphi_2 p_2 \ln p_2 + \varphi_2 p_2 \\ & + \varphi_2(1 - p_2)^2 \sum_{r_{2j}=1}^{\infty} p_2^{r_{2j}-1} \ln \frac{\sigma_{r_{2j}}}{\delta_{r_{2j}}} \left. \right\} \\ & + \frac{\tilde{T}\varphi_2}{rN(1 - p_1)} \left\{ (p_2 - p_1) \ln \tilde{\rho} + (1 - p_1) \ln \varphi_1(1 - p_1)^2 \right. \\ & + p_1 \ln p_1 + (1 - p_1)^2 \sum_{r_{1j}} p_1^{r_{1j}-1} \ln \frac{\sigma_{r_{1j}}}{\delta_{r_{1j}}} \\ & - (1 - p_2) \ln \varphi_2(1 - p_2)^2 - p_2 \ln p_2 \\ & \left. - (1 - p_2)^2 \sum_{r_{2j}} p_2^{r_{2j}-1} \ln \frac{\sigma_{r_{2j}}}{\delta_{r_{2j}}} \right\} \tag{B9} \end{aligned}$$

$$\begin{aligned} \frac{\partial^2 \varepsilon^*}{\partial N_1^2} = & \frac{2\varphi_2}{[rN(1 - p_1)]^2} \{ \varphi_2(\varepsilon_{11}^* - 2\varepsilon_{12}^* + \varepsilon_{22}^*) \\ & - 2[\varphi_1(\varepsilon_{11}^* - \varepsilon_{12}^*) + \varphi_2(\varepsilon_{12}^* - \varepsilon_{22}^*)] \} \tag{B10} \end{aligned}$$

$$\begin{aligned} \frac{\partial^2 \tilde{G}}{\partial N_1^2} = & \left\{ -1 - \frac{\tilde{P}}{\tilde{\rho}^2} - \frac{\tilde{T} \ln(1 - \tilde{\rho})}{\tilde{\rho}^2} - \frac{\tilde{T}}{\tilde{\rho}} \right. \\ & + \left. \frac{\tilde{T}}{\tilde{\rho}} [\varphi_1(1 - p_1) + \varphi_2(1 - p_2)] \right\} \frac{\partial^2 \tilde{\rho}}{\partial N_1^2} \\ & + \frac{1}{\tilde{\rho}} \frac{\partial^2 \tilde{P}}{\partial N_1^2} + \frac{\partial^2 \tilde{T}}{\partial N_1^2} \left\{ \frac{1 - \tilde{\rho}}{\tilde{\rho}} \ln(1 - \tilde{\rho}) \right. \end{aligned}$$

$$\begin{aligned} & + [\varphi_1(1 - p_1) + \varphi_2(1 - p_2)] \ln \tilde{\rho} \\ & + \varphi_1(1 - p_1) \ln \varphi_1(1 - p_1)^2 + \varphi_1 p_1 \ln p_1 \\ & + \varphi_1 p_1 + \varphi_1(1 - p_1)^2 \sum_{r_{1j}} p_1^{r_{1j}-1} \ln \frac{\sigma_{r_{1j}}}{\delta_{r_{1j}}} \\ & + \varphi_2(1 - p_2) \ln \varphi_2(1 - p_2)^2 + \varphi_2 p_2 \ln p_2 \\ & + \varphi_2 p_2 + \varphi_2(1 - p_2)^2 \sum_{r_{2j}} p_2^{r_{2j}-1} \ln \frac{\sigma_{r_{2j}}}{\delta_{r_{2j}}} \left. \right\} \\ & + \left\{ \frac{2\tilde{P}}{\tilde{\rho}^3} + \frac{2\tilde{T}}{\tilde{\rho}^3} \ln(1 - \tilde{\rho}) + \frac{\tilde{T}}{\tilde{\rho}^2(1 - \tilde{\rho})} + \frac{\tilde{T}}{\tilde{\rho}^2} \right. \\ & - \left. \frac{\tilde{T}}{\tilde{\rho}^2} [\varphi_1(1 - p_1) + \varphi_2(1 - p_2)] \right\} \\ & \times \left(\frac{\partial \tilde{\rho}}{\partial N_1} \right)^2 - \frac{2}{\tilde{\rho}^2} \frac{\partial \tilde{\rho}}{\partial N_1} \frac{\partial \tilde{P}}{\partial N_1} + 2 \left\{ -\frac{1}{\tilde{\rho}^2} \ln(1 - \tilde{\rho}) - \frac{1}{\tilde{\rho}} \right. \\ & + \left. \frac{1}{\tilde{\rho}} [\varphi_1(1 - p_1) + \varphi_2(1 - p_2)] \right\} \frac{\partial \tilde{\rho}}{\partial N_1} \frac{\partial \tilde{T}}{\partial N_1} \\ & + \frac{2\varphi_1(p_2 - p_1)\tilde{T}}{rN(1 - p_1)\tilde{\rho}} \frac{\partial \tilde{\rho}}{\partial N_1} + 2 \left\{ (p_2 - p_1) \ln \tilde{\rho} \right. \\ & + (1 - p_1) \ln \varphi_1(1 - p_1)^2 + p_1 \ln p_1 \\ & + (1 - p_1)^2 \sum_{r_{1j}} p_1^{r_{1j}-1} \ln \frac{\sigma_{r_{1j}}}{\delta_{r_{1j}}} - (1 - p_2) \ln \varphi_2(1 - p_2)^2 \\ & - p_2 \ln p_2 - (1 - p_2)^2 \sum_{r_{2j}} p_2^{r_{2j}-1} \ln \frac{\sigma_{r_{2j}}}{\delta_{r_{2j}}} \left. \right\} \frac{\varphi_2}{rN(1 - p_1)} \frac{\partial \tilde{T}}{\partial N_1} \\ & + \frac{\varphi_2 \tilde{T}}{[rN(1 - p_1)]^2} \left\{ \varphi_2 \left[\frac{1 - p_1}{\varphi_1} + \frac{1 - p_2}{\varphi_2} \right] \right. \\ & - 2[(p_2 - p_1) \ln \tilde{\rho} + (1 - p_1) \ln \varphi_1(1 - p_1)^2 + p_1 \ln p_1 \\ & + (1 - p_1)^2 \sum_{r_{1j}} p_1^{r_{1j}-1} \ln \frac{\sigma_{r_{1j}}}{\delta_{r_{1j}}} - (1 - p_2) \ln \varphi_2(1 - p_2)^2 \\ & \left. - p_2 \ln p_2 - (1 - p_2)^2 \sum_{r_{2j}} p_2^{r_{2j}-1} \ln \frac{\sigma_{r_{2j}}}{\delta_{r_{2j}}} \right\} \tag{B11} \end{aligned}$$

where

$$\begin{aligned} \frac{\partial \tilde{\rho}}{\partial N_1} = & \frac{\varphi_2 \tilde{T} \tilde{\rho}}{rN(1 - p_1)} (p_2 - p_1) - \frac{\partial \tilde{P}}{\partial N_1} - \frac{\partial \tilde{T}}{\partial N_1} [\ln(1 - \tilde{\rho}) + (\varphi_1 p_1 + \varphi_2 p_2) \tilde{\rho}] \\ = & \frac{\tilde{T}}{2\tilde{\rho} - \frac{\tilde{T}}{1 - \tilde{\rho}}} + \tilde{T}(\varphi_1 p_1 + \varphi_2 p_2) \tag{B12} \end{aligned}$$

$$\begin{aligned} \frac{\partial \tilde{P}}{\partial N_1} = & \frac{P\varphi_2}{rN(1 - p_1)\varepsilon^{*2}} \\ & \times \{ \varepsilon^*(v_1^* - v_2^*) - 2v^*[\varphi_1(\varepsilon_{11}^* - \varepsilon_{12}^*) + \varphi_2(\varepsilon_{12}^* - \varepsilon_{22}^*)] \} \tag{B13} \end{aligned}$$

$$\frac{\partial \tilde{T}}{\partial N_1} = -\frac{2\varphi_2 kT}{rN(1 - p_1)\varepsilon^{*2}} [\varphi_1(\varepsilon_{11}^* - \varepsilon_{12}^*) + \varphi_2(\varepsilon_{12}^* - \varepsilon_{22}^*)] \tag{B14}$$

$$\begin{aligned}
 \frac{\partial^2 \tilde{\rho}}{\partial N_1^2} = & \left\{ -\frac{\partial^2 \tilde{P}}{\partial N_1^2} - \frac{\partial^2 \tilde{T}}{\partial N_1^2} [\ln(1-\tilde{\rho}) + (\varphi_1 p_1 + \varphi_2 p_2) \tilde{\rho}] \right. \\
 & + \left[\frac{\tilde{T}}{(1-\tilde{\rho})^2} - 2 \right] \left(\frac{\partial \tilde{\rho}}{\partial N_1} \right)^2 \\
 & + 2 \left[\frac{1}{1-\tilde{\rho}} - (\varphi_1 p_1 + \varphi_2 p_2) \right] \frac{\partial \tilde{T}}{\partial N_1} \frac{\partial \tilde{\rho}}{\partial N_1} \\
 & + \frac{2(p_2 - p_1) \varphi_2 \tilde{\rho}}{rN(1-p_1)} \frac{\partial \tilde{T}}{\partial N_1} + \frac{2(p_2 - p_1) \varphi_2 \tilde{T}}{rN(1-p_1)} \frac{\partial \tilde{\rho}}{\partial N_1} \\
 & - \frac{2(p_2 - p_1) \varphi_2 \tilde{T} \tilde{\rho}}{[rN(1-p_1)]^2} \left. \right\} \\
 & \times \left[2\tilde{\rho} - \frac{\tilde{T}}{1-\tilde{\rho}} + (\varphi_1 p_1 + \varphi_2 p_2) \tilde{T} \right]^{-1} \quad (B15)
 \end{aligned}$$

$$\begin{aligned}
 \frac{\partial^2 \tilde{P}}{\partial N_1^2} & = \frac{2P\varphi_2}{[rN(1-\rho_1)\varepsilon^*]^2} \left\{ \frac{4\varphi_2 v^*}{\varepsilon^*} [\varphi_1(\varepsilon_{11}^* - \varepsilon_{12}^*) + \varphi_2(\varepsilon_{12}^* - \varepsilon_{22}^*)]^2 \right. \\
 & + 2[v^* - \varphi_2(v_1^* - v_2^*)][\varphi_1(\varepsilon_{11}^* - \varepsilon_{12}^*) + \varphi_2(\varepsilon_{12}^* - \varepsilon_{22}^*)] \\
 & \left. - \varepsilon^*(v_1^* - v_2^*) - \varphi_2 v^*(\varepsilon_{11}^* - 2\varepsilon_{12}^* + \varepsilon_{22}^*) \right\} \quad (B16) \\
 \frac{\partial^2 \tilde{T}}{\partial N_1^2} & = \frac{2\varphi_2 kT}{[rN(1-\rho_1)\varepsilon^*]^2} \left\{ \frac{4\varphi_2}{\varepsilon^*} [\varphi_1(\varepsilon_{11}^* - \varepsilon_{12}^*) + \varphi_2(\varepsilon_{12}^* - \varepsilon_{22}^*)]^2 \right. \\
 & + 2[\varphi_1(\varepsilon_{11}^* - \varepsilon_{12}^*) + \varphi_2(\varepsilon_{12}^* - \varepsilon_{22}^*)] \\
 & \left. - \varphi_2(\varepsilon_{11}^* - 2\varepsilon_{12}^* + \varepsilon_{22}^*) \right\} \quad (B17)
 \end{aligned}$$

The expressions for $(\partial/\partial N_{II})(rN)$, $\partial\varepsilon^*/\partial N_{II}$, $\partial\tilde{G}/\partial N_{II}$, $\partial^2\varepsilon^*/\partial N_{II}^2$ and $\partial^2\tilde{G}/\partial N_{II}^2$ are easily obtained by interchanging the indices 1 and 2 or I and II.