聚合物-溶剂A-溶剂B

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$$\frac{\Delta G_{mix}}{RT} = \sum_{i=1}^{m} n_i \ln\varphi_i + \sum_{i=1}^{m}\sum_{j>i} \chi_{ij} n_i \varphi_j$$

这一式子来自 Flory 的书 p.549 脚注
J.Chem.Phys. 12:425(1944) 同时推导了双组份和多组份

m=3 时

$$\frac{\Delta G_{mix}}{RT} = n_1\ln\varphi_1 + n_2\ln\varphi_2 + n_3\ln\varphi_3 + \chi_{12}n_1\varphi_2 + \chi_{13}n_1\varphi_3 + \chi_{23}n_2\varphi_3$$

$\varphi_1 = \frac{n_1 v_1}{n_1v_1+n_2v_2+n_3v_3}$ … 等等是体积分数，v_i是摩尔体积（不考虑偏摩尔体积）

$$\frac{\partial\varphi_1}{\partial n_1} = (1-\varphi_1)\frac{v_1}{V}, \quad \frac{\partial\varphi_1}{\partial n_2} = -\varphi_1\frac{v_2}{V}, \quad 等等.$$

另外 χ_{ij} 也常常依赖组成 u_j，其中 $u_j = \varphi_j/(\varphi_i+\varphi_j)$。$\chi_{ij}(u_j)$的数据要查资料。

$$\frac{\partial\chi_{12}}{\partial n_1} = \frac{\partial\chi_{12}}{\partial u_2}\frac{\partial u_2}{\partial n_1}, \quad \frac{\partial u_2}{\partial n_1} = \frac{\partial}{\partial n_1}\left(\frac{\varphi_2}{\varphi_1+\varphi_2}\right) = -u_2\frac{v_1}{V(\varphi_1+\varphi_2)}$$

$$\frac{\partial u_2}{\partial n_2} = \frac{v_2}{V}\frac{u_1}{\varphi_1+\varphi_2}, \quad \frac{\partial u_2}{\partial n_3} = 0$$

假设只有χ_{12}依赖u_2.（这是 Altena and Smolders, M 15:1491 (1982) 的做法）

$$\frac{\Delta\mu_1}{RT} = \frac{\partial\Delta G_{mix}}{RT\partial n_1} = \ln\varphi_1 + n_1\varphi_1^{-1}\frac{\partial\varphi_1}{\partial n_1} + n_2\varphi_2^{-1}\frac{\partial\varphi_2}{\partial n_1} + n_3\varphi_3^{-1}\frac{\partial\varphi_3}{\partial n_1} + \frac{\partial\chi_{12}}{\partial n_1}n_1\varphi_2 + n_1\chi_{12}\frac{\partial\varphi_2}{\partial n_1}$$
$$+\chi_{12}\varphi_2 + n_1\chi_{13}\frac{\partial\varphi_3}{\partial n_1} + \chi_{13}\varphi_3 + \chi_{23}n_2\frac{\partial\varphi_3}{\partial n_1}$$
$$= \ln\varphi_1 + 1 - \varphi_1 - s\varphi_2 - r\varphi_3 - u_1u_2\varphi_2\frac{\partial\chi_{12}}{\partial u_2} - \chi_{12}\varphi_1\varphi_2 + \chi_{12}\varphi_2$$
$$-\chi_{13}\varphi_1\varphi_3 + \chi_{13}\varphi_3 - s\chi_{23}\varphi_2\varphi_3$$
$$= \ln\varphi_1 + 1 - \varphi_1 - s\varphi_2 - r\varphi_3 - u_1u_2\varphi_2\frac{\partial\chi_{12}}{\partial u_2} + \chi_{12}\varphi_2(1-\varphi_1)$$
$$+\chi_{13}\varphi_3(1-\varphi_1) - s\chi_{23}\varphi_2\varphi_3$$

$$\frac{\Delta\mu_2}{RT} = n_1\varphi_1^{-1}\frac{\partial\varphi_1}{\partial n_2} + \ln\varphi_2 + n_2\varphi_2^{-1}\frac{\partial\varphi_2}{\partial n_2} + n_3\varphi_3^{-1}\frac{\partial\varphi_3}{\partial n_2} + n_1\varphi_2\frac{\partial\chi_{12}}{\partial n_2} + n_1\chi_{12}\frac{\partial\varphi_2}{\partial n_2} + \chi_{13}n_1\frac{\partial\varphi_3}{\partial n_2}$$
$$+\chi_{23}\varphi_3 + n_2\chi_{23}\frac{\partial\varphi_3}{\partial n_2}$$
$$= -s^{-1}\varphi_1 + \ln\varphi_2 + 1 - \varphi_2 - \frac{r}{s}\varphi_3 + s^{-1}\varphi_1 u_1u_2\frac{\partial\chi_{12}}{\partial u_2} + s^{-1}\varphi_1(1-\varphi_2)\chi_{12} - \chi_{13}\varphi_3\varphi_1 s^{-1}$$
$$+\chi_{23}\varphi_3 - \chi_{23}\varphi_2\varphi_3$$

$$\frac{s\Delta\mu_2}{RT} = s\ln\varphi_2 + s - \varphi_1 - s\varphi_2 - r\varphi_3 + (1-\varphi_2)(\chi_{12}\varphi_1 + s\chi_{23}\varphi_3) - \chi_{13}\varphi_1\varphi_3 + u_1u_2\varphi_1\frac{\partial\chi_{12}}{\partial u_2}$$

$$\frac{\Delta\mu_3}{RT} = n_1\varphi_1^{-1}\frac{\partial\varphi_1}{\partial n_3} + n_2\varphi_2^{-1}\frac{\partial\varphi_2}{\partial n_3} + \ln\varphi_3 + n_3\varphi_3^{-1}\frac{\partial\varphi_3}{\partial n_3} + n_1\chi_{12}\frac{\partial\varphi_2}{\partial n_3} + n_1\chi_{13}\frac{\partial\varphi_3}{\partial n_3} + n_2\chi_{23}\frac{\partial\varphi_3}{\partial n_3}$$
$$= -\varphi_1 r^{-1} - \varphi_2\frac{s}{r} + \ln\varphi_3 + 1 - \varphi_3 - r^{-1}\chi_{12}\varphi_1\varphi_2 + r^{-1}\chi_{13}\varphi_1(1-\varphi_3) + \chi_{23}\varphi_2(1-\varphi_3)\frac{s}{r}$$

$$\frac{r\Delta\mu_3}{RT} = r\ln\varphi_3 + r - \varphi_1 - s\varphi_2 - r\varphi_3 - \chi_{12}\varphi_1\varphi_2 + (\chi_{13}\varphi_1 + s\chi_{23}\varphi_2)(1-\varphi_3)$$

其中 $s = \frac{v_1}{v_2}$，$r = \frac{v_1}{v_3}$

设液液相分离有两相，组成分别为 $\varphi_1', \varphi_2', \varphi_3'$，$\varphi_1'', \varphi_2'', \varphi_3''$，3个组份的化学势分别为 $\Delta\mu_1, \Delta\mu_2, \Delta\mu_3$

其中 $s = \nu_2$，$r = \nu_3$

设液-液相分离有两相，组成分别为 $\varphi_1', \varphi_2', \varphi_3'$，$\varphi_1'', \varphi_2'', \varphi_3''$，3个组份的化学势分别为 $\Delta\mu_1', \Delta\mu_2', \Delta\mu_3'$，$\Delta\mu_1'', \Delta\mu_2'', \Delta\mu_3''$，相平衡时

$$\begin{cases} \Delta\mu_1' = \Delta\mu_1'' \\ \Delta\mu_2' = \Delta\mu_2'' \\ \Delta\mu_3' = \Delta\mu_3'' \\ \varphi_1' + \varphi_2' + \varphi_3' = 1 \\ \varphi_1'' + \varphi_2'' + \varphi_3'' = 1 \end{cases}$$

固定 φ_1' 的值，则其余5个体积分数都可以确定。变化 φ_1' 的值可描出双节线。

假设体系被半透膜隔开，只允许组份1，2通过。设半透膜外溶液组成 φ_1^{bath}，φ_2^{bath}，

$$\varphi_2^{bath} = \frac{n_2^{bath}\nu_2}{n_1^{bath}\nu_1 + n_2^{bath}\nu_2}, \quad \varphi_2^{bath} = 1 - \varphi_1^{bath} \qquad \frac{\partial \varphi_2^{bath}}{\partial n_2^{bath}} = (1-\varphi_2^{bath})\frac{\nu_2}{V^{bath}}, \quad \frac{\partial \varphi_1^{bath}}{\partial n_2} = \varphi_1^{bath}\frac{\nu_2}{V^{bath}}$$

$$\frac{\Delta G_{mix}^{bath}}{RT} = n_1^{bath}\ln\varphi_1^{bath} + n_2^{bath}\ln\varphi_2^{bath} + \chi_{12}n_1^{bath}\varphi_2^{bath}$$

$$\frac{\Delta\mu_1^{bath}}{RT} = \ln\phi_1^b + \phi_2^b - s\phi_2^b - \frac{\partial\chi_{12}}{\partial\phi_2^b}\phi_1^b(\phi_2^b)^2 + \chi_{12}\phi_2^b - \chi_{12}\phi_1\phi_2$$
$$= \ln\phi_1^b + (1-s)\phi_2^b + \chi_{12}(\phi_2^b)^2 - \frac{\partial\chi_{12}}{\partial\phi_2^b}\phi_1^b(\phi_2^b)^2$$

$$\frac{\Delta\mu_2^{bath}}{RT} = n_1^b\varphi_1^{b-1}\frac{\partial\varphi_1^b}{\partial n_2^b} + \ln\varphi_2^b + n_2^b\varphi_2^{b-1}\frac{\partial\varphi_2^b}{\partial n_2^b} + n_1^b\frac{\partial\chi_{12}}{\partial n_2^b}\varphi_2^b + n_1^b\chi_{12}\frac{\partial\varphi_2^b}{\partial n_2^b}$$

$$= \ln\phi_2^b - s^{-1}\phi_1^b + \phi_1^b + s^{-1}\frac{\partial\chi_{12}}{\partial\phi_2^b}(\phi_1^b)^2\phi_2^b + s^{-1}\chi_{12}(\phi_1^b)^2$$

$$\frac{s\Delta\mu_2^b}{RT} = s\ln\phi_2^b - (1-s)\phi_1^b + \chi_{12}(\phi_1^b)^2 + \frac{\partial\chi_{12}}{\partial\varphi_2^b}(\phi_1^b)^2\phi_2^b$$

这两个化学势通过 $\varphi_1^b = 1 - \varphi_2^b$ 可表达为仅含 φ_2^b 的表达式，消去 φ_2，则 $\Delta\mu_1^b$ 与 $\Delta\mu_2^b$ 满足一个方程。知道 $\Delta\mu_1^b$ 能求 $\Delta\mu_2^b$。相平衡时，由于

$$\begin{cases} \Delta\mu_1' = \Delta\mu_1'' = \Delta\mu_1^b \\ \Delta\mu_2' = \Delta\mu_2'' = \Delta\mu_2^b \end{cases}$$

因此 $\Delta\mu_1'$ 与 $\Delta\mu_2'$ 之间也互相关联并非独立，这为旋节线分离添加了约束。

一些计算实践问题：

Macromol. Theory Simul. 4:449(1995) 5:789(1996)