

PDTOOL: Interactive Computation of Binary Phase Diagrams

J. A. Dantzig
University of Illinois at Urbana-Champaign
and
Ecole Polytechnique Fédérale de Lausanne

April 28, 2009

Introduction

PDTOOL is an interactive tool for computing binary alloy phase diagrams, based on a regular solution model for both the liquid and solid phases. The following sections describe the theoretical basis for the calculations, and the implementation in MATLAB. Users are encouraged to report any problems to `dantzig@illinois.edu`.

Background

In the regular solution model, the molar free energy of mixing in the liquid and solid states are given by

$$G_\ell^m(X_B, T) = RT(X_B \ln X_B + (1 - X_B) \ln(1 - X_B)) + \Omega_\ell X_B(1 - X_B) \quad (1)$$

$$G_s^m(X_B, T) = (1 - X_B)\Delta S_f^A(T - T_f^A) + X_B\Delta S_f^B(T - T_f^B) + RT(X_B \ln X_B + (1 - X_B) \ln(1 - X_B)) + \Omega_s X_B(1 - X_B) \quad (2)$$

where x is the composition expressed as atomic fraction, R is the ideal gas constant, T is the temperature, ΔS_f^A and ΔS_f^B are the entropies of fusion of pure components A and B, respectively, T_f^A and T_f^B are their respective melting points, and Ω_ℓ and Ω_s are the regular solution model parameters for the liquid and solid, respectively.

Consider the case of an *ideal solution*, where both Ω_s and Ω_ℓ are zero. At some temperature between T_f^A and T_f^B , the free energy curves for the solid and liquid will intersect, as shown in Figure 1, at a location called the T_0 point. At that point, the free energy of the liquid and solid phases are equal, and this indicates that there is a region of two-phase coexistence containing the point x_0 .

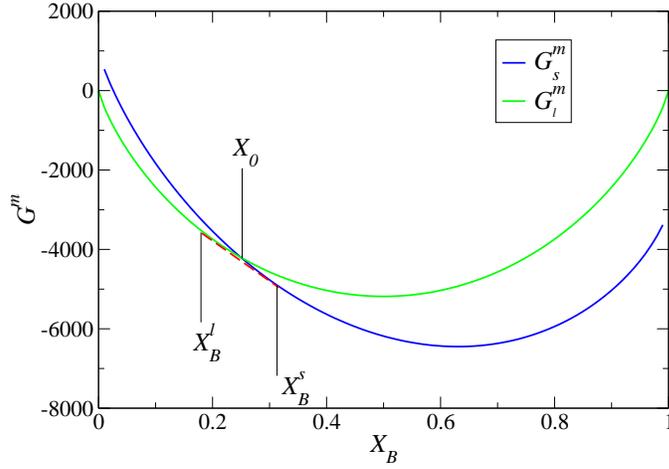


Figure 1: Free energy of mixing for liquid and solid for an ideal mixture at a temperature between their two melting points. The common tangent is shown as a red dashed line.

Gibbs phase rule tells us that the concentrations of the solid and liquid in equilibrium for any composition in the two-phase region, including of course X_0 , will be the same. Let us denote these by X_s and X_ℓ . The lever rule then allows us to compute the fraction of each phase present as

$$f_s = \frac{X_B^\ell - X_0}{X_B^\ell - X_B^s} \quad (3)$$

$$f_\ell = \frac{X_0 - X_B^s}{X_B^\ell - X_B^s} \quad (4)$$

Using these data, we can now compute the total free energy of the two-phase mixture as

$$G^m(X_0, T; [X_B^s, X_B^\ell]) = f_s G_s^m(X_B^s, T) + f_\ell G_\ell^m(X_B^\ell, T) \quad (5)$$

where we have explicitly indicated the parametric dependence of G^m on the phase compositions X_B^s and X_B^ℓ .

The equilibrium phase compositions are those which minimize G^m . We can thus pose this as an optimization problem: find those values of X_B^s and X_B^ℓ that minimize G^m in Eq. (5). The optimization problem has side constraints. For the example shown in Figure 1, we have $0 \leq X_B^\ell < X_0$ and $X_0 < X_B^s \leq 1$. Note that if the two curves cross in the opposite sense, i.e. $G_\ell^m > G_s^m$ for $X_B < X_0$, then the bounds on X_B^s and X_B^ℓ are reversed. The equilibrium values for X_B^s and X_B^ℓ are also the points on the two curves which share a common tangent, as indicated in the figure.

There are numerous cases that become somewhat more interesting, but also more complicated to sort out, when Ω_s and Ω_ℓ are non-zero. Table 1 lists several types of phase diagrams

that appear for various values of the solution parameters. The basic idea of solving an optimization problem to find the compositions corresponding to the minimum free energy is the same. PDTOOL allows the user to explore the parameter space, and thus achieve a better understanding of the relationship between solution thermodynamics and phase diagrams. The implementation is described in the next section.

Table 1: Some example phase diagrams found for various values of the regular solution parameters. The pure material properties are fixed at $T_f^A = 800$, $T_f^B = 1200$, $\Delta S_f^A = 10$ and $\Delta S_f^B = 10$.

Ω_s	Ω_ℓ	Phase Diagram	Example
0	0	Isomorphous	Cu-Ni
0	-15000	Liquidus minimum	Nb-Mo
15000	-15000	Eutectic	Ag-Cu
10000	10000	Isomorphous with spinodal	Au-Pt
15000	10000	Peritectic	Ag-Pt
10000	30000	Syntectic with spinodal	Na-Zn
30000	20000	Eutectic and Monotectic	Al-In

PDTOOL

PDtool is a GUI-based MATLAB implementation of the phase diagram computation algorithm described above. The program is mostly self-explanatory, and so just a brief description is included here. It is easiest to understand with reference to the GUI shown in Figure 2.

The user selects the material property data for the pure materials: ΔS_f and T_f and the parameters for the regular solutions Ω_s and Ω_ℓ . Computation of the phase diagram is initiated by pressing the “Compute Phase Diagram” button. The program computes and displays the free energy curves for temperatures in the range $T_{min} \leq T \leq T_{max}$ in increments of dT . The user can re-probe specific temperatures to examine the free energy, without recomputing the phase diagram, by selecting the temperature (Temp on the GUI) and then pressing the “Plot G(T)” button.

Liquid-solid two phase equilibria are shown in red, solid-solid two phase equilibria are shown in blue, and liquid-liquid two phase equilibria are shown in green. Single phase regions are white. The program does not explicitly find three phase (invariant) points, so it may be necessary to narrow the search range and use a smaller temperature increment to locate such points more precisely.

There are a few other minor controls that affect the display. The radio button labeled “Show T0” allows the user to select whether the set of T_0 points in the liquid-solid phase region is displayed. Similarly, “Show Grid” determines the appearance of the graphs. Finally, plotting in MATLAB can be slow, so the update frequency for the plots can also be set by the user.

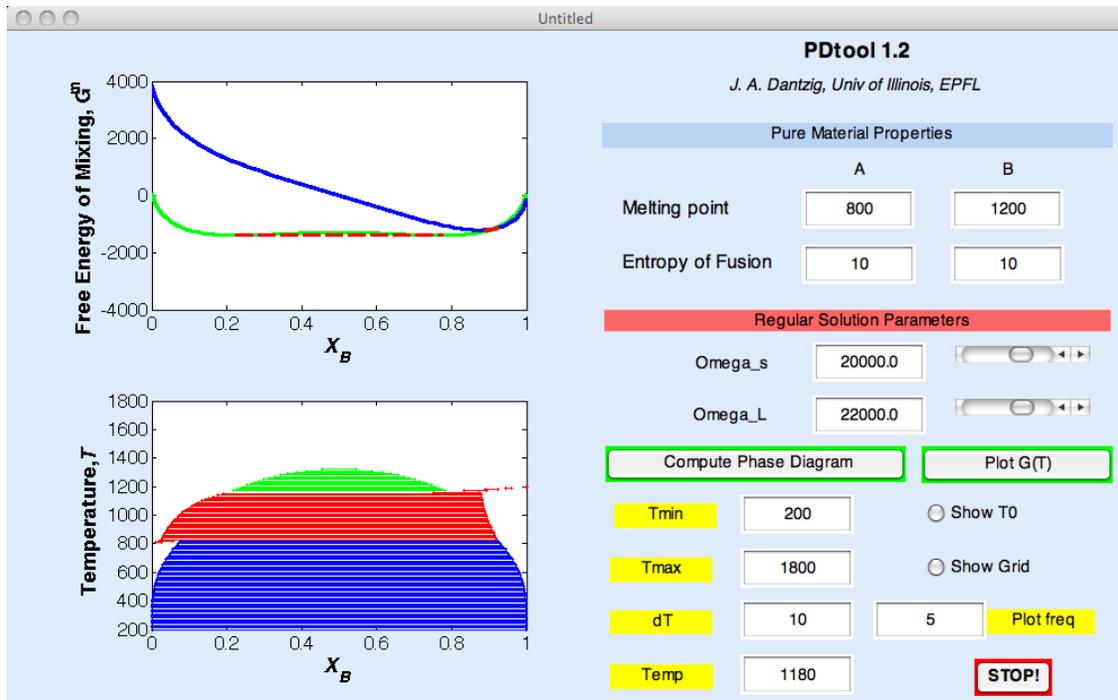


Figure 2: PDtool GUI, showing a computed phase diagram for a regular solution, with parameters that lead to peritectic and monotectic reactions. The blue region corresponds to two immiscible solids, red region indicates $L+S$, and green indicates two immiscible liquids.

After each computation of a phase diagram, PDTOOL outputs a file called `PhaseDiagram.dat` in XMGRACE format for plotting. This is a half-hearted effort to produce a printable phase diagram that needs to be cleaned up for publication.

The button marked "STOP!" does just that.

Installation

PDtool is distributed in executable form. Installation is relatively straightforward. There are distributions available for Windows, Linux, and Mac OS/X. Follow the download instructions for each distribution.

The program loads rather slowly, because it is loading a bunch of MATLAB libraries.