

Combining Multiphysics Modeling and Solution Thermodynamics Using M4Dlib, an External Library

Tanai L. Marin-Alvarado*¹

¹M4Dynamics Inc.

*Corresponding author: 1120 Finch Ave. W. Suite 701, Toronto, ON, M3J3H7,
tanai.marin@m4dynamics.com

Abstract: An external library, M4Dlib [1], has been developed to solve multiphysics problems coupled to solution thermodynamics. This approach extends the concept of local equilibrium [2] to multiphysics modeling by incorporating a full Gibbs energy minimization routine at each numerical node to calculate the thermodynamic equilibrium based on global temperature, enthalpy or concentration conditions. The application of M4Dlib allows for complex multiphysics simulations involving multicomponent systems, ideal and non-ideal solutions systems, speciation, reactive flow, multiphase flow, solidification or precipitation processes.

In this paper, the development of the thermodynamic library and the application to multiphysics modeling is described in detail. Examples of problems involving solidification in multicomponent non-ideal systems are described and the results are compared to the 0D classical equilibrium thermodynamic approaches such as equilibrium solidification or Scheil cooling as well as to previous approaches to multiphysics solidification simulation [3,4].

The implementation of M4Dlib to solve coupled multiphysics and thermodynamic models is demonstrated as an external library or by a user interface built using COMSOL Application Builder.

Even though M4Dlib has been created to be applied to extractive metallurgy areas, involving complex thermodynamic solution models such as high temperature systems (pyrometallurgy), it is also applicable to a wide range of chemical processing industries.

Keywords: Gibbs energy minimization, pyrometallurgy, casting, thermodynamic equilibrium, solidification, external library, phase transition, multiphase systems

1. Introduction

The concept of local equilibrium has been developed for 0D thermodynamic process simulation [2], taking advantage of the rigorous

application of Gibbs free energy minimization to chemical process metallurgy simulation. The present library, M4Dlib, developed by M4Dynamics, extends this approach to 1, 2 or 3D multiphysics modeling. The concept of local equilibrium applied to process simulation consists of breaking down a given process into one or more sub-processes, each represented by an “Equilibrium Reactor” in which Gibbs minimization routines solve the phase stability problem given adequate number of system conditions (Temperature, concentration or pressure). The relationship between several “Equilibrium Reactors” can be made by interconnecting them using “stream”, “mixers”, “phase splitters”, etc. Therefore, a process that from a macroscopic point of view is not at chemical equilibrium can be represented by the use of the local equilibrium concept.

One of the advantages of this approach is the enhanced prediction capabilities of the simulator as there is less dependance in assumptions needed to generate the simulator. In addition, there is no need to define chemical reactions or extent of reactions as it is sufficient to just define a thermodynamic database that represents all the possible species present in the process. However, one of the limitations of this concept is that it is not capable of simulating process at a microscopic level in which space distribution is of interest. Furthermore, even though, time dependant or dynamic simulations are possible using the local equilibrium concept, still a full time discretization of the simulation is not possible.

To overcome the limitations mentioned above and to incorporate full solution thermodynamic capabilities to multiphysics simulation, the present work describes the extension of the local equilibrium concept to 1, 2 or 3D and its application to multiphysics. In order to accomplish this, assume that a process simulated by a series of “equilibrium reactors” is refined further and further into smaller and smaller units until it resembles the spacial discretization generated in numerical approximation of the physics conservation

equations such as momentum, heat and mass transport. The interaction between reactors units is then given by convective or diffusive transport mechanism for temperature and concentration. Therefore, by solving the Gibbs minimization routines on each Gauss point of the multiphysics problem, the extension of the local equilibrium concept to space domain is achieved. An schematic of the main concept is shown in Figure 1.

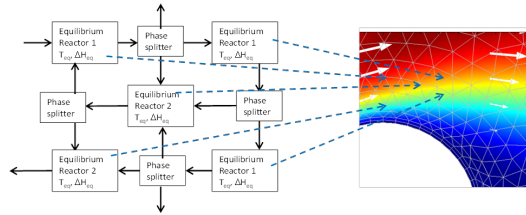


Figure 1. Schematic showing the extension of the local equilibrium concept to a 2D multiphysics simulation.

When modeling real multicomponent-multiphase chemical systems it is often the case that a mixture of various phases can be present depending on the local thermodynamic conditions. For example, in the simple case of a binary system A-B with chemical solutions in both liquid and solid states, it is possible that at a given temperature and global composition of components A and B, the thermodynamic equilibrium is represented by the mixture of both solid and liquid solutions, each having different compositions of A and B, such as during the solidification of a liquid alloy. Figure 2 shows a typical example of the Integral Gibbs free energy for both solid and liquid solutions of AB over the entire range of composition at a fixed temperature. The close up view in Figure 2 shows the case in which the Gibbs free energy of the system would be minimize by a mixture of the two phases rather than by any of the single solutions.

In more complex cases, the presence of miscibility gaps can exist within the same phase or among different phases, which will result in the coexistence of two or more solid or liquid phases at the same time. This is often the case in high temperature chemical systems such as liquid metal, mattes or slags and typically present during calcining, smelting, converting or refining processes. The advantage of using M4Dlib to simulate solidification or phase transition processes over previous models [3,4] is that the simulation is not limited to just binary systems.

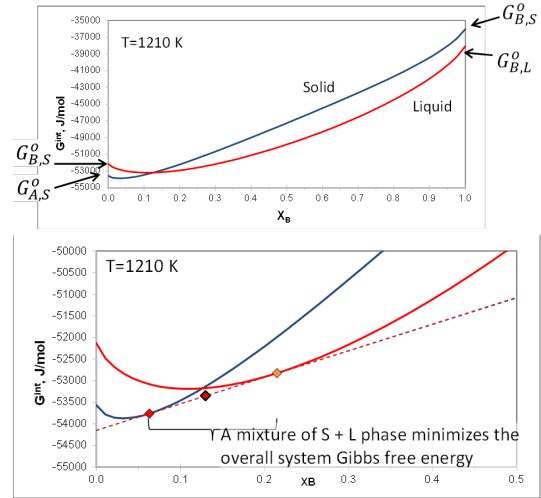


Figure 2. Plot of Integral Gibbs free energy as a function of composition at a given $T = 1210\text{K}$ for both solid and liquid solutions. Top: full range view; Bottom: close up view for X_B from 0 to 0.5 showing the range of concentrations in which System energy is minimized by a mixture of solutions ($S + L$).

1.1 Solution Thermodynamic System Description

The complex minimization routine involves solving a multi-dimension constrained optimization problem for each numerical node in the multiphysics space domain. This process is carried out by M4Dlib which provides COMSOL with all the thermodynamic information required by the model by calling the appropriate function defined in the library, such as the activity of specific components, amount of a given phase, solid fraction, enthalpy of a given component or mixture, etc.

The example described in this paper, represents a binary (2 components: A and B) non-ideal solution system, consisting of the two pure components, A and B , two solution models (solid AB and liquid AB) and five possible mixtures: fully solid, fully liquid, solid + liquid, solid + solid (miscibility gap in solid solution) and liquid + liquid solutions.

For a given solutions, solid or liquid, the integral Gibbs free energy is given by:

$$G^{int} = \sum G_i^o \cdot X_i + G^{mix} \quad (1)$$

The first component on the right hand side of Equation 1 represents the contribution of the pure compounds (standard Gibbs free energy) for either solid or liquid phases, typically defined by a polynomial or other common type of equations depending in a number of parameters found in available thermodynamic databases [5, 6]. X_i is

the fraction of component A or B and G^{mix} is the term associated to the mixing of A and B in the solid or liquid solutions. This last term is expressed by the following equation:

$$G^{mix} = RT \sum (X_i \ln(a_i)) = G^{id} + G^{ex} \quad (2)$$

in which G^{id} and G^{ex} represent the ideal and excess (non ideal) contributions of the mixing term, respectively.

In the case of a regular solution model, the excess Gibbs free energy of mixing is given by Equation 3:

$$G^{ex} = RT \sum (X_i \ln(\gamma_i)) = X_A X_B L_{AB}^{(0)} + X_A X_B L_{AB}^{(1)} (X_A - X_B) + X_A X_B L_{AB}^{(2)} (X_A - X_B)^2 \quad (3)$$

The regular solution parameters $L^{(0)}$, $L^{(1)}$ and $L^{(2)}$ have to be defined by the thermodynamic database for each solution and are typically express in the following form:

$$L_{AB}^{(0)} = a_0 + b_0 T; L_{AB}^{(1)} = a_1 + b_1 T; L_{AB}^{(2)} = a_2 + b_2 T$$

Once the parameters necessary to define the standard Gibbs free energy of pure compounds and those for the regular solution models for both solid and liquids, the Gibbs free energy of the system can be calculated for any temperature (T) and global set of composition (X_A and X_B). For example, in the case of a solid + liquid solution mixture, the mass balance of the system needs to be defined in terms of the global compositions, the compositions of components A and B in the solid and liquid phases ($X_{A,S}$, $X_{B,S}$, $X_{A,L}$ and $X_{B,L}$, respectively) and the fraction of solid and liquid solutions (S_f and L_f), as shown in the following set of equations:

$$\begin{aligned} \text{System variables: } T, X_A, (X_B) \\ X_B = 1 - X_A \end{aligned}$$

$$\begin{aligned} \text{For a given pair of } X_{A,S} \text{ and } S_f \\ L_f = 1 - S_f \end{aligned}$$

$$X_{B,S} = 1 - X_{A,S}$$

$$X_{A,L} = \frac{X_A - S_f X_{A,S}}{1 - S_f}$$

$$X_{B,L} = \frac{1 - X_A - S_f (1 - X_{A,S})}{1 - S_f}$$

Based on the example above, the system's Gibbs free energy can be calculated as a function of two variables, $X_{A,S}$ and S_f , in this case.

The constrained minimization problem for the binary system used in this example is illustrated in Figure 3, where the system's Gibbs free energy of mixing is plotted by a surface plot as a function of S_f and $X_{A,S}$. For the global conditions used in this example and by applying a Newton optimization algorithm, it is found that the mixture of solid and liquid phases that minimize the free energy of the system corresponds to a solid fraction of 58% and a concentration of 85.7% of component A in the solid phase.

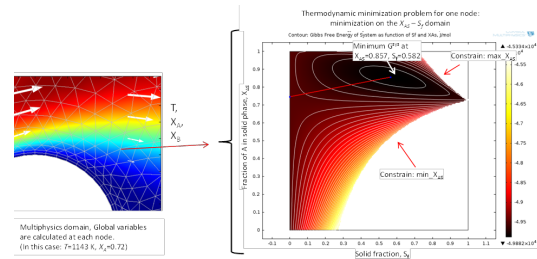


Figure 3. Gibbs free energy of system minimization on the S_f vs $X_{A,S}$ plane for a specific temperature and global concentration ($T=1143$ K and $X_A = 72\%$)

Based on the above results, the rest of the mass balance variables can be calculated as well as other thermodynamic properties, such as enthalpy, entropy, activities of phase constituents, etc. and other properties of the mixture can be calculated.

2. Use of COMSOL Multiphysics

M4Dlib is available as a dynamic library for Windows or OS X and can be called directly from COMSOL Multiphysics by the use of an "external function", allowing for maximum calculation speed since no external application has to be called to perform the Gibbs minimization routines.

The thermodynamic data necessary to describe the chemical system of interest is loaded by the external library during the initialization of the model, allowing the user to solve for various chemical systems by simply specifying the filename of different thermodynamic databases. In its simplest form of application, M4Dlib can be used as a solution or mixtures material library for thermodynamic and physical properties, for example: heat capacity, enthalpy, entropy, thermal conductivity, density, etc.

COMSOL Application Builder, has been used to create an end user application for the

simulation of a binary solution model as described above, with the purpose of creating and verifying the required thermodynamic database to be used. The application allows for the calculation of the system's phase diagram described by the thermodynamic database selected by the user. The phase diagram is expressed as a surface plot of the solid fraction (or mixture fraction) of the system as a function of temperature and global composition of component B. The application also plots the integral Gibbs free energy of mixing for both solid and liquid solutions as a function of temperature (set by a slider control). As an example Figure 4 demonstrates the case in which the solid solution exhibits a strong positive deviation from ideality, resulting in a miscibility gap on the solid solution at low temperatures, generating the classical Eutectic type of phase diagram shown in Figure 5.

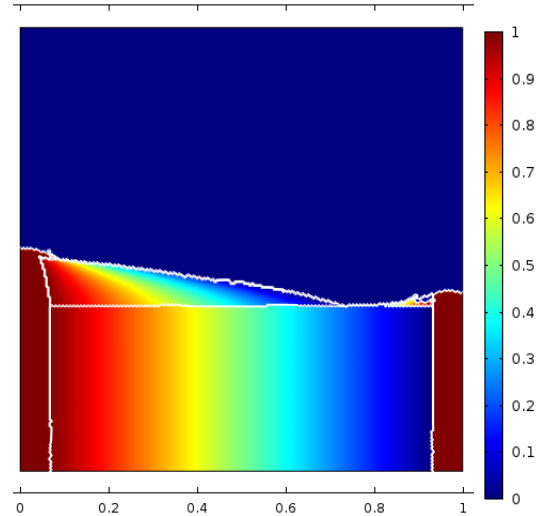


Figure 5. Binary phase diagram for a system exhibiting eutectic properties. Surface plot shows “mixture” fraction (0 = fully liquid solution, 1 = fully solid solution, and values in between representing Solid + Liquid mixtures or Solid - Solid mixture. X axis represents fraction of component B (from 0 to 1) and Y axis is Temperature (273-2273 K)

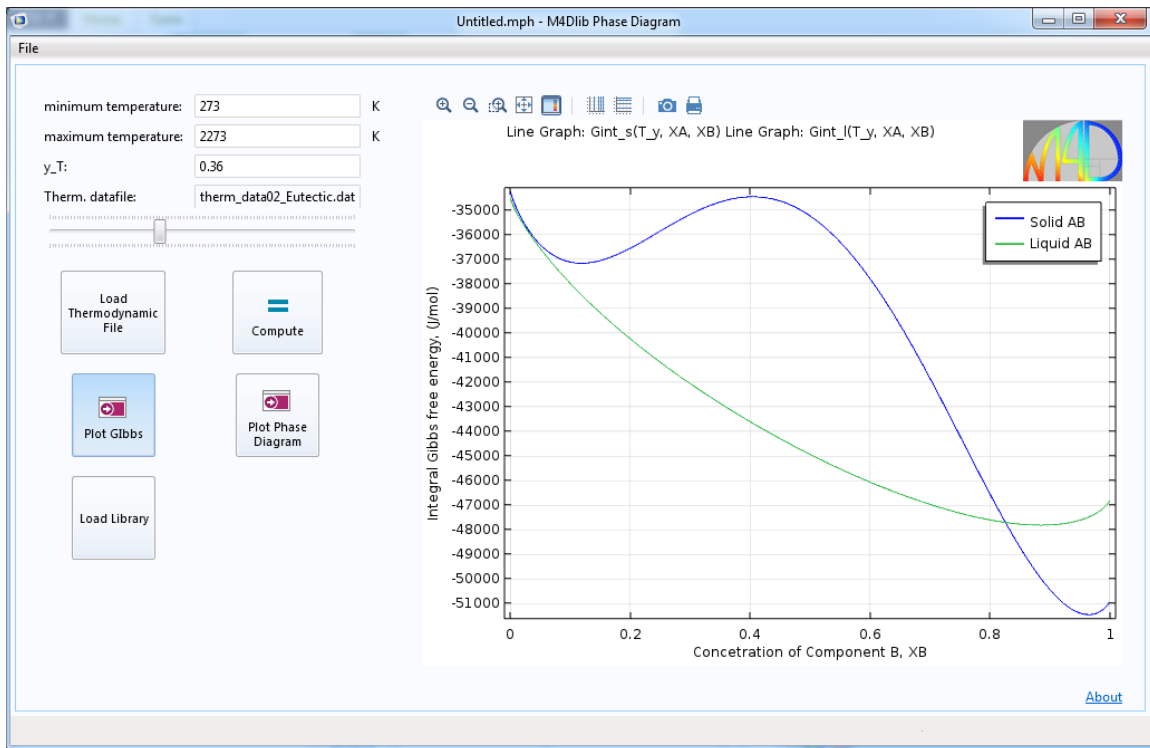


Figure 4. Integral Gibbs free energy of system AB at a given temperature as a function of global concentration of component B viewed on the M4Dlib COMSOL Application. In this case, Solid solution has positive deviation from ideality, resulting in miscibility gap at low temperatures.

3. Results

To demonstrate the use of M4Dlib applied to a coupled thermodynamic and multiphysics

model, lets consider the simulation of the controlled solidification of molten solution A-B ($X_A = 0.9$) inside a crucible starting at an initial temperature ($T_0 = 1300$ K) above the liquidus temperature of the solution (1242.2 K).

Assuming convective heat transfer to be negligible in this case (no natural convection), the problem can be simulated using a time dependant diffusion heat transfer and transport of diluted species model.

The geometry of the system corresponds to the liquid inside the crucible, in this case 5 inches tall and 1.5 inches in radius with round bottom, which can be simulated by using a 2D axial-symmetric model.

Cooling of the crucible is simulated by heat flow boundary conditions around the surface of the crucible, using convective heat transfer ($h = 10$ W/m²K) and an ambient temperature ($T_{amb} = 1073.15$ K) below the solidus temperature of the solution (1176.9 K)

The transient solution of the heat transfer model (T) is shown below at $t = 2160$ s.

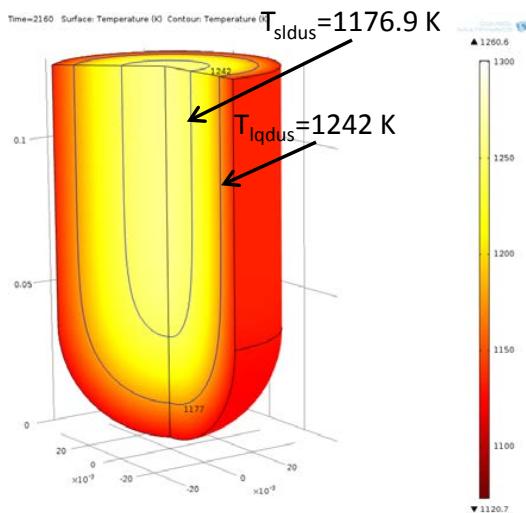


Figure 6. Temperature at $t = 2160$ s inside a crucible during controlled solidification of a liquid binary solution (AB).

As shown in the figure above, it should be expected that everything below the liquidus temperature would be fully solidified, then a transition of solid + liquid solution would be present between the liquidus and solidus temperature contours and everything else would be still fully liquid towards the centre of the crucible. In addition, as the solidification process takes place, the solid phase would be enriched in component A (in this case) and the liquid should become depleted from component A and as the solid fraction at any given location increases, the concentration in the solid phase should approach

the equilibrium amount, provided sufficient time and high enough diffusivity from the solid are given.

This behaviour is observed in Figure 7, in which the solid fraction, calculated by M4Dlib is shown as a surface plot (from 0 to 1) at $t = 2160$ s and the concentration of component A in both solid and liquid solutions is plotted as a function of time at an specific location ($r = 3.2$ cm and $z = 7$ cm)

If the solidification process is fast enough and since the solid diffusivity of component A and B would be very small, then it should be expected that the system would not have time to equilibrate and a gradient of concentrations would be present in the radial direction (ignoring natural convection effects). This effect can be simulated by using M4Dlib if the calculated equilibrium composition is used only as the driving force for the actual species transport of components A and B. This approach would be inline with the 0D Scheil cooling approximation as opposed to perfect equilibrium solidification.

Finally, if convective effects are significant and need to be considered in the liquid phase, then the problem would require to couple fluid flow. The effect of solidification on the Navier-Stokes equations can be simulated by using the approach described by Voller and Prakash [3] in which volumetric forces depending on the calculated S_f are added to the N-S equations. The implementation of this approach is described in [4].

4. Conclusions

The simulation of complex multicomponent multiphase chemical reaction systems can be carried out by the application of M4Dlib. A thermodynamic database including the necessary information of the system components and the appropriate solution model and parameters is necessary as an input. These databases can be created from publicly available information for pure stoichiometric compounds [5, 6] and the specific knowledge of the solution model of interest. Additional mixing models can be added to the thermodynamic database for properties that are non-linear within the mixture, such as density, thermal conductivity, diffusivity, etc. These properties of the mixture can be called directly from COMSOL by the use of a function defined in the external library. Alternatively, private thermodynamic database files can be requested to M4Dynamics for specific applications based on available literature information.

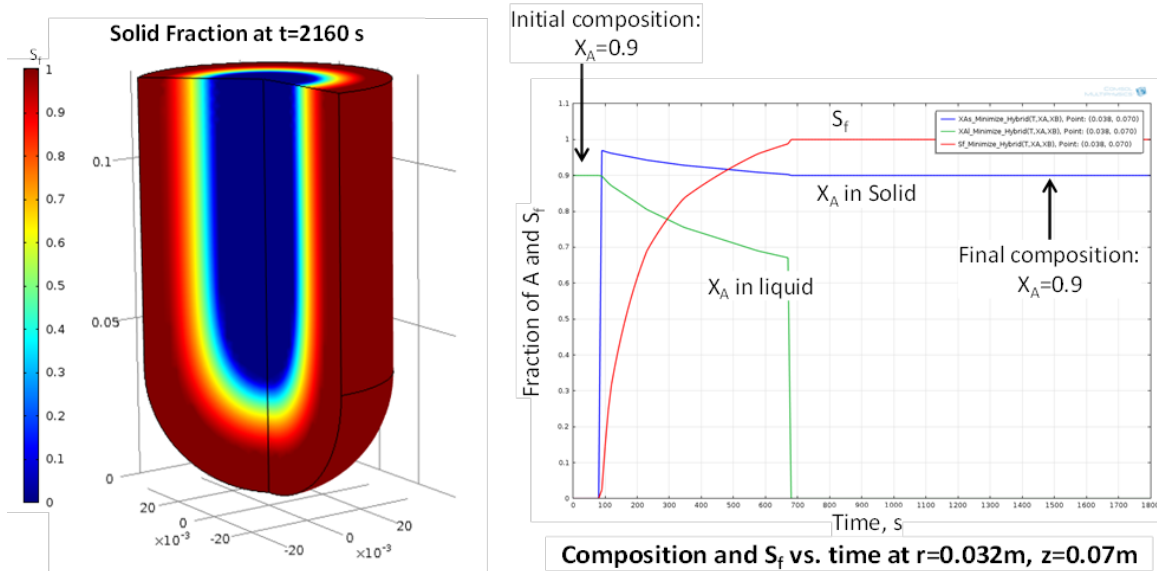


Figure 7. Solidification of a liquid binary solution (AB) inside a crucible. Left: solidification after 2160s; Right: composition of component A in liquid and solid phases as a function of time as well as solid fraction at a fix location inside the crucible.

Finally, M4Dlib can easily be integrated to a custom COMSOL application for specific end-user interfaces, simplifying significantly the simulation of multiphysics problems coupled with solution thermodynamics.

For more information, please visit www.m4dynamics.com

5. Acknowledgements

In memory of Prof. Torstein Utigard.

9. References

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