PLATFORM FOR DESIGNING HIGH FUNCTIONAL MATERIALS

PHASE DIAGRAM GENERATOR

PDFT

USER'S GUIDE

Nagoya University, Doi Project
Research and Development of the Platform
for Designing High Functional Materials

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Contents

Chapter 1

Introduction

This program generates a phase diagram for exact ternary system based on the Flory-Huggins free energy.[**?**] The program requires the input file written by the UDF format which includes three degrees of polymerization, N_1, N_2 and N_3, and three χ parameters, χ_{12}, χ_{13} and χ_{23}. The program writes the information on the phase diagram and the free energy surface in the two types of output files with both the UDF format and the gnuplot format. We call the program as PDFT (Phase Diagram For Ternary).

Chapter 2

Ternary phase diagram

2.1 Flory-Huggins free energy

Under the incompressibility condition,

$$\phi_1 + \phi_2 + \phi_3 = 1, \tag{2.1}$$

the Flory-Huggins free energy of mixing for a exact ternary system is approximated by

$$\begin{aligned}
F &= \frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_2 + \frac{\phi_3}{N_3}\ln\phi_3 + \chi_{12}\phi_1\phi_2 + \chi_{13}\phi_1\phi_3 + \chi_{23}\phi_2\phi_3 \\
&= \frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_2 + \frac{(1-\phi_1-\phi_2)}{N_3}\ln(1-\phi_1-\phi_2) \\
&\quad +\chi_{12}\phi_1\phi_2 + \chi_{13}\phi_1(1-\phi_1-\phi_2) + \chi_{23}\phi_2(1-\phi_1-\phi_2) \\
&= \frac{(1-\phi_2-\phi_3)}{N_1}\ln(1-\phi_2-\phi_3) + \frac{\phi_2}{N_2}\ln\phi_2 + \frac{\phi_3}{N_3}\ln\phi_3 \\
&\quad +\chi_{12}(1-\phi_2-\phi_3)\phi_2 + \chi_{13}(1-\phi_2-\phi_3)\phi_3 + \chi_{23}\phi_2\phi_3 \\
&= \frac{\phi_1}{N_1}\ln\phi_1 + \frac{(1-\phi_1-\phi_3)}{N_2}\ln(1-\phi_1-\phi_3) + \frac{\phi_3}{N_3}\ln\phi_3 \\
&\quad +\chi_{12}\phi_1(1-\phi_1-\phi_3) + \chi_{13}\phi_1\phi_3 + \chi_{23}(1-\phi_1-\phi_3)\phi_3,
\end{aligned} \tag{2.2}$$

where N_i, ϕ_i and χ_{ij} are the degree of polymerization of polymer i, the volume fraction of polymer i and the binary interaction parameter (taken to be independent of composition) between polymer i and polymer j, respectively.

2.2 Chemical potential

Differentiation of the free energy with respect to the volume fraction leads to the chemical potential for the three components.

$$\begin{aligned}
\mu_1 = \frac{\partial F}{\partial\phi_1} &= \frac{1}{N_1}(1+\ln\phi_1) - \frac{1}{N_3}(1+\ln(1-\phi_1-\phi_2)) \\
&\quad +\chi_{12}\phi_2 + \chi_{13}(1-\phi_1-\phi_2) - \chi_{13}\phi_1 - \chi_{23}\phi_2 \\
&= \frac{1}{N_1}(1+\ln\phi_1) - \frac{1}{N_2}(1+\ln(1-\phi_1-\phi_3)) \\
&\quad +\chi_{12}(1-\phi_1-\phi_3) - \chi_{12}\phi_1 + \chi_{13}\phi_3 - \chi_{23}\phi_3
\end{aligned} \tag{2.3}$$

$$\begin{aligned}
\mu_2 = \frac{\partial F}{\partial\phi_2} &= \frac{1}{N_2}(1+\ln\phi_2) - \frac{1}{N_3}(1+\ln(1-\phi_1-\phi_2)) \\
&\quad +\chi_{12}\phi_1 - \chi_{13}\phi_1 + \chi_{23}(1-\phi_1-\phi_2) - \chi_{23}\phi_2 \\
&= -\frac{1}{N_1}(1+\ln(1-\phi_2-\phi_3)) + \frac{1}{N_2}(1+\ln\phi_2) \\
&\quad +\chi_{12}(1-\phi_2-\phi_3) - \chi_{12}\phi_2 - \chi_{13}\phi_3 + \chi_{23}\phi_3
\end{aligned} \tag{2.4}$$

$$\begin{aligned}\mu_3 = \frac{\partial F}{\partial \phi_3} &= -\frac{1}{N_1}(1+\ln(1-\phi_2-\phi_3)) + \frac{1}{N_3}(1+\ln\phi_3) \\ &\quad -\chi_{12}\phi_2 + \chi_{13}(1-\phi_2-\phi_3) - \chi_{13}\phi_3 + \chi_{23}\phi_2 \\ &= -\frac{1}{N_2}(1+\ln(1-\phi_1-\phi_3)) + \frac{1}{N_3}(1+\ln\phi_3) \\ &\quad -\chi_{12}\phi_1 + \chi_{13}\phi_1 + \chi_{23}(1-\phi_1-\phi_3) - \chi_{23}\phi_3 \end{aligned} \tag{2.5}$$

Differentiation of the chemical potential with respect to the volume fraction, which is used in the calculation of spinodal, is as follows.

$$\begin{aligned}G_{11} = \frac{\partial \mu_1}{\partial \phi_1} &= \frac{1}{N_1\phi_1} + \frac{1}{N_3(1-\phi_1-\phi_2)} - 2\chi_{13} \\ &= \frac{1}{N_1\phi_1} + \frac{1}{N_2(1-\phi_1-\phi_3)} - 2\chi_{12}\end{aligned} \tag{2.6}$$

$$\begin{aligned}G_{22} = \frac{\partial \mu_2}{\partial \phi_2} &= \frac{1}{N_2\phi_2} + \frac{1}{N_3(1-\phi_1-\phi_2)} - 2\chi_{23} \\ &= \frac{1}{N_1(1-\phi_2-\phi_3)} + \frac{1}{N_2\phi_2} - 2\chi_{12}\end{aligned} \tag{2.7}$$

$$\begin{aligned}G_{33} = \frac{\partial \mu_3}{\partial \phi_3} &= \frac{1}{N_1(1-\phi_2-\phi_3)} + \frac{1}{N_3\phi_3} - 2\chi_{13} \\ &= \frac{1}{N_2(1-\phi_1-\phi_3)} + \frac{1}{N_3\phi_3} - 2\chi_{23}\end{aligned} \tag{2.8}$$

$$G_{12} = G_{21} = \frac{\partial \mu_1}{\partial \phi_2} = \frac{\partial \mu_2}{\partial \phi_1} = \frac{1}{N_3(1-\phi_1-\phi_2)} + \chi_{12} - \chi_{13} - \chi_{23} \tag{2.9}$$

$$G_{13} = G_{31} = \frac{\partial \mu_1}{\partial \phi_3} = \frac{\partial \mu_3}{\partial \phi_1} = \frac{1}{N_2(1-\phi_1-\phi_3)} - \chi_{12} + \chi_{13} - \chi_{23} \tag{2.10}$$

$$G_{23} = G_{32} = \frac{\partial \mu_2}{\partial \phi_3} = \frac{\partial \mu_3}{\partial \phi_2} = \frac{1}{N_1(1-\phi_2-\phi_3)} - \chi_{12} - \chi_{13} + \chi_{23} \tag{2.11}$$

2.3 Spinodal

Spinodal is given by the condition,

$$J_{s1} \equiv \begin{vmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{vmatrix} = 0 \qquad or \qquad J_{s2} \equiv \begin{vmatrix} G_{22} & G_{23} \\ G_{32} & G_{33} \end{vmatrix} = 0. \tag{2.12}$$

Thus the spinodal equation becomes

$$\begin{aligned}G_{11}G_{22} - G_{21}^2 &= \left(\frac{1}{N_1\phi_1} + \frac{1}{N_3\phi_3} - 2\chi_{13}\right)\left(\frac{1}{N_2\phi_2} + \frac{1}{N_3\phi_3} - 2\chi_{23}\right) \\ &\quad - \left(\frac{1}{N_3\phi_3} + \chi_{12} - \chi_{13} - \chi_{23}\right)^2 = 0.\end{aligned} \tag{2.13}$$

When Eq. (2.13) is multiplied by $N_1N_2N_3\phi_1\phi_2\phi_3$, we can get the following equation.

$$\begin{aligned}&N_1\phi_1 + N_2\phi_2 + N_3\phi_3 - 2N_1N_2\phi_1\phi_2\chi_{12} - 2N_1N_3\phi_1\phi_3\chi_{13} - 2N_2N_3\phi_2\phi_3\chi_{23} \\ &\quad -N_1N_2N_3\phi_1\phi_2\phi_3\left(\chi_{12}^2 + \chi_{13}^2 + \chi_{23}^2 - 2\chi_{12}\chi_{13} - 2\chi_{12}\chi_{23} - 2\chi_{13}\chi_{23}\right) = 0\end{aligned} \tag{2.14}$$

Equation (2.14) can be rewriten as a function of ϕ_2,

$$\begin{aligned}
&[2N_2N_3\chi_{23} + N_1N_2N_3\phi_1 C]\,\phi_2^2 \\
&+[N_2 - N_3 - 2N_2N_3\chi_{23} - 2N_1N_2\chi_{12}\phi_1 + 2N_1N_3\chi_{13}\phi_1 + 2N_2N_3\chi_{23}\phi_1 \\
&-N_1N_2N_3\phi_1 C + N_1N_2N_3\phi_1^2 C]\,\phi_2 \\
&\left[N_3 + N_1\phi_1 - N_3\phi_1 - 2N_1N_3\chi_{13}\phi_1 + 2N_1N_3\chi_{13}\phi_1^2\right] = 0,
\end{aligned} \tag{2.15}$$

where $C = \chi_{12}^2 + \chi_{13}^2 + \chi_{23}^2 - 2\chi_{12}\chi_{13} - 2\chi_{12}\chi_{23} - 2\chi_{13}\chi_{23}$. We can solve Eq.(2.15) for a specified ϕ_1. Thus the entire spinodal curve is obtained by repeating the procedure for different fixed values of ϕ_1.

2.4 Critical Point

The critical point is required to satisfy the following set of conditions.

$$\left\{\begin{array}{l} J_{s1} \equiv \begin{vmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{vmatrix} = 0 \\ \mid J_{c1a} \mid + \mid J_{c1b} \mid = 0 \end{array}\right. ,\left\{\begin{array}{l} J_{s2} \equiv \begin{vmatrix} G_{22} & G_{23} \\ G_{32} & G_{33} \end{vmatrix} = 0 \\ \mid J_{c2a} \mid + \mid J_{c2b} \mid = 0 \end{array}\right. ,\left\{\begin{array}{l} J_{s3} \equiv \begin{vmatrix} G_{33} & G_{31} \\ G_{13} & G_{11} \end{vmatrix} = 0 \\ \mid J_{c3a} \mid + \mid J_{c3b} \mid = 0 \end{array}\right. \tag{2.16}$$

Here

$$J_{c1a} = \begin{vmatrix} \frac{\partial J_{s1}}{\partial \phi_1} & \frac{\partial J_{s1}}{\partial \phi_2} \\ G_{21} & G_{22} \end{vmatrix} \qquad J_{c1b} = \begin{vmatrix} G_{11} & G_{12} \\ \frac{\partial J_{s1}}{\partial \phi_1} & \frac{\partial J_{s1}}{\partial \phi_2} \end{vmatrix} \tag{2.17}$$

$$J_{c2a} = \begin{vmatrix} \frac{\partial J_{s2}}{\partial \phi_2} & \frac{\partial J_{s2}}{\partial \phi_3} \\ G_{32} & G_{33} \end{vmatrix} \qquad J_{c2b} = \begin{vmatrix} G_{22} & G_{23} \\ \frac{\partial J_{s2}}{\partial \phi_2} & \frac{\partial J_{s2}}{\partial \phi_3} \end{vmatrix} \tag{2.18}$$

$$J_{c3a} = \begin{vmatrix} \frac{\partial J_{s3}}{\partial \phi_3} & \frac{\partial J_{s3}}{\partial \phi_1} \\ G_{13} & G_{11} \end{vmatrix} \qquad J_{c3b} = \begin{vmatrix} G_{33} & G_{31} \\ \frac{\partial J_{s3}}{\partial \phi_3} & \frac{\partial J_{s3}}{\partial \phi_1} \end{vmatrix} \tag{2.19}$$

$$J_{s1} = G_{11}G_{22} - G_{21}^2 \tag{2.20}$$

$$J_{s2} = G_{22}G_{33} - G_{32}^2 \tag{2.21}$$

$$J_{s3} = G_{33}G_{11} - G_{13}^2 \tag{2.22}$$

$$\frac{\partial J_{s1}}{\partial \phi_k} = G_{11k}G_{22} + G_{11}G_{22k} - 2G_{21}G_{21k} \tag{2.23}$$

$$\frac{\partial J_{s2}}{\partial \phi_k} = G_{22k}G_{33} + G_{22}G_{33k} - 2G_{32}G_{32k} \tag{2.24}$$

$$\frac{\partial J_{s3}}{\partial \phi_k} = G_{33k}G_{11} + G_{33}G_{11k} - 2G_{13}G_{13k} \tag{2.25}$$

$$G_{111} = -\frac{1}{N_1\phi_1^2} + \frac{1}{N_3\phi_3^2} = -\frac{1}{N_1\phi_1^2} + \frac{1}{N_2\phi_2^2} \tag{2.26}$$

$$G_{222} = -\frac{1}{N_2\phi_2^2} + \frac{1}{N_3\phi_3^2} = -\frac{1}{N_2\phi_2^2} + \frac{1}{N_1\phi_1^2} \tag{2.27}$$

$$G_{333} = -\frac{1}{N_3\phi_3^2} + \frac{1}{N_1\phi_1^2} = -\frac{1}{N_3\phi_3^2} + \frac{1}{N_2\phi_2^2} \tag{2.28}$$

$$G_{112} = G_{221} = G_{211} = G_{212} = \frac{1}{N_3\phi_3^2} \tag{2.29}$$

$$G_{223} = G_{332} = G_{322} = G_{323} = \frac{1}{N_1\phi_1^2} \tag{2.30}$$

$$G_{331} = G_{113} = G_{131} = G_{133} = \frac{1}{N_2\phi_2^2} \tag{2.31}$$

The independent two variables can be calculated numerically with the two set of equations.

2.5 Coexistence curves

2.5.1 Binodal line

The binodal lines are required to satisfy the following conditions.

$$\begin{cases} \mu_1(\phi_{1a}, \phi_{2a}) = \mu_1(\phi_{1b}, \phi_{2b}) \\ \mu_2(\phi_{1a}, \phi_{2a}) = \mu_2(\phi_{1b}, \phi_{2b}) \\ \mu_3(\phi_{1a}, \phi_{2a}) = \mu_3(\phi_{1b}, \phi_{2b}) \end{cases} \tag{2.32}$$

$$\begin{cases} \phi_{1a} + \phi_{2a} + \phi_{3a} = 0 \\ \phi_{1b} + \phi_{2b} + \phi_{3b} = 0 \end{cases} \tag{2.33}$$

The resultant set of equations becomes

$$\begin{cases} F_1 = \phi_{1a} - \phi_{1b} \exp\left(N_1(\Delta F - \Delta\Gamma_1)\right) = 0 \\ F_2 = \phi_{2a} - \phi_{2b} \exp\left(N_2(\Delta F - \Delta\Gamma_2)\right) = 0 \\ F_3 = \phi_{3a} - \phi_{3b} \exp\left(N_3(\Delta F - \Delta\Gamma_3)\right) = 0 \end{cases} . \tag{2.34}$$

Here

$$\Delta F = \left(\frac{\phi_{1a}}{N_1} + \frac{\phi_{2a}}{N_2} + \frac{\phi_{3a}}{N_3}\right) - \left(\frac{\phi_{1b}}{N_1} + \frac{\phi_{2b}}{N_2} + \frac{\phi_{3b}}{N_3}\right) \tag{2.35}$$

$$\begin{cases} \Delta\Gamma_1 = \Gamma_{1a} - \Gamma_{1b} \\ \Delta\Gamma_2 = \Gamma_{2a} - \Gamma_{2b} \\ \Delta\Gamma_3 = \Gamma_{3a} - \Gamma_{3b} \end{cases} \tag{2.36}$$

$$\begin{cases} \Gamma_{1f} = (\chi_{12}\phi_{2f} + \chi_{13}\phi_{3f})(1 - \phi_{1f}) - \chi_{23}\phi_{2f}\phi_{3f} \\ \Gamma_{2f} = (\chi_{12}\phi_{1f} + \chi_{23}\phi_{3f})(1 - \phi_{2f}) - \chi_{13}\phi_{1f}\phi_{3f} \\ \Gamma_{3f} = (\chi_{13}\phi_{1f} + \chi_{23}\phi_{2f})(1 - \phi_{3f}) - \chi_{12}\phi_{1f}\phi_{2f} \end{cases} \tag{2.37}$$

At fixed ϕ_{1a}, the three independent variables can be calculated numerically with the three set of equations. In addition, the obtained binodal lines must be checked with the conditions of thermodynamic stability,

$$\begin{cases} \frac{\partial^2 F}{\partial \phi_1^2} > 0 \\ \begin{vmatrix} \frac{\partial^2 F}{\partial \phi_1^2} & \frac{\partial^2 F}{\partial \phi_1 \partial \phi_2} \\ \frac{\partial^2 F}{\partial \phi_1 \partial \phi_2} & \frac{\partial^2 F}{\partial \phi_2^2} \end{vmatrix} > 0 \end{cases} . \tag{2.38}$$

2.5.2 Trinodal line

The trinodal lines are required to satisfy the following conditions.

$$\begin{cases} \mu_1(\phi_{1a}, \phi_{2a}) = \mu_1(\phi_{1b}, \phi_{2b}) \\ \mu_2(\phi_{1a}, \phi_{2a}) = \mu_2(\phi_{1b}, \phi_{2b}) \\ \mu_3(\phi_{1a}, \phi_{2a}) = \mu_3(\phi_{1b}, \phi_{2b}) \\ \mu_1(\phi_{1a}, \phi_{2a}) = \mu_1(\phi_{1c}, \phi_{2c}) \\ \mu_2(\phi_{1a}, \phi_{2a}) = \mu_2(\phi_{1c}, \phi_{2c}) \\ \mu_3(\phi_{1a}, \phi_{2a}) = \mu_3(\phi_{1c}, \phi_{2c}). \end{cases} \tag{2.39}$$

$$\begin{cases} \phi_{1a} + \phi_{2a} + \phi_{3a} = 0 \\ \phi_{1b} + \phi_{2b} + \phi_{3b} = 0 \\ \phi_{1c} + \phi_{2c} + \phi_{3c} = 0 \end{cases} \tag{2.40}$$

The resultant set of equations becomes

$$\begin{cases} F_1 = \phi_{1a} - \phi_{1b} \exp\left(N_1(\Delta F_{ab} - \Delta\Gamma_{1ab})\right) = 0 \\ F_2 = \phi_{2a} - \phi_{2b} \exp\left(N_2(\Delta F_{ab} - \Delta\Gamma_{2ab})\right) = 0 \\ F_3 = \phi_{3a} - \phi_{3b} \exp\left(N_3(\Delta F_{ab} - \Delta\Gamma_{3ab})\right) = 0 \\ F_4 = \phi_{1a} - \phi_{1c} \exp\left(N_1(\Delta F_{ac} - \Delta\Gamma_{1ac})\right) = 0 \\ F_5 = \phi_{2a} - \phi_{2c} \exp\left(N_2(\Delta F_{ac} - \Delta\Gamma_{2ac})\right) = 0 \\ F_6 = \phi_{3a} - \phi_{3c} \exp\left(N_3(\Delta F_{ac} - \Delta\Gamma_{3ac})\right) = 0 \end{cases} \tag{2.41}$$

Here

$$\begin{cases} \Delta F_{ab} = \left(\frac{\phi_{1a}}{N_1} + \frac{\phi_{2a}}{N_2} + \frac{\phi_{3a}}{N_3}\right) - \left(\frac{\phi_{1b}}{N_1} + \frac{\phi_{2b}}{N_2} + \frac{\phi_{3b}}{N_3}\right) \\ \Delta F_{ac} = \left(\frac{\phi_{1a}}{N_1} + \frac{\phi_{2a}}{N_2} + \frac{\phi_{3a}}{N_3}\right) - \left(\frac{\phi_{1c}}{N_1} + \frac{\phi_{2c}}{N_2} + \frac{\phi_{3c}}{N_3}\right) \end{cases} \tag{2.42}$$

$$\begin{cases} \Delta\Gamma_{1ab} = \Gamma_{1a} - \Gamma_{1b} \\ \Delta\Gamma_{2ab} = \Gamma_{2a} - \Gamma_{2b} \\ \Delta\Gamma_{3ab} = \Gamma_{3a} - \Gamma_{3b} \\ \Delta\Gamma_{1ac} = \Gamma_{1a} - \Gamma_{1c} \\ \Delta\Gamma_{2ac} = \Gamma_{2a} - \Gamma_{2c} \\ \Delta\Gamma_{3ac} = \Gamma_{3a} - \Gamma_{3c} \end{cases} \tag{2.43}$$

$$\begin{cases} \Gamma_{1f} = \left(\chi_{12}\phi_{2f} + \chi_{13}\phi_{3f}\right)\left(1 - \phi_{1f}\right) - \chi_{23}\phi_{2f}\phi_{3f} \\ \Gamma_{2f} = \left(\chi_{12}\phi_{1f} + \chi_{23}\phi_{3f}\right)\left(1 - \phi_{2f}\right) - \chi_{13}\phi_{1f}\phi_{3f} \\ \Gamma_{3f} = \left(\chi_{13}\phi_{1f} + \chi_{23}\phi_{2f}\right)\left(1 - \phi_{3f}\right) - \chi_{12}\phi_{1f}\phi_{2f} \end{cases} \tag{2.44}$$

The independent six variables can be calculated numerically with the six set of equations.

The numerical calculations are carried out with the multidimensional Secant method of the Broyden's method.[?]

References

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