薄膜合成之 spinodal decomposition

計劃主持人：鄭廖平、林博中　　執行機構：淡江大學化學工程學系

中文摘要

本研究探討恒溫浸漬－沈澱製膜程序中，spinodal decomposition 之可能性，我們發現在 spinodal 處必須滿足(1)所有質傳通量為零或(2) $J_1/J_2 = D_{11}/D_{21} = D_{12}/D_{22}$。此外我們也考慮局部濃度擾動的效應，推導含擾動效應之質傳方程式，並計算擴散路徑。

ABSTRACT

The possibility of spinodal decomposition during isothermal immersion precipitation for membrane formation was studied. It was found that the diffusional fluxes at the spinodal must obey (1) all fluxes are zero, or (2) $J_1/J_2 = D_{11}/D_{21} = D_{12}/D_{22}$. In addition, the effects from local random concentration fluctuations on the diffusional fluxes were considered. And the diffusion trajectories were computed.

1. Flux Equations for Multi-component Systems

As a homogeneous multi-component solution with its initial composition outside the spinodal envelope is subject to external concentration boundary conditions, isothermal mass transfer of each component take place, and there will be some circumstances under which the system may be forced to approach the spinodal. In such instance, it is interesting to return to the question of whether the spinodal condition of the ternary system places any restriction on the diffusional flux of each component.

Considering a "c+1" component system undergoes isothermal mass transfer. There are, in this case, only "c" independent diffusion flows, since one of the components is selected as the reference component, and all other diffusion flows are determined by their velocities relative to the reference component. The phenomenological expressions for these diffusion fluxes are given by[1]

$$- J_i = \sum_{j=1}^{c} L_{ij} \nabla \mu_j \qquad (i, j = 1, 2, \ldots, c) \qquad (1)$$

where J_i is the molar flux of component i relative to the velocity of the reference component, L_{ij} is the phenomenological coefficient, which satisfies the Onsager's relation[1], i.e. $L_{ij}=L_{ji}$, and μ_j is the chemical potential of component j, which is assumed depends only on concentrations. The one-dimensional chemical potential gradient of component-j can be obtained

$$\frac{\partial \mu_j}{\partial x} = \sum_{k=1}^{c} \frac{\partial \mu_j}{\partial \phi_k} \frac{\partial \phi_k}{\partial x} \qquad (j = 1, 2, \ldots., c) \qquad (2)$$

From Eqn. (2), the relative one dimension diffusional fluxes of component-i can be expressed as

$$- J_i = \sum_{k=1}^{c} \sum_{j=1}^{c} L_{ij} \frac{\partial \mu_j}{\partial \phi_k} \frac{\partial \phi_k}{\partial x} = \sum_{k=1}^{c} D_{ik} \frac{\partial \phi_k}{\partial x} \qquad (3)$$

where D_{ik} is the diffusion coefficient. Eqn (3) can be rewritten in matrix form:

$$D\varphi = -J \qquad (4)$$

where D is a c × c coefficient matrix composed of D_{ik} terms, φ is a c-dimensional column vector composed of $\partial \phi_k / \partial x$ terms, and J is a c-dimensional column vector. Coefficient matrix D can be shown to be equivalent to the products of the matrices given in Eqn. (5).

$$D = L\mu = \begin{pmatrix} L_{11} & L_{12} & \cdots\cdots & L_{1c} \\ L_{21} & L_{22} & \cdots\cdots & L_{2c} \\ \cdots & \cdots & \cdots\cdots & \cdots \\ L_{i1} & L_{i2} & \cdots\cdots & L_{ic} \\ \cdots & \cdots & \cdots\cdots & \cdots \\ L_{c1} & L_{c2} & \cdots\cdots & L_{cc} \end{pmatrix} \begin{pmatrix} \frac{\partial \mu_1}{\partial \phi_1} & \frac{\partial \mu_1}{\partial \phi_2} & \cdots\cdots & \frac{\partial \mu_1}{\partial \phi_c} \\ \frac{\partial \mu_2}{\partial \phi_1} & \frac{\partial \mu_2}{\partial \phi_2} & \cdots\cdots & \frac{\partial \mu_2}{\partial \phi_c} \\ \cdots & \cdots & & \cdots \\ \frac{\partial \mu_j}{\partial \phi_1} & \frac{\partial \mu_j}{\partial \phi_2} & \cdots & \frac{\partial \mu_j}{\partial \phi_c} \\ \cdots & \cdots & & \cdots \\ \frac{\partial \mu_c}{\partial \phi_1} & \frac{\partial \mu_c}{\partial \phi_2} & \cdots & \frac{\partial \mu_c}{\partial \phi_c} \end{pmatrix} \qquad (5)$$

where L is the matrix containing only L_{ij} terms which satisfies the Onsager's conditions so that its determinant is > 0. μ is the matrix composed of $\partial \mu_j / \partial \phi_k$ terms.

Eqn. (4) is said to be consistent (i.e., has at least one solution) if and only if the rank of the coefficient matrix D, r(D), is equal to the rank of the augmented matrix, r($D | J$), where $D | J$ is defined in Eqn .(6).

$$D | J = \begin{pmatrix} D_{11} & D_{12} & \cdots\cdots & D_{1c} & J_1 \\ D_{21} & D_{22} & \cdots\cdots & D_{2c} & J_2 \\ \cdots & \cdots & \cdots\cdots & \cdots & \cdots \\ D_{i1} & D_{i2} & \cdots\cdots & D_{ic} & J_i \\ \cdots & \cdots & \cdots\cdots & \cdots & \cdots \\ D_{c1} & D_{c1} & \cdots\cdots & D_{cc} & J_c \end{pmatrix} \qquad (6)$$

More specifically, Eqn (4) has
 (i) no solution if and only if $r(D) \neq r(D | J)$;
 (ii) a unique solution if and only if $r(D) = r(D | J) = c$;
 (iii) a (c-r)-parameter family of solutions if and only if $r(D) = r(D | J) \equiv r$ is less than c.

If systems are in the stable region, matrix μ is positive definite. From Eqn (5), matrix D must be positive definite. Therefore, matrix D is not singular and is of rank c. It can be shown from Eqn (6) that $r(D) = r(D | J) = c$. Therefore, Eqn (4) is always consistent.

However, if systems are at the limit of stability, Eqn (5) shows that the coefficient matrix D becomes positive semi-definite since matrix μ is positive

semi-definite. Matrix D is said to be positive semi-definite if it is singular and all of its principle minors are zero or still positive. Therefore, the rank of the coefficient matrix D is equal to c-1 if all its principle minors are positive. Now, for Eqn. (4) to be consistent, the rank of the augmented matrix $r(D \mid J)$ must be also equal to c-1. If all fluxes approach zero at spinodal compositions, in such instance Eqn. (4) becomes a homogeneous system:

$$D\varphi = 0 \qquad (7)$$

For a homogeneous system, it must surely be true that $r(D) = r(D \mid J) = c - 1$. Since matrix D is singular at the limit of stability, Eqn. (7) is always consistent. Hence, spinodal is a barrier for isothermal mass transfer if all fluxes are zero at spinodal compositions, and the system of equations $D\varphi = 0$ is consistent.

However, if all the fluxes in the augmented matrix $D \mid J$ are nonzero, for $r(D \mid J) = c - 1$, it must follow that at least, any two rows or columns in the matrix $D \mid J$ are proportional to each other, i.e.,

$$\frac{D_{i-11}}{D_{i1}} = \frac{D_{i-12}}{D_{i2}} = \ldots = \frac{D_{i-1c}}{D_{ic}} = \frac{J_{i-1}}{J_i} \qquad (8)$$

Hence, Eqn. (4) is still consistent and there exists a one-parameter family of solutions. Since fluxes exist as the system approaches spinodal compositions, the latter is not an absolute barrier to isothermal mass transfer.

Lets first consider the one dimensional diffusion problem encountered in the formation of a membrane from isothermal precipitation process. The polymer solution used in the process consists of nonsolvent (1)-solvent(2)-polymer(3). Initially, the homogeneous polymer solution is immersed in the nonsolvent bath at time zero. Because of the chemical potential gradients, nonsolvent diffuses into and solvent diffuses out of the membrane with fluxes J_1 and J_2, respectively. Consider a thin layer l of polymer solution in the membrane, which moves with the same velocity as the polymer. At time zero, the composition of this layer is essentially the initial polymer concentration, which is represented by point A in the phase diagram shown in Figure 1. At time t', mass transfer process brings the composition of this layer from point A to point B as shown in Figure 1. At time t'', the composition of this layer reaches a spinodal composition represented by point S in Figure 1. At point S, the diffusion coefficient matrix becomes singular and hence is of rank 1. Hence, the rank augmented matrix, $r(D \mid J)$, given in Eqn (9), must be equal to 1.

$$r(D \mid J) = \begin{vmatrix} D_{11} & D_{12} & J_1 \\ D_{21} & D_{22} & J_2 \end{vmatrix} \qquad (9)$$

The condition for $r(D \mid J) = 1$ is: (i) both fluxes approach zero at spinodal compositions; or (ii) if J_1 and J_2 are both nonzero J_1 and J_2 must follow:

$$\frac{D_{11}}{D_{21}} = \frac{D_{12}}{D_{22}} = \frac{J_1}{J_2} \qquad (10)$$

Since fluxes may exist as layer l approaches spinodal, mass transfer process is allowed in this layer.
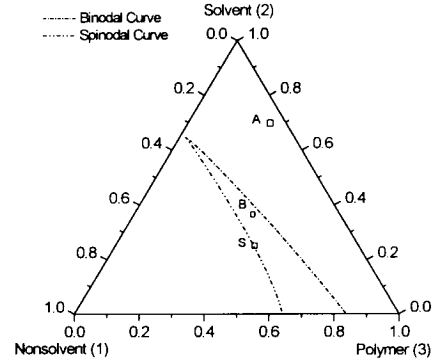

Fig. 1: Compositions of layer l at different time after immersion. (a) t = 0, point A; (b) t = t', point B c) t = t'', point S.

2. Cahn-Hilliard Theory For Ternary Mixtures

The free energy due to composition fluctuation can be expressed in terms of the gradients of volume fractions giving a relation of the form

$$\Delta g_v' = \Delta g_v^0 + k_1(\nabla\phi_1)^2 + k_2(\nabla\phi_2)^2 + k_{12}(\nabla\phi_1)(\nabla\phi_2) \qquad (11)$$

where $\Delta g_v'$ is the extended Gibbs free energy of mixing per volume that includes the contributions of volume fraction fluctuations, Δg_v^0 is the homogeneous expression of the Gibbs free energy of mixing per volume, and $k_1(\nabla\phi_1)^2 + k_2(\nabla\phi_2)^2 + k_{12}(\nabla\phi_1)(\nabla\phi_2)$ is the gradient energy terms arising from local fluctuations of the volume fractions, where k_1, k_2, and k_{12} are the gradient energy parameters[2,3] and they are all assumed to be non-negative; otherwise another kind of instability may exist[4].

The total Gibbs energy of mixing for ternary system including contribution from the volume fraction fluctuation can then be expressed by the so-called Landau-Ginzburg functional[2]:

$$\Delta G = \int_v \left\{ \Delta g_v^0 + k_1(\nabla\phi_1)^2 + k_2(\nabla\phi_2)^2 + k_{12}(\nabla\phi_1)(\nabla\phi_2) \right\} dV \qquad (12)$$

We follow the procedure of Cahn and Hilliard[4] to determine the corresponding generalized chemical potentials for a system whose free energy of mixing of a phase is given by Eqn. (12). These generalized chemical potentials must satisfy two requirements: (1) they must reduce to the classical $\partial\Delta g_v^0 / \partial\phi_i$'s when the gradient energy parameters are zero; (2) at equilibrium, they are constant throughout the system. In a ternary system, the free energy can be expressed in terms of two component volume fractions since one of the component volume fractions is a dependent variable. However, there is no need to decide a priori which one of the three volume fractions is a dependent variable. The ordinary rules for partial differentiation are applied whether or not ϕ_3 appears explicitly in the function being differentiated. Therefore, all three variables are treated as though they were independent until a specific choice of dependent variable is made.

Since a system at equilibrium has minimum free energy, the required potentials should minimize Eqn. (12) subject to the following material balance constrains:

$$\frac{1}{V}\int_V \phi_1 dV = \bar{\phi}_1 \qquad (13)$$

$$\frac{1}{V}\int_V \phi_2 dV = \bar{\phi}_2 \qquad (14)$$

$$\frac{1}{V}\int_V \phi_3 dV = \bar{\phi}_3 \qquad (15)$$

where $\bar{\phi}_i$ $(i = 1 \sim 3)$ are the average volume fractions of the system. Minimization of Eqn. (12) subject to the constrains given by Eqn. (13)-(15) is a classical problem in the calculus of variations, and this will give the partial differential forms of Euler-Lagrange equations with the assumption that k_{ij} are constant[2,3]

$$\left(\frac{\partial \Delta g_v^0}{\partial \phi_1}\right)_{\phi_2,\phi_3} - 2k_1\nabla^2\phi_1 - k_{12}\nabla^2\phi_2 = \gamma_1 \quad \text{(a constant) (16)}$$

$$\left(\frac{\partial \Delta g_v^0}{\partial \phi_2}\right)_{\phi_1,\phi_3} - 2k_2\nabla^2\phi_2 - k_{12}\nabla^2\phi_1 = \gamma_2 \quad \text{(a constant) (17)}$$

$$\left(\frac{\partial \Delta g_v^0}{\partial \phi_3}\right)_{\phi_1,\phi_2} = \gamma_3 \quad \text{(a constant) (18)}$$

These generalized chemical potentials are the necessary conditions for ΔG to be a minimum and they remain true regardless of when material constrain $\sum \varphi_i = 1$ is used. Suppose that all the partial derivatives are non-zero, then the chain rule gives

$$\frac{d\Delta g_v^0}{d\phi_1} = \left(\frac{\partial \Delta g_v^0}{\partial \phi_1}\right)_{\phi_2,\phi_3}\frac{d\phi_1}{d\phi_1} + \left(\frac{\partial \Delta g_v^0}{\partial \phi_2}\right)_{\phi_1,\phi_3}\frac{d\phi_2}{d\phi_1} + \left(\frac{\partial \Delta g_v^0}{\partial \phi_3}\right)_{\phi_1,\phi_2}\frac{d\phi_3}{d\phi_1} \qquad (19)$$

$$\frac{d\Delta g_v^0}{d\phi_2} = \left(\frac{\partial \Delta g_v^0}{\partial \phi_1}\right)_{\phi_2,\phi_3}\frac{d\phi_1}{d\phi_2} + \left(\frac{\partial \Delta g_v^0}{\partial \phi_2}\right)_{\phi_1,\phi_3}\frac{d\phi_2}{d\phi_2} + \left(\frac{\partial \Delta g_v^0}{\partial \phi_3}\right)_{\phi_1,\phi_2}\frac{d\phi_3}{d\phi_2} \qquad (20)$$

We now set $\phi_3 = 1 - \phi_1 - \phi_2$ to obtain

$$\left(\frac{\partial \Delta g_v^0}{\partial \phi_1}\right)_{\phi_2} = \left(\frac{\partial \Delta g_v^0}{\partial \phi_1}\right)_{\phi_2,\phi_3} - \left(\frac{\partial \Delta g_v^0}{\partial \phi_3}\right)_{\phi_1,\phi_2} = \gamma_1 - \gamma_3 + 2k_1\nabla^2\phi_1 + k_{12}\nabla^2\phi_2 \qquad (21)$$

$$\left(\frac{\partial \Delta g_v^0}{\partial \phi_2}\right)_{\phi_1} = \left(\frac{\partial \Delta g_v^0}{\partial \phi_2}\right)_{\phi_1,\phi_3} - \left(\frac{\partial \Delta g_v^0}{\partial \phi_3}\right)_{\phi_1,\phi_2} = \gamma_2 - \gamma_3 + 2k_2\nabla^2\phi_2 + k_{12}\nabla^2\phi_1 \qquad (22)$$

Integration of Eqn. (16)-(18) will give, respectively

$$\Delta g_v^0 = \phi_1\gamma_1 + k_1(\nabla\phi_1)^2 + k_{12}(\nabla\phi_1)(\nabla\phi_2) + f_1(\phi_2,\phi_3) \quad (23)$$

$$\Delta g_v^0 = \phi_2\gamma_2 + k_2(\nabla\phi_2)^2 + k_{12}(\nabla\phi_1)(\nabla\phi_2) + f_2(\phi_1,\phi_3) \quad (24)$$

$$\Delta g_v^0 = \phi_3\gamma_3 + f_3(\phi_1,\phi_2) \qquad (25)$$

Comparing these equations and choosing ϕ_3 as dependent variable will give

$$\Delta g_v^0 = \phi_1\gamma_1 + \phi_2\gamma_2 + \phi_3\gamma_3 + k_1(\nabla\phi_1)^2 + k_2(\nabla\phi_2)^2 + k_{12}(\nabla\phi_1)(\nabla\phi_2)$$
$$= (\gamma_1 - \gamma_3)\phi_1 + (\gamma_2 - \gamma_3)\phi_2 + \gamma_3 + k_1(\nabla\phi_1)^2 + k_2(\nabla\phi_2)^2 + k_{12}(\nabla\phi_1)(\nabla\phi_2) \qquad (26)$$

Solving Eqn. (21),(22), and (26) for γ_1, γ_2, and γ_3 gives

$$\gamma_1 = \Delta g_v^0 + (1-\phi_1)\left.\frac{\partial \Delta g_v^0}{\partial \phi_1}\right|_{\phi_2} - \phi_2\left.\frac{\partial \Delta g_v}{\partial \phi_2}\right|_{\phi_1} - \left[k_1(\nabla\phi_1)^2 + k_2(\nabla\phi_2)^2 + k_{12}(\nabla\phi_1)(\nabla\phi_2)\right]$$
$$- (1-\phi_1)(2k_1\nabla^2\phi_1 + k_{12}\nabla^2\phi_2) - \phi_2(2k_2\nabla^2\phi_2 + k_{12}\nabla^2\phi_1)]$$

(27)

$$\gamma_2 = \Delta g_v^0 - \phi_1\left.\frac{\partial \Delta g_v^0}{\partial \phi_1}\right|_{\phi_2} + (1-\phi_2)\left.\frac{\partial \Delta g_v}{\partial \phi_2}\right|_{\phi_1} - \left[k_1(\nabla\phi_1)^2 + k_2(\nabla\phi_2)^2 + k_{12}(\nabla\phi_1)(\nabla\phi_2)\right]$$
$$- (1-\phi_2)(2k_2\nabla^2\phi_2 + k_{12}\nabla^2\phi_1) - \phi_1(2k_1\nabla^2\phi_1 + k_{12}\nabla^2\phi_2)]$$

(28)

$$\gamma_3 = \Delta g_v^0 - \phi_1\left.\frac{\partial \Delta g_v^0}{\partial \phi_1}\right|_{\phi_2} - \phi_2\left.\frac{\partial \Delta g_v}{\partial \phi_2}\right|_{\phi_1} - \left[k_1(\nabla\phi_1)^2 + k_2(\nabla\phi_2)^2 + k_{12}(\nabla\phi_1)(\nabla\phi_2)\right]$$
$$+ \phi_1(2k_1\nabla^2\phi_1 + k_{12}\nabla^2\phi_2) + \phi_2(2k_2\nabla^2\phi_2 + k_{12}\nabla^2\phi_1)]$$

(29)

These equations can also be expressed in terms of chemical potential changes[2,3]

$$\gamma_1 = \frac{\Delta\mu_1}{v_1} = \frac{\Delta\mu_1^0}{v_1} - \left[k_1(\nabla\phi_1)^2 + k_2(\nabla\phi_2)^2 + k_{12}(\nabla\phi_1)(\nabla\phi_2)\right]$$
$$- \left[(1-\phi_1)(2k_1\nabla^2\phi_1 + k_{12}\nabla^2\phi_2) - \phi_2(2k_2\nabla^2\phi_2 + k_{12}\nabla^2\phi_1)\right]$$

(30)

$$\gamma_2 = \frac{\Delta\mu_2}{v_2} = \frac{\Delta\mu_2^0}{v_2} - \left[k_1(\nabla\phi_1)^2 + k_2(\nabla\phi_2)^2 + k_{12}(\nabla\phi_1)(\nabla\phi_2)\right]$$
$$- \left[(1-\phi_2)(2k_2\nabla^2\phi_2 + k_{12}\nabla^2\phi_1) - \phi_1(2k_1\nabla^2\phi_1 + k_{12}\nabla^2\phi_2)\right]$$

(31)

$$\gamma_3 = \frac{\Delta\mu_3}{v_3} = \frac{\Delta\mu_3^0}{v_3} - \left[k_1(\nabla\phi_1)^2 + k_2(\nabla\phi_2)^2 + k_{12}(\nabla\phi_1)(\nabla\phi_2)\right]$$
$$+ \left[\phi_1(2k_1\nabla^2\phi_1 + k_{12}\nabla^2\phi_2) + \phi_2(2k_2\nabla^2\phi_2 + k_{12}\nabla^2\phi_1)\right]$$

(32)

where superscript "0" refers to homogeneous property. Eqn. (30)-(32) are the generalized chemical potential changes that include the gradient energy terms arising from local fluctuations of the volume fractions. Cheng[5,6] have studied the ternary mass transfer processes from for membrane formations by isothermal immersion precipitation in nonsolvent(1)-solvent(2)-polymer(3) systems. If the gradient energy contributions due to the local volume fluctuations of components are included, the diffusional flux equations used by Cheng have to be modified. Using the generalized expressions for chemical potential change given in Eqn. (30)-(32) the one-dimensional diffusional fluxes $(J_i')_3$ can be expressed as

$$-(J_i')_3 = -\left[(J_i)_3 - \sum_{j=1}^2 \Psi_{ij}\frac{\partial^3\phi_j}{\partial x^3}\right] \quad (i = 1, 2) \qquad (33)$$

where $(J_i)_3$ is the diffusional flux used by Cheng, and Ψ_{ij}, which account for the contributions from local volume fluctuations, are equal to

$$\Psi_{11} = 4[L_{11}v_2\phi_1 - L_{11}v_1(1-\phi_1)]k_1 + 2[L_{11}v_1\phi_2 - L_{12}v_2(1-\phi_2)]k_{12}$$

(34)

$$\Psi_{12} = 2[L_{11}v_2\phi_1 - L_{11}v_1(1-\phi_1)]k_{12} + 4[L_{11}v_1\phi_2 - L_{12}v_2(1-\phi_2)]k_2$$

(35)

$$\Psi_{21} = 4[L_{22}v_2\phi_1 - L_{12}v_1(1-\phi_1)]k_1 + 2[L_{12}v_1\phi_2 - L_{22}v_2(1-\phi_2)]k_{12}$$

(36)

$$\Psi_{12} = 2[L_{22}v_2\phi_1 - L_{12}v_1(1-\phi_1)]k_{12} + 4[L_{12}v_1\phi_2 - L_{22}v_2(1-\phi_2)]k_2$$

(37)

The diffusion equations for the membrane solution used by Cheng can be modified by replacing the classic diffusional fluxes with the generalized form, and this gives

$$\frac{\partial\left(\frac{\phi_i}{\phi_3}\right)}{\partial t} = -v_i\left[\frac{\partial(J_i)_3}{\partial m} - \phi_3\frac{\partial^3\phi_3\sum_{j=1}^2\Psi_{ij}\frac{\partial^3\phi_j}{\partial m^3}}{\partial m}\right] \quad (i = 1, 2) \quad (38)$$

Eqn. (38) can be non-dimensionalized by introducing

$$\tau = \frac{D_0 t}{M^2} \qquad (39)$$

$$\eta = \frac{m}{M} \qquad (40)$$

where D_0 (cm^2/s) is a scaling factor for numerical procedure. M is the total volume per unit area of the initial membrane solution.

$$\frac{\partial \begin{pmatrix} \phi_i \\ \phi_3 \end{pmatrix}}{\partial \tau} = -\frac{v_i}{D_0} \left[\partial \phi_3 \sum_{j=1}^{2} L_{ij} \frac{\partial \mu_j}{\partial \eta} - \frac{\phi_3}{M^2} \partial \phi_3^3 \sum_{j=1}^{2} \Psi_{ij} \frac{\partial^3 \phi_j}{\partial \eta^3} \right] \quad (41)$$

Using Eqn.(41), the concentration profiles for immersion procedure can be calculated. By comparing the concentration profiles calculated by Cheng and that by Eqn. (41), we can estimate the contribution from local concentration fluctuations for each precipitation stage.

3. Gradient Energy Parameters for Nonsolvent -Solvent-Polymer systems

The gradient energy parameters, k_i and k_{ij}, given in Eqn. (11) are known to have both enthalpic and entropic components[4,7]:

$$k_i = k_{iH} + k_{iS} \qquad (42)$$

$$k_{ij} = k_{ijH} + k_{ijS} \qquad (43)$$

Here subscripts H and S refer to enthalpic and entropic contributions to the gradient energy parameters, and subscripts i and j refer to solvent or nonsolvent components of the system. The enthalpic contribution is due to interactions between different molecules in the system, while the entropic contribution is due to the arrangements of the chains that constitute the polymer molecules[8,9]. For small molecules, the entropic contribution does not exist.

Following Ariyapadi et al[8,10] for a system consisting of nonsolvent (1)-solvent (2)-polymer (3), the gradient energy parameters are summarized as follows:

$$k_i = \frac{1}{6} \frac{R_{Gi}^2}{v_i} \left[\chi_{i3} + \frac{3}{(1-\phi_i)} \right] \qquad (i = 1, 2) \quad (44)$$

$$k_{12} = \frac{1}{6} \left(R_{G1}^2 \frac{\chi_{13}}{v_1} + R_{G2}^2 \frac{\chi_{23}}{v_2} \right) \qquad (45)$$

where R_{Gi} (i = 1, 2) is the radius of gyration of a polymer molecule dissolved in solvent i, and can be evaluated by[xxx]

$$R_{Gi} = \frac{1}{6} \alpha_i^2 \beta^2 N \qquad (46)$$

where α_i is an empirical function[11], which depends strongly on solvent, β is the effective segment length of the polymer molecules, and N is the degree of polymerization of the polymer. For poor solvent $\alpha \approx 1$ and for ideal or concentrated solution $\alpha = 1$.

4. Concentration fluctuation for the immersion precipitation process

The Flory-Huggins interaction parameters for

water(1)-formic acid(2)-polyamide(3) systems, are given by Cheng[6]. The gradient energy parameters are evaluated by Eqn. (44)-(45). The concentration fluctuations for different precipitation stages are given in Figures 2 and 3.
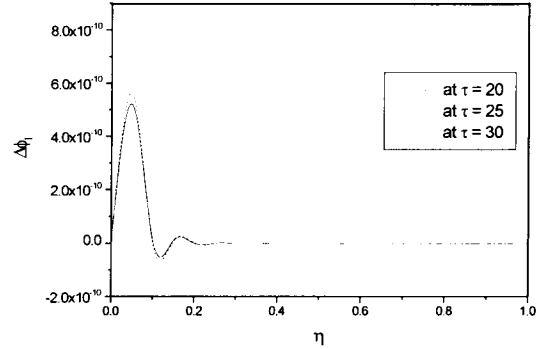
Fig. 2. Concentration fluctuation profiles o component 1 as a function of distance fro membrane-bath interface for the water(1)-formi acid(2)-polyamide(3) system for dope C [in ref. 6 into a pure water bath.
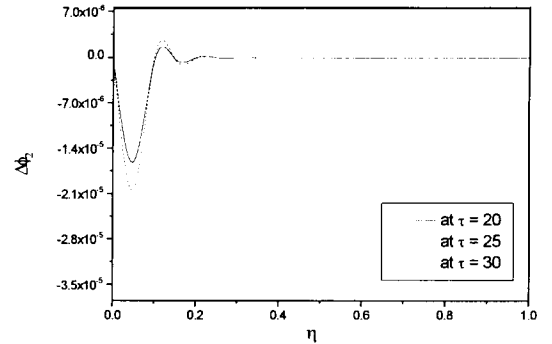
Fig. 3. Concentration fluctuation profiles o component 2 as a function of distance fro membrane-bath interface for the water(1)-formic acid(2)-polyamide(3) system for dope C [in ref. 6 into a pure water bath.

Reference

1. D.D. Fitts, Nonequilibrium Thermodynamics, McGraw-Hill, NY, 1962.
2. M.V. Ariyapadi et al, J. Polym. Sci., B:30, 535, 1990.
3. Bobba et al, J. Polym. Sci., B:32, 671, 1994.
4. J.W. Cahn et al, J. Chem. Phys., 28, 258, 1958.
5. L.P. Cheng et al, J. Polym. Sci., B:33, 211, 1995.
6. L.P. Cheng et al, J. Polym. Sci., B:33, 223, 1995.
7. P.G. de Gennes et al, J. Chem. Phys., 72, 4756, 1971.
8. M.V. Ariyapadi et al, J. Polym. Sci., B:27, 2637, 1989.
9. Ariyapadi et al, J. Polym. Sci., B:28, 2395, 1990.
10. N. Balsara et al, J. Polym. Sci., B:26, 1077, 1987
11. Tanford, Physical Chemistry of Macromolecules, Wiley, 1966.