Statistical thermodynamics of polydisperse polymer systems in the framework of lattice fluid model: Effect of molecular weight and its distribution on the spinodal in polymer solution

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Statistical thermodynamics of polydisperse polymer systems in the framework of lattice fluid model: Effect of molecular weight and its distribution on the spinodal in polymer solution

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With the aid of thermodynamics of Gibbs, the expression of the spinodal was derived for the polydisperse polymer-solvent system in the framework of Sanchez–Lacombe Lattice Fluid Theory (SLLFT). For convenience, we considered that a model polydisperse polymer contains three sub-components. According to our calculation, the spinodal depends on both weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights of the polydisperse polymer, but the z-average molecular weight ($\bar{M}_z$) dependence on the spinodal is invisible. The dependence of free volume on composition, temperature, molecular weight, and its distribution results in the effect of $\bar{M}_n$ on the spinodal. Moreover, it has been found that the effect of changing $\bar{M}_w$ on the spinodal is much bigger than that of changing $\bar{M}_n$ and the extrema of the spinodal increases with the rise of the weight-average molecular weight of the polymer in the solutions with upper critical solution temperature (UCST). However, the effect of polydispersity on the spinodal can be neglected for the polymer with a considerably high weight-average molecular weight. A more simple expression of the spinodal for the polydisperse polymer solution in the framework of SLLFT was also derived under the assumption of $v^* = v_1^* = v_2^*$ and $(1/r_1^0) - (1/r_{2i}^0) \rightarrow (1/r_1^0)$. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1424320]

I. INTRODUCTION

The polydispersity of polymers always attracts polymer physicists' attention due to the existence of many industrially important polydisperse systems such as crude oil, polymers, commercial surfactants, and colloidal suspensions. The thermodynamics and the phase-separation behavior of such systems, which underlie, at least in part, important processing characteristics, storage stability, and other properties, have been a well-established subject since Gibbs.[1]

As far as we know, there are several different procedures to deal with the polydispersity of systems. The first one is the multi-component procedure in which each of the components in the polydisperse system is divided into a finite number of sub-components. Koningsveld and Kleintjens[2–7] have given a thorough description of the statistical thermodynamics of polydisperse systems using this procedure. Their starting points are the definitions of the thermodynamics for the multi-component system advanced by Gibbs.[8] Using different theoretical framework and deduction of mathematics, they derived the expression of the spinodal and other thermodynamic properties and discussed the effects of polydispersity, such as molecular weight and its distribution, on phase-separation behavior. They pointed out that the spinodal

depended only on the weight-average molecular weight and the alternation of z-average molecular weight can only change critical point.[2] The second one is the functional method developed primarily by Rätzsch and co-workers.[9,10] Thermodynamically, a polydisperse system can be considered as a system with a continuously infinite species.[11–14] So, in their theory, the thermodynamic functions were defined for continuous mixtures. The expressions of chemical potential, the spinodal, and critical point were derived by means of functional theory. Some useful results have been obtained by using that method.[15–19] Although the functional method is attractive due to its mathematical integrity, it is still in a stage of development and its reliability should often be checked with the results obtained by the discrete approach because the monomer has a finite size. There are also some other theories to deal with the polydisperse systems. Sanchez[20] used volume fluctuating theory and found that the polydisperse polymer solution had a less stability than the corresponding monodisperse polymer solution. More recently, Warren[21] advanced a new method to treat statistical mechanics of a polydisperse system and obtained the exact spinodal, critical points, cloud point curve, and shadow curve using some approximation in general case. Sollich and Cates[22] gave a rational procedure for projecting the infinite-dimensional free energy surface of a polydisperse system onto a subspace comprising a finite number of linear combinations of densities. Their method is computationally robust, giving new geometrical insights into the thermodynamics of polydispersity.

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An *et al.*[23,24] have applied the Sanchez–Lacombe Lattice Fluid Theory (SLLFT)[25–28] to the polydisperse polymer mixtures and obtained some theoretical results for the mixtures of polymers with special distribution. Owing to the thermodynamic stability criteria of zero approximation used, the results obtained miss seemingly some generality. In this paper, the generalized phase-separation condition and one of its approximations, which are based on that advanced by Gibbs,[8] were derived for the polydisperse polymer solution by virtue of SLLFT. The spinodals for different molecular weights and their distributions were calculated and the effects of polydispersity on the spinodals are discussed and compared with the results calculated under the assumptions of $v^* = v_1^* = v_2^*$ and $(1/r_1^0) - (1/r_{2i}^0) \rightarrow (1/r_1^0)$.

II. THEORY BACKGROUND

The Gibbs energy and equation of state for the polydisperse polymer solutions, on the basis of SLLFT, can be expressed as follows:[23,24]

$$G = rN\varepsilon^* \left\{ -\tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T}\left[(\tilde{v}-1)\ln(1-\tilde{\rho}) + \frac{1}{r}\ln\tilde{\rho} \right. \right.$$
$$\left. \left. + \frac{\phi_1^0}{r_1^0}\ln\frac{\phi_1^0}{\omega_1^0} + \sum_i \frac{\phi_{2i}^0}{r_{2i}^0}\ln\frac{\phi_{2i}^0}{\omega_{2i}^0} \right] \right\}, \tag{1}$$

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1-\tilde{\rho}) + (1-1/r)\tilde{\rho}] = 0, \tag{2}$$

where subscripts 1 and 2 represent solvent and polydisperse polymer, respectively. The symbols which appear in Eqs. (1) and (2) and in the following discussions are defined as:

G: the Gibbs energy of the solution with volume V.

ε^*: the average interaction energy per lattice site occupied.

r: the average number of lattice sites occupied by one molecule in the polymer solution.

N: the total number of molecules in the polymer solution.

N_{2i} and N_1: the number of the molecules of the sub-component $2i$ in the polydisperse polymer and of solvent.

r_{2i}^0 and r_1^0: the numbers of lattice sites occupied by one chain of the sub-component $2i$ and by one solvent molecule in their corresponding pure states.

r_{2i} and r_1: the numbers of lattice sites occupied by one chain of the sub-component $2i$ and by one solvent molecule in the polymer solution.

ω_{2i}^0 and ω_1^0: the numbers of configurations available to r_{2i}^0-mer and r_1^0-mer in the corresponding close-packed pure states.

ω_{2i} and ω_1: the numbers of configurations available to r_{2i}-mer and r_1-mer in the close-packed states of the polymer solution.

ϕ_{2i} and ϕ_1: the close-packed volume fractions of sub-component $2i$ of a polydisperse polymer and of the solvent in a polymer solution, whose definitions are

$$\phi_{2i} = \frac{r_{2i}N_{2i}}{rN}, \quad \phi_1 = \frac{r_1N_1}{rN}, \tag{3}$$

$$\phi_{2i}^0 = \frac{r_{2i}^0 N_{2i}}{rN}, \quad \phi_1^0 = \frac{r_1^0 N_1}{rN}, \tag{4}$$

$$N = N_1 + \sum_i N_{2i}, \tag{5}$$

$$rN = r_1^0 N_1 + \sum_i r_{2i}^0 N_{2i} = r_1 N_1 + \sum_i r_{2i} N_{2i}, \tag{6}$$

$$\frac{1}{r} = \frac{\phi_1}{r_1} + \sum_i \frac{\phi_{2i}}{r_{2i}} = \frac{\phi_1^0}{r_1^0} + \sum_i \frac{\phi_{2i}^0}{r_{2i}^0}. \tag{7}$$

The reduced variables in Eqs. 1 and 2 are written as

$$\tilde{X} = X/X^*, \tag{8}$$

where $X = T$, P, v on the left hand side and $X = T$, P, V on the right hand side, respectively; the stared variables are the scaling parameters and can be expressed as

$$T^* = \varepsilon^*/k, \quad P^* = \varepsilon^*/v^*, \tag{9}$$

$$V^* = rNv^* = \left(r_1 N_1 + \sum_i r_{2i} N_{2i} \right)v^*. \tag{10}$$

k is the Boltzmann constant, v^* is the volume of a lattice site in the polymer solution, and the reduced density reads

$$\tilde{\rho} = 1/\tilde{v} = V^*/V. \tag{11}$$

Equation (1) is slightly different from the original one just by substituting

$$\sum_{i,j} \frac{\phi_{ij}^0}{r_{ij}^0}\ln\frac{\phi_{ij}^0}{\omega_{ij}^0}$$

for

$$\sum_{i,j} \frac{\phi_{ij}}{r_{ij}}\ln\frac{\phi_{ij}}{\omega_{ij}}$$

(see Refs. 23, 24). It can be easily known that there is no difference between them if the symmetry numbers for polymer and solvent are the same in solutions and in pure states, i.e., $\sigma_1 = \sigma_1^0$, $\sigma_{2i} = \sigma_{2i}^0$, and the flexibility parameter characteristics[25] are assumed to be the maximum, i.e., $\delta_{ij} = \delta_{ij}^{max}$, $\delta_{ij}^0 = \delta_{ij}^{0\,max}$, where

$$\omega_{ij} = \delta_{ij}r_{ij}/\sigma_{ij}e^{r_{ij}-1}, \quad \omega_{ij}^0 = \delta_{ij}^0 r_{ij}^0/\sigma_{ij}^0 e^{r_{ij}^0-1} \tag{12}$$

subscript ij represents either the sub-component $2i$ of the polydisperse polymer or that of the solvent.[23,24]

For polydisperse polymer solutions, the scaling parameters ε^* and v^* could be obtained by using "combining rules,"[23,24] whose expressions are

$$\varepsilon^* = \phi_1^2 \varepsilon_{11}^* + \phi_1 \sum_{i=1}^l \phi_{2i}\varepsilon_{12,1i}^* + \phi_1 \sum_{i=1}^l \phi_{2i}\varepsilon_{21,i1}^*$$
$$+ \sum_{i=1}^l \sum_{j=1}^l \phi_{2i}\phi_{2j}\varepsilon_{22,ij}^*, \tag{13}$$

$$v^* = \phi_1^0 v_1^* + \sum_{i=1}^l \phi_{2i}^0 v_{2i}^*, \tag{14}$$

where $Y^* = (z/2)Y$ ($Y = \varepsilon_{11}$, $\varepsilon_{12,1i}$, $\varepsilon_{21,i1}$, or $\varepsilon_{22,ij}$), Y is the interaction energy between a mer occupied by solvent (or sub-component $2i$) and its nearest-neighbor mer occupied by sub-component $2i$ (or solvent, or sub-component $2j$); z is the coordination number; l is the number of the sub-components of the polydisperse polymer. If we assume that there are no influence of chain-length on Y^* and the close-packed volume of the polymer, then $\varepsilon_{22,ij}^* = \varepsilon_{22}^*$, $\varepsilon_{12,1i}^* = \varepsilon_{21,i1}^* = \varepsilon_{12}^*$ and $v_{2i}^* = v_2^*$. Therefore the above two equations can be simplified, i.e.,

$$\varepsilon^* = \phi_1^2 \varepsilon_{11}^* + 2\phi_1\phi_2\varepsilon_{12}^* + \phi_2^2\varepsilon_{22}^*, \tag{15}$$

$$v^* = \phi_1^0 v_1^* + \phi_2^0 v_2^*, \tag{16}$$

where ε_{ij}^*, which is symmetrical, is the interaction energy of a mer belonging to component i when it is surrounded by z mers belonging to component j. Equations (15) and (16) are similar to those in monodisperse mixture.[26]

Let

$$g = \frac{G}{rNkT} = \frac{\bar{\bar{G}}}{kT}, \tag{17}$$

where $\bar{\bar{G}}$ is the Gibbs energy per lattice site occupied according to SLLFT. Then the following expression can be easily obtained:

$$g = \frac{-\tilde{\rho} + \tilde{P}\tilde{v}}{\tilde{T}} + (\tilde{v} - 1)\ln(1 - \tilde{\rho}) + \frac{1}{r}\ln\tilde{\rho} + \frac{\phi_1^0}{r_1^0}\ln\frac{\phi_1^0}{\omega_1^0}$$

$$+ \sum_i^l \frac{\phi_{2i}^0}{r_{2i}^0}\ln\frac{\phi_{2i}^0}{\omega_{2i}^0}, \tag{18}$$

where

$$\phi_1^0 + \sum_{i=1}^l \phi_{2i}^0 = 1. \tag{19}$$

According to the spinodal criteria advanced by Gibbs,[8] i.e.,

$$J_{sp} = |\partial^2 \zeta / \partial m_i \partial m_j| = 0 \quad (i,j = 1,2,...,n-1), \tag{20}$$

where J_{sp} is a $(n-1) \times (n-1)$ determinant under the condition of intensive energy ζ and composition fractions $m_{i(or\,j)}$, the polydisperse polymer solution is given as

$$J_{sp} = \begin{vmatrix} \dfrac{\partial^2 \bar{\bar{G}}}{\partial \phi_{21}^{0^2}}, & \dfrac{\partial^2 \bar{\bar{G}}}{\partial \phi_{21}^0 \partial \phi_{22}^0}, & \cdots\cdots & , \dfrac{\partial^2 \bar{\bar{G}}}{\partial \phi_{21}^0 \partial \phi_{2l}^0} \\[2mm] \dfrac{\partial^2 \bar{\bar{G}}}{\partial \phi_{22}^0 \partial \phi_{21}^0}, & \dfrac{\partial^2 \bar{\bar{G}}}{\partial \phi_{22}^{0^2}}, & \cdots\cdots & , \dfrac{\partial^2 \bar{\bar{G}}}{\partial \phi_{22}^0 \partial \phi_{2l}^0} \\[1mm] \vdots & \vdots & & \vdots \\[1mm] \vdots & \vdots & & \vdots \\[2mm] \dfrac{\partial^2 \bar{\bar{G}}}{\partial \phi_{2l}^0 \partial \phi_{21}^0}, & \dfrac{\partial^2 \bar{\bar{G}}}{\partial \phi_{2l}^0 \partial \phi_{22}^0}, & \cdots\cdots & , \dfrac{\partial^2 \bar{\bar{G}}}{\partial \phi_{2l}^{0^2}} \end{vmatrix}$$

$$= 0. \tag{21}$$

In the above determinant J_{sp}, it is seen that $(\partial^2 \bar{\bar{G}})/(\partial \phi_{2i}^0 \partial \phi_{2j}^0)$ is the general term. The above determinant can be reduced to the spinodal of SLLFT[26] for the monodisperse polymer solution. This general term can be written as (see Appendix A for further details)

$$\frac{\partial^2 \bar{\bar{G}}}{\partial \phi_{2i}^0 \partial \phi_{2j}^0} = kT \frac{\partial^2 g}{\partial \phi_{2i}^0 \partial \phi_{2j}^0}, \tag{22}$$

$$\frac{\partial^2 g}{\partial \phi_{2i}^0 \partial \phi_{2j}^0}$$

$$= \begin{cases} -\tilde{\rho}\Theta + \dfrac{1}{r_1^0\phi_1^0} - \tilde{\rho}\tilde{T}P^*\beta\psi_{2i}\psi_{2j} & (i \neq j) \\[3mm] -\tilde{\rho}\Theta + \dfrac{1}{r_1^0\phi_1^0} + \dfrac{1}{r_{2i}^0\phi_{2i}^0} - \tilde{\rho}\tilde{T}P^*\beta\psi_{2i}^2 & (i = j) \end{cases}, \tag{23}$$

where

$$\Theta = \frac{2v_1^* v_2^*}{v^{*3}}\left[\frac{\chi v_1^* v_2^*}{v^*} - \lambda_{12}(v_2^* - v_1^*)\right]. \tag{24}$$

The volume fraction in close-packed state could be assumed as that in normal state,[29,30] that is, we can use ϕ to represent the actual volume fraction in polymer solutions. Therefore, Eqs. (21)–(24) can be used to calculate the spinodal of polydisperse systems with the aid of computer programming.

For convenience, two assumptions are made to get a clearer expression of the criteria of the spinodal.

Assumption I: $v^* = v_1^* = v_2^*$

Under this assumption, we have

$$\frac{\partial^2 g}{\partial \phi_{2i}^{0^2}} = -2\tilde{\rho}\chi + \left(\frac{1}{r_{2i}^0\phi_{2i}^0} + \frac{1}{r_1^0\phi_1^0}\right)$$

$$- \tilde{\rho}\tilde{T}P^*\beta\left[\tilde{\rho}\lambda_{12} - \left(\frac{1}{r_{2i}^0} - \frac{1}{r_1^0}\right)\right]^2, \tag{25}$$

$$\frac{\partial^2 g}{\partial \phi_{2i}^0 \partial \phi_{2j}^0} = -2\tilde{\rho}\chi + \frac{1}{r_1^0\phi_1^0} - \tilde{\rho}\tilde{T}P^*\beta\left[\tilde{\rho}\lambda_{12}\right.$$

$$\left. - \left(\frac{1}{r_{2i}^0} - \frac{1}{r_1^0}\right)\right]\left[\tilde{\rho}\lambda_{12} - \left(\frac{1}{r_{2j}^0} - \frac{1}{r_1^0}\right)\right]. \tag{26}$$

Assumption II: $1/r_1^0 - 1/r_{2i}^0 \to 1/r_1^0 (r_{2i}^0 \gg r_1^0)$

Under those two assumptions, we have

$$\frac{\partial^2 g}{\partial \phi_{2i}^{0^2}} = -2\tilde{\rho}\chi + \left(\frac{1}{r_{2i}^0\phi_{2i}^0} + \frac{1}{r_1^0\phi_1^0}\right)$$

$$- \tilde{\rho}\tilde{T}P^*\beta\left(\tilde{\rho}\lambda_{12} + \frac{1}{r_1^0}\right)^2, \tag{27}$$

$$\frac{\partial^2 g}{\partial \phi_{2i}^0 \partial \phi_{2j}^0} = -2\tilde{\rho}\chi + \frac{1}{r_1^0\phi_1^0} - \tilde{\rho}\tilde{T}P^*\beta\left(\tilde{\rho}\lambda_{12} + \frac{1}{r_1^0}\right)^2. \tag{28}$$

If we let

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$$J_{11} = -2\tilde{\rho}\chi + \frac{1}{r_1^0\phi_1^0} - \tilde{\rho}\tilde{T}P^*\beta\psi_s^2, \quad (29)$$

$$L_{2i} = \frac{1}{r_{2i}^0\phi_{2i}^0}, \quad (30)$$

where

$$\psi_s = \tilde{\rho}\lambda_{12} + \frac{1}{r_1^0}, \quad (31)$$

then,

$$\frac{\partial^2 g}{\partial\phi_{2i}^{0^2}} = J_{11} + L_{2i}, \quad (32)$$

$$\frac{\partial^2 g}{\partial\phi_{2i}^0 \partial\phi_{2j}^0} = J_{11}. \quad (33)$$

Thus,

$$(kT)^{-l+1}J_{sp}$$

$$= \begin{vmatrix} J_{11}+L_{21} & J_{11} & \cdots & \cdots & J_{11} \\ J_{11} & J_{11}+L_{22} & \cdots & \cdots & J_{11} \\ \vdots & \vdots & & & \vdots \\ \vdots & \vdots & & & \vdots \\ J_{11} & J_{11} & \cdots & \cdots & J_{11}+L_{2l} \end{vmatrix} = 0. \quad (34)$$

From this determinant, we can obtain[2]

$$1 + J_{11}\sum_{i=1}^{k} L_{2i}^{-1} = 0. \quad (35)$$

The spinodal of polymer solutions is written as (see Appendix B for details)

$$\frac{1}{r_1\phi_1} + \frac{1}{r_{w,2}\phi_2} = \tilde{\rho}(2\chi + \tilde{T}\psi_s^2 P^*\beta). \quad (36)$$

If the system is reduced into monodisperse system, i.e., $r_{w,2} = r_2$, then the spinodal is

$$\frac{1}{r_1\phi_1} + \frac{1}{r_2\phi_2} = \tilde{\rho}(2\chi + \tilde{T}\psi_s^2 P^*\beta). \quad (37)$$

The expression of the spinodal is identical with that obtained by Sanchez and Lacombe.[26] It can be also seen from Eq. (36) that the spinodal can only depend on the weight-average chain length (weight-average molecular weight) under the assumption of $(1/r_1^0) - (1/r_{2i}^0) \rightarrow (1/r_1^0)$. In Sec. III we will give it in details.

III. RESULTS AND DISCUSSION

By means of the method developed in the previous section, we can calculate the spinodals of representative polymer solutions according to the determinant and the approximate expression. In order to discuss the effect of molecular weight and its distribution on the spinodal, a model system based on the polystyrene (PS)/cyclohexane (CH) solution has been introduced. The scaling parameters are listed in Table I. We used Assumption I ($v^* = v_1^* = v_2^*$) in this work to simplify the calculation. The interaction energy parameter

TABLE I. Scaling parameters of model system (Ref. 30) (based on PS/CH solution).

	P^*(MPa)	ρ^*(kg/m^3)	T^*(K)
Polymer[a]	446.1[b]	1148.3	597.7
Solvent	385.9	917.0	517.0

[a]The scaling parameters of polymer are obtained by fitting the PVT data of the polymer and those of solvent are obtained from the reference directly (Ref. 30).
[b]P^* of polymer should be 529.6 MPa in Ref. 30. The data listed in Table I were obtained under the assumption of $v^* = v_1^* = v_2^*$.

(ε_{12}^*/k) between polymer and solvent is assumed to be independent of molecular weight, which equals to 546.8 K. The molecular weight of the solvent is 0.084 kg/mol. For convenience, we considered that a model polydisperse polymer contains three sub-components. They can be obtained from the following three equations:

$$\frac{w_{21}}{M_{21}} + \frac{w_{22}}{M_{22}} + \frac{w_{23}}{M_{23}} = \frac{1}{\bar{M}_n}, \quad (38)$$

$$w_{21}M_{21} + w_{22}M_{22} + w_{23}M_{23} = \bar{M}_w, \quad (39)$$

$$w_{21}M_{21}^2 + w_{22}M_{22}^2 + w_{23}M_{23}^2 = \bar{M}_w\bar{M}_z, \quad (40)$$

where M_{2i} and w_{2i} ($i = 1,2,3$) are the molecular weight and the weight fraction of sub-component $2i$ of the polydisperse polymer; $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_z$ correspond to the number-average, the weight-average, and the z-average molecular weight.

A. Effect of $\bar{M}_z$ on the spinodal at the fixed $\bar{M}_w$ and $\bar{M}_n$

In order to testify whether $\bar{M}_z$ has an effect on the spinodal, the spinodals for different $\bar{M}_z$ at the same $\bar{M}_w$ and $\bar{M}_n$ were calculated by means of Eq. (21). The corresponding characters are listed in Table II. According to our calculation, all of the spinodals calculated are almost coincident with each other for the same $\bar{M}_n$ and $\bar{M}_w$ as shown in Fig. 1. This indicates that the $\bar{M}_z$ effect on the position of the spinodal at fixed $\bar{M}_n$ and $\bar{M}_w$ is invisible. We used Assumption II to calculate the spinodals at the same $\bar{M}_n$ and $\bar{M}_w$ for different $\bar{M}_z$; the spinodals are coincident with each other, but the results are deviated from the actual ones. Furthermore, this difference decreases with the increase of the molecular weight.

B. Effect of $\bar{M}_n$ on the spinodal at the fixed $\bar{M}_w$

Koningsveld[2] pointed out that the spinodal does not shift if $\bar{M}_w$ is fixed according to the original Flory–Huggins Lattice Theory. From Eq. (36) (under the condition of Assumptions I and II) we can also prove that. In order to testify the effects of the introduction of Assumption II on the spinodal, we also calculated the spinodal when $\bar{M}_w$($= 5$ kg/mol) was fixed as shown in Fig. 2 by using Eq. (21). The polydispersity indexes ($\eta_{w/n} = \bar{M}_w/\bar{M}_n$) of the polymer are 1, 2, 5, 10,

TABLE II. Characters of the polydisperse polymer in solution at fixed $\bar{M}_w$ (=5 kg/mol) and $\bar{M}_n$ (=1.25 kg/mol).[a]

Model	$\bar{M}_z$ of polymer (kg/mol)	M_{21} (kg/mol)	M_{22} (kg/mol)	M_{23} (kg/mol)	$w_{21}(\%)$	$w_{22}(\%)$	$w_{23}(\%)$
1A		0.374	4.65	10.33	0.25	0.5	0.25
1B	7.5	0.164	4.37	14.92	0.1	0.8	0.1
1C		0.309	4.47	11.30	0.2	0.6	0.2
2A		0.404	3.07	13.45	0.25	0.5	0.25
2B	10	0.172	3.77	19.65	0.1	0.8	0.1
2C		0.331	3.31	14.73	0.2	0.6	0.2
3A		0.470	1.99	15.55	0.25	0.5	0.25
3B	12.5	0.180	3.33	23.15	0.1	0.8	0.1
3C		0.365	2.50	17.14	0.2	0.6	0.2

[a]All of the molecular weights' items should be multiplied by factor of 40 when they are applied in Fig. 1(b).

20, and 50, respectively. Figure 2(a) shows the spinodals at different number-average molecular weights and Fig. 2(b) the maxima of spinodal temperatures versus polydispersity indices. From Fig. 2 it is seen that when the $\bar{M}_n$ decreases, i.e., the polydispersity index increases, the phase separation area and the maximum of the spinodal are increased. But this increment is quite small compared with the phase separation temperature. Moreover, Eq. (36) only presents the approximate results. The effect of $\bar{M}_n$ on the spinodal does exist even though it is very small. This conclusion is different from Koningsveld's one based on the Flory–Huggins (FH) theory.[2] It is well known that SLLFT is different from the Flory–Huggins theory in the following two aspects:

(1) The close-packed volume (v^*) in a mixture is different from that in its pure component and is a function of composition in SLLFT.
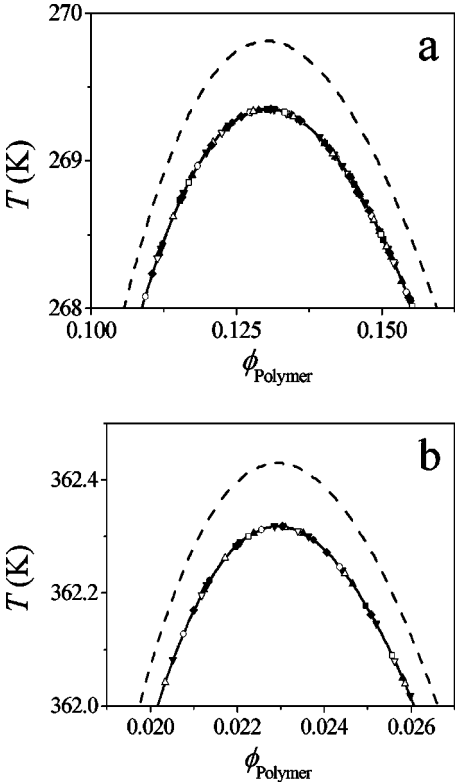

FIG. 1. Effect of $\bar{M}_z$ on the spinodal at constant $\bar{M}_n$ and $\bar{M}_w$. The molecular weight of each sub-component of model 1A, 1B, ..., and 3C are shown in Table II. The dashed line refers to the spinodal when Assumption II is used. (a) $\bar{M}_n = 1.25$ kg/mol and $\bar{M}_w = 5$ kg/mol. (b) $\bar{M}_n = 50$ kg/mol and $\bar{M}_w = 200$ kg/mol.

♦ 1A;   □ 1B;   ▼ 1C;   ▽ 2A;
● 2B;   ○ 2C;   ▲ 3A;   △ 3B;
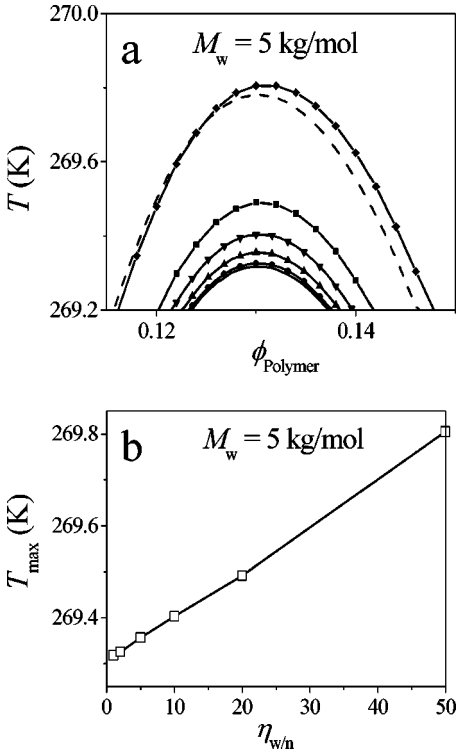■ 3C;   -----Assumption II applied.

FIG. 2. Effect of $\bar{M}_n$ on the spinodal at the fixed $\bar{M}_w$ (5 kg/mol). (a) The spinodals at different number-average molecular weights; (b) The maxima of spinodals vs polydispersity indices.

♦ $\eta_{w/n}=50$;   ■ $\eta_{w/n}=20$;   ▼ $\eta_{w/n}=10$;
▲ $\eta_{w/n}=5$;   ● $\eta_{w/n}=2$; $\eta_{w/n}=1$;
- - - - Assumption II applied.

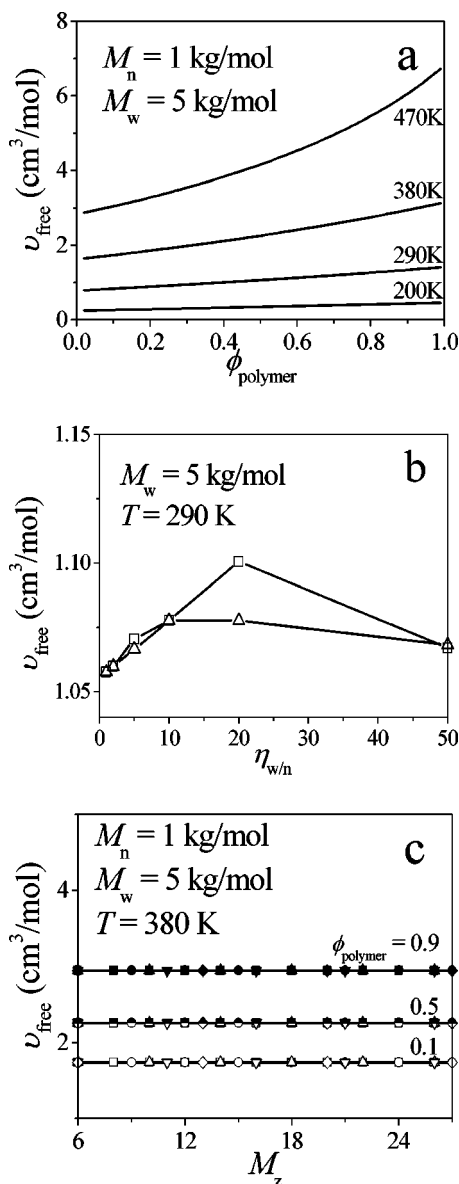FIG. 4. Effect of $\bar{M}_n$ on the spinodals at the fixed $\bar{M}_w$ (5 kg/mol) under $\tilde{\rho}$ $=1$ where the different symbols represent the spinodals of polymer solutions at different polydispersity index.

weight and molecular weight distribution. We can see that the free volume (i.e., the compressibility) of polymer solutions increases with the volume fraction of polymer and temperature [Fig. 3(a)]. In Fig. 3(b), it is found that there are two series of number-average molecular weights for a given $\eta_{w/n}$ when the $\bar{M}_w$ is fixed. Moreover, the maximum of free volume can be observed for the different series of $\bar{M}_n$'s, respectively. Meanwhile it is obvious that the relationship between free volume and $\bar{M}_z$ is invisible when the $\bar{M}_n$ and $\bar{M}_w$ are fixed at the given composition and temperature [Fig. 3(c)], i.e., the free volume only depends on $\bar{M}_n$ and $\bar{M}_w$ according to our calculation when the temperature and composition are constants. Furthermore, the influence of composition of and molecular weight of sub-components on free volume vanishes for the fixed $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$.

If we further assume that the free volume in this system is independent on the composition, temperature, molecular weight and its distribution, i.e., the $\tilde{\rho}$ is constant, under those assumptions, SLLFT could be simplified to the model similar to FH theory. From the calculated results shown in Fig. 4 (where the situation of $\tilde{\rho}=1$ is only given for convenience), we can see that the effect of $\bar{M}_n$ on the spinodal vanishes. So the dependence of free volume (or compressibility) on the composition, temperature, molecular weight, and its distribution in polymer solution is the major reason for the influence of $\bar{M}_n$ on the spinodal.

C. Effect of $\bar{M}_w$ on the spinodal at the fixed $\bar{M}_n$

Let $\bar{M}_n(=10\,\text{kg/mol})$ remains a constant and $\bar{M}_w$ varies in a large range, as shown in Fig. 5. The polydispersity indexes of the polymer used in this section are 1, 2, 5, 10, and 20, respectively. Comparing Fig. 5 with Fig. 2, we can find that the effect of changing $\bar{M}_w$ on the spinodal is much bigger than that of changing $\bar{M}_n$. Also, with the increase of $\bar{M}_w$, i.e., the increase of the $\eta_{w/n}$, the trend of the increase of the phase separation areas decreases [Fig. 5(b)] and the

FIG. 3. Dependence of free volume on composition, temperature, polydispersity index, z-average molecular weight, and molecular weight distribution in the polydisperse polymer solution. (a) Free volume at different volume fraction of polymer and at different temperature where $\bar{M}_n=1$ kg/mol and $\bar{M}_w=5$ kg/mol. (b) Free volume at different polydispersity index where $\bar{M}_w=5$ kg/mol. The different symbols in this figure represent two series of number-average molecular weights at a given polydispersity index. (c) Free volume at different $\bar{M}_z$ and different distribution where $\bar{M}_n=1$ kg/mol and $\bar{M}_w=5$ kg/mol. Squares: $w_{21}=0.25$, $w_{22}=0.50$, $w_{23}=0.25$; circles: $w_{21}=0.20$, $w_{22}=0.60$, $w_{23}=0.20$; up-triangles: $M_{21}=0.50$ kg/mol, $M_{22}=1.0$ kg/mol; down-triangles: $M_{22}=1.5$ kg/mol, $M_{23}=2.0$ kg/mol; diamonds: $M_{21}=0.8$ kg/mol, $M_{23}=3.0$ kg/mol.

(2) The compressibility of polymer system is introduced in SLLFT.

In this paper, we have assumed that $v_1^*=v_2^*=v^*$, which is similar to that of FH theory, so the effect of $\bar{M}_n$ on the spinodal should be caused by the introduction of compressibility of system. Figure 3 shows the dependence of free volume, which is defined by $(\tilde{v}-1)\cdot v^*$, on composition, temperature and polydispersity index, z-average molecular
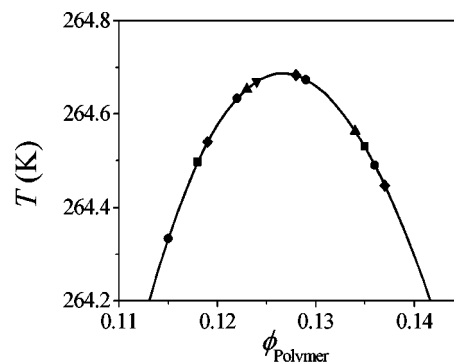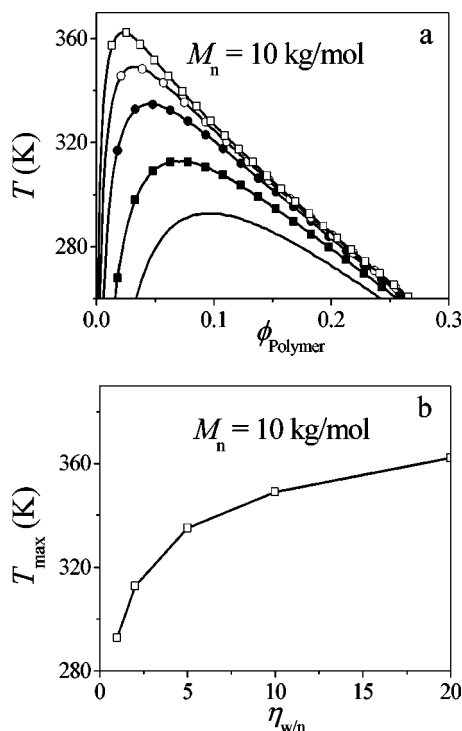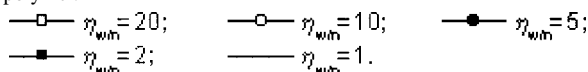
FIG. 5. Effect of $\bar{M}_w$ on the spinodals at the fixed $\bar{M}_n$ (10 kg/mol) where the different symbols represent the spinodals at different polydispersity index of the polymer.

left branch of the spinodal is getting much closer to the pure solvent boundary [Fig. 5(a)]. This is similar to that presented by Koningsveld *et al.*[2]

D. Effect of polydispersity on the spinodal at different molecular weight

Three different polydispersity indexes (η= 1, 2, and 5) were chosen at the same $\bar{M}_n$'s to study the effect of molecular weight on the spinodal. The results for different $\bar{M}_n$ are shown in Fig. 6. It is seen that with the increase of the molecular weight, the effect of polydispersity on the spinodal decreases. For a considerably high number-average molecular weight, we can think that the effect of polydispersity on
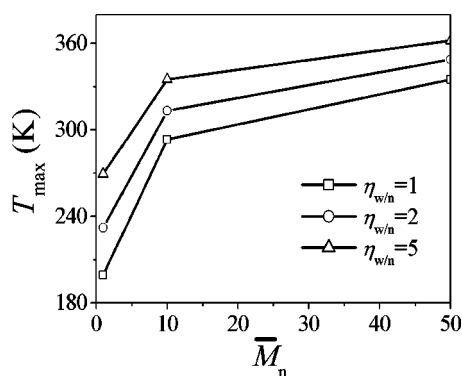

FIG. 6. Dependence of the maximum temperature of the spinodals on molecular weights at different polydispersity indexes.
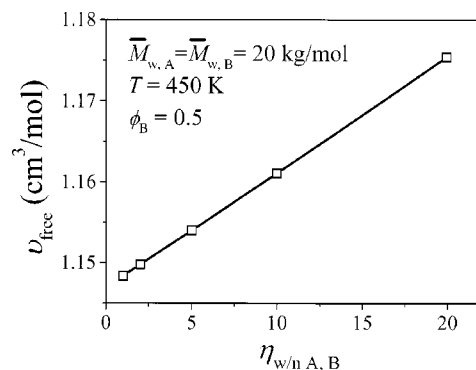

FIG. 7. Relationship between the free volume and polydispersity index at $\phi_B = 0.5$ and $T = 450$ K, where $\bar{M}_{w,A} = \bar{M}_{w,B} = 20$ kg/mol.

the spinodal in polymer solution will be ignored. Moreover, the spinodal moves upward with the increase of the molecular weight of the polymer and the maxima of the spinodals move toward the solvent side when the molecular weight of the polymer increases [as seen in Fig. 5(a)]. This indicates that the phase separation occurs in the relative dilute solution of the polymer with high molecular weight at the same temperature and pressure.

E. Extension for quasi-binary polydisperse polymer mixture

It is easy to extend the above equations into the quasi-binary polydisperse polymer mixtures so long as we consider the solvent into the other polydisperse polymer, i.e., replacing subscript 1 by $1j$ and summing the corresponding term [Eqs. (1), (5), (6), (7), (10), (13), (14), (18), and (19)] or changing subscript 1 into $1j$ [Eqs. (3) and (4)] or substituting $r_{w,1}$ for r_1 [Eq. (36)]. The spinodal, Eq. (21), becomes a $(l+h-1) \times (l+h-1)$ determinant, where h is the number of sub-components of the other polydisperse polymer. Furthermore, the dependence of the spinodals with the lower critical solution temperature (LCST) on number-average, weight-average, z-average molecular weights, and polydispersity are calculated for a model polydisperse polymer mixture based on the polyethersulfone (PES)/phenoxy system, each of the polymer contains three different molecular weight sub-components. The three scaling parameters for PES and phenoxy can be obtained from Ref. 31 and the interaction energy parameter (ε^*_{12}/k) is equals to 790.4 K. The similar conclusions are given according to our calculation. However, the effect of polydispersity index on free volume in the polymer mixture is different from that in the polymer solution (shown in Fig. 7). The maxima in the polymer solutions are not visible in the polymer mixtures. It is obvious that the maxima in Fig. 3(b) is only a consequence of our modeling for polymer solutions for the given parameters in this calculation.

IV. CONCLUSIONS

From above discussion, the following conclusions are obtained:

(1) The polydispersity can make the phase separation areas increase; this effect decreases with the increase of the molecular weight of polymer.

(2) Either the change of $\bar{M}_w$ or that of $\bar{M}_n$ can affect the shape and the extrema of the spinodal, but the effect of changing $\bar{M}_w$ is much bigger than that of changing $\bar{M}_n$. Only when $\bar{M}_w$ and $\bar{M}_n$ are fixed, is the shift of the spinodal invisible.

(3) We derived a simple expression of the spinodal for polydisperse polymer solutions and mixtures in the framework of SLLFT. This approximate expression can be used since it has only a small deviation from the exact determinant expression.

(4) It is pointed out that the dependence of free volume on the composition, temperature, molecular weight and its distribution results in the effect of $\bar{M}_n$ on the spinodal.

(5) The effect of polydispersity on the spinodal can be neglected for the polymer with a considerably high number-average molecular weight.

ACKNOWLEDGMENTS

APPENDIX A: DERIVATION OF THE SECOND PARTIAL DERIVATES OF GIBBS ENERGY WITH RESPECT TO CORRESPONDING ϕ_{2i}^0.

Equation (18) can be expressed as $g = g(\varphi_{2i}^0, \tilde{\rho})$, so

$$\frac{\partial g}{\partial \phi_{2i}^0} = \frac{\partial g}{\partial \phi_{2i}^0}\bigg|_{\tilde{\rho}} + \frac{\partial g}{\partial \tilde{\rho}}\frac{\partial \tilde{\rho}}{\partial \phi_{2i}^0} = \frac{\partial g}{\partial \phi_{2i}^0}\bigg|_{\tilde{\rho}}$$

$$(g_{\tilde{\rho}} = 0, \text{ i.e., equation of state}), \tag{A1}$$

$$\frac{\partial^2 g}{\partial \phi_{2i}^0 \partial \phi_{2j}^0} = \frac{\partial^2 g}{\partial \phi_{2i}^0 \partial \phi_{2j}^0}\bigg|_{\tilde{\rho}} + \frac{\partial^2 g}{\partial \phi_{2i}^0 \partial \tilde{\rho}}\frac{\partial \tilde{\rho}}{\partial \phi_{2j}^0}, \tag{A2}$$

where

$$\frac{\partial g}{\partial \phi_{2i}^0} = -\tilde{\rho}\frac{\partial(\varepsilon^*/kT)}{\partial \phi_{2i}^0} + \frac{P}{kT\tilde{\rho}}\frac{\partial v^*}{\partial \phi_{2i}^0} + \left(\frac{1}{r_{2i}^0} - \frac{1}{r_1^0}\right)\ln \tilde{\rho}$$

$$+ \frac{1}{r_{2i}^0}\ln\frac{\phi_{2i}^0}{\omega_{2i}^0} + \frac{1}{r_{2i}^0} - \frac{1}{r_1^0}\ln\frac{\phi_1^0}{\omega_1^0} - \frac{1}{r_1^0}, \tag{A3}$$

$$\frac{\partial^2 g}{\partial \phi_{2i}^0 \partial \phi_{2j}^0}\bigg|_{\tilde{\rho}} = -\tilde{\rho}\frac{\partial^2(\varepsilon^*/kT)}{\partial \phi_{2i}^0 \partial \phi_{2j}^0} + \frac{P}{kT\tilde{\rho}}\frac{\partial^2 v^*}{\partial \phi_{2i}^0 \partial \phi_{2j}^0}$$

$$+ \frac{\partial}{\partial \phi_{2j}^0}\left(\frac{1}{r_{2i}^0}\ln\frac{\phi_{2i}^0}{\omega_{2i}^0}\right) + \frac{1}{r_1^0 \phi_1^0}, \tag{A4}$$

$$\frac{\partial^2 g}{\partial \phi_{2i}^0 \partial \tilde{\rho}} = -\frac{\partial(\varepsilon^*/kT)}{\partial \phi_{2i}^0} - \frac{P}{kT\tilde{\rho}^2}\frac{\partial v^*}{\partial \phi_{2i}^0} + \left(\frac{1}{r_{2i}^0} - \frac{1}{r_1^0}\right)\frac{1}{\tilde{\rho}}, \tag{A5}$$

$$\frac{\partial \tilde{\rho}}{\partial \phi_{2i}^0} = \tilde{\rho}^2 \psi_{2i}\tilde{T}P^*\beta, \tag{A6}$$

$$\psi_{2i} = \tilde{\rho}\frac{\partial(\varepsilon^*/kT)}{\partial \phi_{2i}^0} + \frac{P}{kT\tilde{\rho}}\frac{\partial v^*}{\partial \phi_{2i}^0} - \left(\frac{1}{r_{2i}^0} - \frac{1}{r_1^0}\right), \tag{A7}$$

$$P^*\beta = \frac{1}{\tilde{\rho}\left[\tilde{T}\left(\dfrac{\tilde{\rho}}{1-\tilde{\rho}} + \dfrac{1}{r}\right) - 2\tilde{\rho}\right]} > 0, \tag{A8}$$

where $(\partial \tilde{\rho}/\partial \phi_{2i}^0)$ is derived from Eq. (2).

According to Eqs. (13) and (14) and considering $\varepsilon_{12,1i}^* = \varepsilon_{21,i1}^*$, we have

$$\frac{\partial(\varepsilon^*/kT)}{\partial \phi_{2i}}$$

$$= \left[2\sum_{j=1}^{l} \phi_{2j}(\varepsilon_{22,ij}^* - \varepsilon_{12,1j}^*) + 2\phi_1(\varepsilon_{12,1i}^* - \varepsilon_{11}^*)\right]\bigg/ kT, \tag{A9}$$

$$\frac{\partial v^*}{\partial \phi_{2i}^0} = v_{2i}^* - v_1^*. \tag{A10}$$

If it is assumed that $\varepsilon_{22,ij}^* = \varepsilon_{22}^*$, $\varepsilon_{12,ij}^* = \varepsilon_{12}^*$, and $v_{2i}^* = v_2^*$, then

$$\frac{\partial(\varepsilon^*/kT)}{\partial \phi_{2i}} = [2\phi_2(\varepsilon_{22}^* - \varepsilon_{12}^*) + 2\phi_1(\varepsilon_{12}^* - \varepsilon_{11}^*)]/kT$$

$$= \lambda_{12}, \tag{A11}$$

$$\frac{\partial v^*}{\partial \phi_{2i}^0} = v_2^* - v_1^*. \tag{A12}$$

According to SLLFT,[23,24]

$$\phi_1 = \phi_1^0 \frac{v_1^*}{v^*}, \quad \phi_{2i} = \phi_{2i}^0 \frac{v_{2i}^*}{v^*}. \tag{A13}$$

So,

$$\frac{\partial(\varepsilon^*/kT)}{\partial \phi_{2i}^0} = \sum_{j=1}^{l} \frac{\partial(\varepsilon^*/kT)}{\partial \phi_{2j}}\frac{\partial \phi_{2j}}{\partial \phi_{2i}^0} = \lambda_{12}\frac{v_1^* v_2^*}{v^{*2}}, \tag{A14}$$

$$\frac{\partial^2(\varepsilon^*/kT)}{\partial \phi_{2i}^0 \partial \phi_{2j}^0} = \frac{\partial}{\partial \phi_{2j}^0}\left(\frac{\partial(\varepsilon^*/kT)}{\partial \phi_{2i}^0}\right)$$

$$= \frac{2v_1^* v_2^*}{v^{*3}}\left[\frac{\chi v_1^* v_2^*}{v^*} - \lambda_{12}(v_2^* - v_1^*)\right] = \Theta, \tag{A15}$$

$$\frac{\partial^2 v^*}{\partial \phi_{2i}^0 \partial \phi_{2j}^0} = 0, \tag{A16}$$

$$\chi = \frac{1}{2}\frac{\partial \lambda_{12}}{\partial \phi_{2i}} = (\varepsilon_{11}^* - 2\varepsilon_{12}^* + \varepsilon_{22}^*)/kT. \tag{A17}$$

From above equations, we have

$$\frac{\partial^2 g}{\partial \phi_{2i}^0 \partial \phi_{2j}^0}$$

$$= \begin{cases} -\widetilde{\rho}\Theta + \dfrac{1}{r_1^0 \phi_1^0} - \widetilde{\rho}\widetilde{T}P^*\beta\psi_{2i}\psi_{2j} & (i \neq j) \\[2ex] -\widetilde{\rho}\Theta + \dfrac{1}{r_1^0 \phi_1^0} + \dfrac{1}{r_{2i}^0 \phi_{2i}^0} - \widetilde{\rho}\widetilde{T}P^*\beta\psi_{2i}^2 & (i = j) \end{cases}.$$

$$(A18)$$

APPENDIX B: DERIVATION OF THE EXPRESSION OF THE SPINODAL

Substituting J_{11} and L_{2i} into Eq. (34), the following is given:

$$1 + \left[(-2\widetilde{\rho}\chi - \widetilde{\rho}\widetilde{T}P^*\beta\psi_s^2) + \frac{1}{r_1^0 \phi_1^0} \right] \sum_{i=1}^{l} r_{2i}^0 \phi_{2i}^0 = 0. \quad (B1)$$

All of the superscript ''0'' can be removed because of the assumption, $v^* = v_1^* = v_2^*$, and

$$\sum_{i=1}^{l} r_{2i}\phi_{2i} = r_{w,2}\phi_2, \quad (B2)$$

where $r_{w,2}$ are the weight-average chain length of polymer, and ϕ_2 is the volume fraction of polymer in the solution. So the criteria of the spinodal can be written as follows:

$$\frac{1}{r_1\phi_1} + \frac{1}{r_{w,2}\phi_2} = \widetilde{\rho}(2\chi + \widetilde{T}P^*\beta\psi_s^2). \quad (B3)$$

[1] R. T. Dehoff, *Thermodynamics in Material Science* (McGraw-Hill, New York, 1992).

[2] R. Koningsveld, H. A. G. Chermin, and M. Gordon, Proc. R. Soc. London, Ser. A **319**, 331 (1970).

[3] R. Koningsveld and L. A. Kleintjens, Macromolecules **4**, 637 (1971).

[4] R. Koningsveld, L. A. Kleintjens, and A. R. Schultz, J. Polym. Sci., Part A-2, 1261 (1970).

[5] L. A. Kleintjens and R. Koningsveld, J. Electrochem. Soc. **127**, 2352 (1980); L. A. Kleintjens, Fluid Phase Equilib. **10**, 183 (1983).

[6] R. Koningsveld, L. A. Kleintjens, and A. M. Leblans-Vinck, J. Phys. Chem. **91**, 6423 (1987).

[7] L. A. Kleintjens and R. Koningsveld, Colloid Polym. Sci. **258**, 711 (1980); K. Šolc and R. Koningsveld, Collect. Czech. Chem. Commun. **60**, 1689 (1995); S. Vanhee, R. Koningsveld, H. Berghmans, K. Šolc, and W. H. Stockmayer, Macromolecules **33**, 3924 (2000).

[8] *The Collected Works of J. Willard Gibbs* (Yale University Press, New Haven, 1957).

[9] S. Beerbaum, J. Bergmann, H. Kehlen, and M. T. Rätzsch, J. Macromol. Sci., Chem. **24**, 1445 (1987).

[10] J. Bergmann, H. Teichert, H. Kehlen, and M. T. Rätzsch, J. Macromol. Sci., Chem. **29**, 371 (1992).

[11] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).

[12] J. A. Gualtieri, J. M. Kincaid, and G. Morrison, J. Chem. Phys. **77**, 521 (1982).

[13] L. Blum and G. Stell, J. Chem. Phys. **71**, 42 (1979).

[14] J. J. Salacuse, J. Chem. Phys. **81**, 2468 (1984).

[15] Y. Hu and X. Ying, Fluid Phase Equilib. **127**, 21 (1997).

[16] D. Browarzik and M. Kowalewski, Fluid Phase Equilib. **163**, 43 (1999).

[17] H. C. de Sousa and L. P. N. Rebelo, J. Polym. Sci., Part B: Polym. Phys. **38**, 632 (2000).

[18] S. Enders, A. Hinrichs, R. Horst, and B. A. Wolf, J. Macromol. Sci., Chem. **33**, 1097 (1996).

[19] W. E. McMullen and K. F. Freed, J. Chem. Phys. **92**, 1413 (1990).

[20] I. C. Sanchez, Macromolecules **24**, 908 (1991).

[21] P. B. Warren, Phys. Rev. Lett. **80**, 1369 (1998).

[22] P. Sollich and M. E. Cates, Phys. Rev. Lett. **80**, 1365 (1998).

[23] L. An, X. Kou, R. Ma, X. Tang, and B. Jiang, Polymer **34**, 2989 (1993).

[24] L. An, B. Jiang, Z. Jiang, Y. Hu, and X. Tang, Macromol. Theory Simul. **3**, 751 (1994).

[25] I. C. Sanchez and R. H. Lacombe, J. Phys. Chem. **80**, 2352 (1976).

[26] R. H. Lacombe and I. C. Sanchez, J. Phys. Chem. **80**, 2568 (1976).

[27] I. C. Sanchez and R. H. Lacombe, Macromolecules **11**, 1145 (1978).

[28] I. C. Sanchez and A. C. Balazs, Macromolecules **22**, 2325 (1989).

[29] L. An, R. Horst, and B. A. Wolf, J. Chem. Phys. **107**, 2597 (1997).

[30] Z. Sun, H. Li, L. An, Z. Jiang, and Z. Wu, Macromol. Theory Simul. **10**, 692 (2001); P. Zoller and D. J. Walsh, *Standard Pressure-Volume-Temperature Data For Polymers* (Technomic Publishing Co. Ltd., 1995).

[31] Z. Sun, L. An, R. Ma, Z. Jiang, and Z. Wu, J. Macromol. Sci., Phys. **38**, 67 (1999).