Isothermobaric Ternary Phase Diagrams

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It is always useful to view the thermodynamic phase diagram as a sanity check on kinetic simulations. This is commonly done for binary alloy systems. The process for generating a correct ternary phase diagram is less routine; this document summarizes the derivation from the system free energy functional as a constrained minimization problem.

An exposition of the method is given in part on math.stackexchange.com. The Python source code in this repository provides a complete implementation.

Binary Two-Phase

We seek to minimize the free energy of the total system with two constraints:

$$G(x_A, x_B) = f_A G_A(x_A) + f_B G_B(x_B) \tag{1}$$
$$f_A + f_B = 1 \tag{2}$$
$$f_A x_A + f_B x_B = x \tag{3}$$

where A and B label phases, 1 and 2 label components, and x is the system composition.

The system functional and integrand are

$$\mathcal{S}[x_A, x_B, f_A, f_B] = \int_V \mathcal{L}\mathrm{d}V \tag{4}$$
$$\mathcal{L}(x_A, x_B, f_A, f_B) = f_A G_A(x_A) + f_B G_B(x_B) - \lambda_1(f_A x_A + f_B x_B - x) - \lambda_2(f_A + f_B - 1). \tag{5}$$

Therefore, the system of Euler-Lagrange Equations is

$$\frac{\delta \mathcal{S}}{\delta x_A} = \frac{\partial \mathcal{L}}{\partial x_A} = 0 = f_A \frac{\partial G_A}{\partial x_A} - \lambda_1 f_A \tag{6}$$
$$\frac{\delta \mathcal{S}}{\delta x_B} = \frac{\partial \mathcal{L}}{\partial x_B} = 0 = f_B \frac{\partial G_B}{\partial x_B} - \lambda_1 f_B \tag{7}$$
$$\frac{\delta \mathcal{S}}{\delta f_A} = \frac{\partial \mathcal{L}}{\partial f_A} = 0 = G_A(x_A) - \lambda_1 x_A - \lambda_2 \tag{8}$$
$$\frac{\delta \mathcal{S}}{\delta f_B} = \frac{\partial \mathcal{L}}{\partial f_B} = 0 = G_B(x_B) - \lambda_1 x_B - \lambda_2 \tag{9}$$

Assuming non-zero f_A and f_B (hence no division-by-zero), Eqns. 6 & 7 give

$$\lambda_1 = \frac{\partial G_A}{\partial x_A} \tag{10}$$
$$\lambda_1 = \frac{\partial G_B}{\partial x_B} \tag{11}$$
$$\therefore \frac{\partial G_A}{\partial x_A} = \frac{\partial G_B}{\partial x_B}. \tag{12}$$

Subtracting Eqns. 8−9 gives

$$G_A(x_A) - G_B(x_B) = \lambda_1(x_A - x_B) \tag{13}$$

$$\therefore G_B(x_B) = G_A(x_A) - \frac{\partial G_A}{\partial x_A}(x_A - x_B)\,. \tag{14}$$

Eqn. 12 represents equality of chemical potential, while Eqn. 14 represents equality of grand potential energy. This pair of equations can be solved to determine the two unknown compositions needed to specify the equilibrium tie line containing points $G_A(x_A)$, $G(x)$, and $G_B(x_B)$. These are similar to Nana's derivation, but in a reduced system.

Ternary Two-Phase

We seek to minimize the free energy of the total system with three constraints:

$$G(x_1^A, x_2^A, x_1^B, x_2^B) = f_A G_A(x_1^A, x_2^A) + f_B G_B(x_1^B, x_2^B) \tag{15}$$

$$f_A x_1^A + f_B x_1^B = x_1 \tag{16}$$

$$f_A x_2^A + f_B x_2^B = x_2 \tag{17}$$

$$f_A + f_B = 1 \tag{18}$$

where A and B label phases, 1 and 2 label components, x_1 and x_2 are the system compositions, and compositions with labels x_i^j represent the composition of component i in phase j.

The integrand is

$$\begin{aligned}\mathcal{L}(x_1^A, x_2^A, x_1^B, x_2^B) = {} & f_A G_A(x_1^A, x_2^A) + f_B G_B(x_1^B, x_2^B) \\ & - \lambda_1(f_A x_1^A + f_B x_1^B - x_1) \\ & - \lambda_2(f_A x_2^A + f_B x_2^B - x_2) \\ & - \lambda_3(f_A + f_B - 1)\end{aligned} \tag{19}$$

The system of Euler-Lagrange Equations becomes

$$\frac{\partial \mathcal{L}}{\partial x_1^A} = 0 = f_A \frac{\partial G_A}{\partial x_1^A} - \lambda_1 f_A \tag{20}$$

$$\frac{\partial \mathcal{L}}{\partial x_1^B} = 0 = f_B \frac{\partial G_B}{\partial x_1^B} - \lambda_1 f_B \tag{21}$$

$$\frac{\partial \mathcal{L}}{\partial x_2^A} = 0 = f_A \frac{\partial G_A}{\partial x_2^A} - \lambda_2 f_A \tag{22}$$

$$\frac{\partial \mathcal{L}}{\partial x_2^B} = 0 = f_B \frac{\partial G_B}{\partial x_2^B} - \lambda_2 f_B \tag{23}$$

$$\frac{\partial \mathcal{L}}{\partial f_A} = 0 = G_A - \lambda_1 x_1^A - \lambda_2 x_2^A - \lambda_3 \tag{24}$$

$$\frac{\partial \mathcal{L}}{\partial f_B} = 0 = G_B - \lambda_1 x_1^B - \lambda_2 x_2^B - \lambda_3 \tag{25}$$

Assuming non-zero f_A and f_B (to prevent division by zero), combining Eqns. 20 & 21 gives

$$\lambda_1 = \frac{\partial G_A}{\partial x_1^A} \tag{26}$$

$$\lambda_1 = \frac{\partial G_B}{\partial x_1^B} \tag{27}$$

$$\therefore \frac{\partial G_A}{\partial x_1^A} = \frac{\partial G_B}{\partial x_1^B} \tag{28}$$

This represents equality of chemical potential of component 1. Likewise, Eqns. 22 & 23 gives

$$\lambda_2 = \frac{\partial G_A}{\partial x_2^A} \tag{29}$$

$$\lambda_2 = \frac{\partial G_B}{\partial x_2^B} \tag{30}$$

$$\therefore \frac{\partial G_A}{\partial x_2^A} = \frac{\partial G_B}{\partial x_2^B} \tag{31}$$

This represents equality of chemical potential of component 2.

Subtracting Eqn. 24−25 gives

$$G_A - \lambda_1(x_1^A - x_1^B) - \lambda_2(x_2^A - x_2^B) = G_B \tag{32}$$

$$\therefore G_B = G_A - \frac{\partial G_A}{\partial x_1^A}(x_1^A - x_1^B) - \frac{\partial G_A}{\partial x_2^A}(x_2^A - x_2^B). \tag{33}$$

This represents equality of the grand potential of phases A and B.

The fourth equation comes from combining the three constraints to recover the lever rule:

$$x_1 = f_A x_1^A + (1 - f_A)x_1^B = f_A(x_1^A - x_1^B) + x_1^B \tag{34}$$

$$x_2 = f_A x_2^A + (2 - f_A)x_2^B = f_A(x_2^A - x_2^B) + x_2^B \tag{35}$$

$$\therefore \frac{x_1 - x_1^B}{x_1^A - x_1^B} = \frac{x_2 - x_2^B}{x_2^A - x_2^B}. \tag{36}$$

The system of Eqns. 28, 31, 33 & 36 can be solved to determine the two unknown composition pairs needed to specify the equilibrium tie line containing the points $G_A(x_1^A, x_2^A)$, $G(x_1, x_2)$, and $G_B(x_1^B, x_2^B)$. *This represents the full set of equations Nana provided.*

Ternary Three-Phase

We seek to minimize the free energy of the total system with three constraints:

$$
\begin{aligned}
G(x_1^A, x_1^B, x_1^C, x_2^A, x_2^B, x_2^C) &= f_A G_A(x_1^A, x_2^A) + f_B G_B(x_1^B, x_2^B) + f_C G_C(x_1^C, x_2^C && (37)\\
f_A x_1^A + f_B x_1^B + f_C x_1^C &= x_1 && (38)\\
f_A x_2^A + f_B x_2^B + f_C x_2^C &= x_2 && (39)\\
f_A + f_B + f_C &= 1 && (40)
\end{aligned}
$$

where A and B label phases, 1 and 2 label components, x_1 and x_2 are the system compositions, and compositions with labels x_i^j represent the composition of component i in phase j. The integrand is

$$
\begin{aligned}
\mathcal{L}(x_1^A, x_1^B, x_1^C, x_2^A, x_2^B, x_2^C) = {} & f_A G_A(x_1^A, x_2^A) + f_B G_B(x_1^B, x_2^B) + f_B G_C(x_1^C, x_2^C) \\
& - \lambda_1 (f_A x_1^A + f_B x_1^B + f_C x_1^C - x_1) \\
& - \lambda_2 (f_A x_2^A + f_B x_2^B + f_C x_2^C - x_2) \\
& - \lambda_3 (f_A + f_B + f_C - 1) \qquad (41)
\end{aligned}
$$

The system of Euler-Lagrange Equations becomes

$$
\begin{aligned}
\frac{\partial \mathcal{L}}{\partial x_1^A} &= 0 = f_A \frac{\partial G_A}{\partial x_1^A} - \lambda_1 f_A && (42)\\
\frac{\partial \mathcal{L}}{\partial x_1^B} &= 0 = f_B \frac{\partial G_B}{\partial x_1^B} - \lambda_1 f_B && (43)\\
\frac{\partial \mathcal{L}}{\partial x_1^C} &= 0 = f_C \frac{\partial G_C}{\partial x_1^C} - \lambda_1 f_C && (44)\\
\frac{\partial \mathcal{L}}{\partial x_2^A} &= 0 = f_A \frac{\partial G_A}{\partial x_2^A} - \lambda_2 f_A && (45)\\
\frac{\partial \mathcal{L}}{\partial x_2^B} &= 0 = f_B \frac{\partial G_B}{\partial x_2^B} - \lambda_2 f_B && (46)\\
\frac{\partial \mathcal{L}}{\partial x_2^C} &= 0 = f_C \frac{\partial G_C}{\partial x_2^C} - \lambda_2 f_C && (47)\\
\frac{\partial \mathcal{L}}{\partial f_A} &= 0 = G_A - \lambda_1 x_1^A - \lambda_2 x_2^A - \lambda_3 && (48)\\
\frac{\partial \mathcal{L}}{\partial f_B} &= 0 = G_B - \lambda_1 x_1^B - \lambda_2 x_2^B - \lambda_3 && (49)\\
\frac{\partial \mathcal{L}}{\partial f_C} &= 0 = G_C - \lambda_1 x_1^C - \lambda_2 x_2^C - \lambda_3 && (50)
\end{aligned}
$$

Assuming non-zero f_A and f_B (to prevent division by zero), combining Eqns. 42 & 43 and Eqns. 42 & 44 gives

$$
\begin{aligned}
\lambda_1 = \frac{\partial G_A}{\partial x_1^A} &= \frac{\partial G_B}{\partial x_1^B} = \frac{\partial G_C}{\partial x_1^C} && (51)\\
\therefore \frac{\partial G_A}{\partial x_1^A} &= \frac{\partial G_B}{\partial x_1^B} && (52)\\
\frac{\partial G_A}{\partial x_1^A} &= \frac{\partial G_C}{\partial x_1^C} && (53)
\end{aligned}
$$

Eqns. 52 & 53 represent equality of chemical potential of component 1 in pairs of phases $A-B$ and $A-C$. Similarly, combining Eqns. 45 & 46 and Eqns. 46 & 47 gives

$$\lambda_2 = \frac{\partial G_A}{\partial x_2^A} = \frac{\partial G_B}{\partial x_2^B} = \frac{\partial G_C}{\partial x_2^C} \tag{54}$$

$$\therefore \frac{\partial G_A}{\partial x_2^A} = \frac{\partial G_B}{\partial x_2^B} \tag{55}$$

$$\frac{\partial G_A}{\partial x_2^A} = \frac{\partial G_C}{\partial x_2^C} \tag{56}$$

Eqns. 55 & 56 represent equality of chemical potential of component 2 in pairs of phases $A-B$ and $A-C$. Taking the differences between Eqns. 48−49 and Eqns. 48−50 gives

$$G_B = G_A - \frac{\partial G_A}{\partial x_1^A}(x_1^A - x_1^B) - \frac{\partial G_A}{\partial x_2^A}(x_2^A - x_2^B) \tag{57}$$

$$G_C = G_A - \frac{\partial G_A}{\partial x_1^A}(x_1^A - x_1^C) - \frac{\partial G_A}{\partial x_2^A}(x_2^A - x_2^C) \tag{58}$$

These represent equality of the grand potentials between pairs of phases $A-B$ and $A-C$.

- The system of Eqns. 52, 53, 55, 56, 57 & 58 represents 6 equations for 6 unknowns, which can be solved for the equilibrium plane containing the points $G_A(x_1^A, x_2^A)$, $G(x_1, x_2)$, $G_B(x_1^B, x_2^B)$ and $G_C(x_1^C, x_2^C)$
- This will *only* find the plane of 3-phase coexistence. Any other points will need to be found using the 2-phase ternary system of equations.